



*Synthesis and radiation stability of silicone elastomers.*

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SYNTHESIS AND RADIATION STABILITY

OF SILICONE ELASTOMERS

by

DAVID TIMOTHY ASTILL BSc

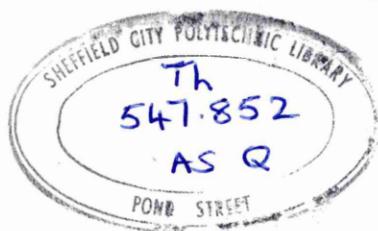
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by

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ABSTRACT

A wide range of polymer samples based upon polydimethylsiloxane (PDMS) have been subject to gamma irradiation, and the subsequent effects analysed using a variety of techniques. The preparation of a series of blends and block copolymers of PDMS containing small amounts of polystyrene (PS) is described, and their characterisation by spectroscopic and thermal analytical methods is discussed.

A PDMS gum gave a  $G(X)$  value of 2.8 which is in good agreement with other reported values. Thermal analysis revealed a shift of 20°C in the glass transition temperature, and disappearance of the exotherm band, upon onset of gelation. Within the sol component of a cross-linked sample, a complex range of reactions are evident which are related to the absorbed dose.

It was found with PS-PDMS blends, upon absorption of low doses of radiation, that the amount of gel produced is very much lower than that observed with PDMS. A substantial degree of radiation protection was observed with a 3% <sup>w</sup>/w PS blend, which required a gelation dose of almost five times that of homopolymer PDMS. A selected number of block copolymers were irradiated and the gelation dose was again found to be far greater than would be expected of PDMS of similar relative molecular mass.

Morphological studies allowed calculation of the size of the PS average domain size which increased with % <sup>w</sup>/w PS in the blend or copolymer. It is proposed that the radiation protection observed with polymers containing PS is related to the PS average domain size. The large surface area/volume ratio found with a 3% <sup>w</sup>/w PS blend would facilitate a considerable degree of miscibility of PS with PDMS, thereby decreasing the susceptibility of PDMS to cross-link formation.

## DEDICATION

To my wife Denise, whose love and  
encouragement was essential to the  
completion of this thesis.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Radiation

In February 1896 Henri Becquerel reported<sup>1</sup> that crystals of uranyl salts emitted a radiation which was found to blacken a photographic plate, even though it was enclosed in black paper. Pierre and Marie Curie summarised the results of this new area,<sup>2</sup> by stating that,

"These rays from uranium were atomic phenomenon, characteristic of the element but not dependent on its chemical or physical state."

When uranium was enclosed in the dark and isolated from any energy source, Becquerel found that emission of radiation took place for many years, with little or no decrease in intensity. Almost simultaneously with this discovery, the Curies quantified the heating effect due to radiation emitted from radium, as almost  $100 \text{ cal h}^{-1} \text{ g}^{-1}$  of radium. ( $420 \text{ Jh}^{-1} \text{ g}^{-1}$ ). The source of this power was then unknown, but an article in the St. Louis Post Dispatch of October 4th 1905, in a far-sighted, almost prophetic, discussion, suggested;

"This mysterious new power could be utilised as an instrument of war."

It was during the Manhattan Project (1942), that the first controlled nuclear chain reaction took place, this signalled the birth of the Atomic Age; a new era had arrived! The immediate beneficial effect of this nuclear reaction, was the harnessing of the immense amount of energy produced. In a relatively short time, the United Kingdom has

become dependent on nuclear energy to the extent that, in 1982, 16.4%<sup>3</sup> of our national grid capability is nuclear in origin.

It was during the course of the development of nuclear reactors that there was found a need for polymeric materials which were able to withstand the emitted radiation from nuclear related installations.

## 1.2 The Irradiation of Polymers

Exposure of polymers (which may be plastic or elastomeric in nature) to high-energy radiation can result in a number of physical and chemical changes. These changes are not due to alterations in the structure of the nucleus, but are a consequence of the formation of new electronic configurations, which give rise to chemical reactions. By high-energy radiation, is meant photons or other particles whose energies are higher than the binding energy of the orbital electrons. In the past, X-ray<sup>4a</sup> or accelerated electrons<sup>5</sup> have been the main irradiation source, but in recent years gamma ( $\gamma$ ) rays have become the standard irradiation facility in both research and production areas.

$\gamma$ -radiation is a form of high energy electromagnetic radiation. A beam of high energy electromagnetic radiation behaves as though it were a stream of particles (photons) having zero charge, zero mass and travelling at the velocity of light. In the passage of the  $\gamma$ -radiation through a material it comes into close contact with the atoms, and this interaction results in a transfer of energy from the incident radiation to the material. In the case of metal irradiation, the imported energy results in an increase in temperature of the metal, but in the case of polymeric materials, this absorbed energy is available for numerous reactions, which will be studied in further detail later.

A polymer molecule may undergo:

a) crosslinking - The formation of a bond between different molecules, to give a 3 Dimensional-network structure.

b) scission - The cleavage of bonds resulting in fragmentation of the polymer molecule.<sup>6-10</sup>

The crosslinking and scission reactions result in a change in the physical properties of the material. The type and rate of change depends on the competition between the crosslinking and scission reactions. Net scission will cause one kind of property change, whilst net-crosslinking will have a much different effect.<sup>11</sup>

Crosslinking increases the molecular weight of a polymer, decreases the solubility, and increases the softening temperature. A liquid, soft, amorphous polymer will change to a rubbery material and then to a hard glassy 'gel'. Whereas, scission decreases the molecular weight, solubility is increased, and the softening point is lowered. In some materials the softening effect is so large, that it results in a great increase in viscous flow.

### 1.2.1 The Use of Radiation in the Processing of Polymers

#### 1.2.1.1 Polymerisation

The first experimental evidence demonstrating that the vinyl monomers could be polymerised by irradiation was obtained by Hopwood and Phillips.<sup>12</sup> Numerous studies have since revealed that most common monomers, such as styrene and methyl methacrylate,<sup>13</sup> polymerise when exposed to radiation at room temperature. The reaction pathways were found to be mainly of the type which proceed via a radical mechanism. Later, it was found that ionic polymerisation, both anionic and cationic mechanisms, could be initiated by irradiation. In 1956,

Lawton and coworkers<sup>14</sup> successfully polymerised a cyclic siloxane to obtain a polydimethylsiloxane.

In certain specific applications, radiation-induced initiation has become the main method of polymerisation. With respect to synthesis, irradiation is so often the preferred method for the following reasons:

- i) closely defined initiation of polymerisation;
- ii) fine process control;
- iii) lack of catalyst residue;
- iv) initiation of systems where conventional initiations fail, i.e. at low temperatures.

Wilson<sup>2b</sup> gives excellent coverage of solid-state polymerisation using irradiation, in one of the latest reviews on this subject. Radiation as a processing tool, has continued to find acceptance in many applications and geographic locations. This is due to:

- i) higher powered sources;
- ii) lower Radiation costs;
- iii) escalating alternative energy costs.

The early <sup>60</sup>Co plants of ½ Megacurie are now being replaced with increased 4 Megacurie capacity, this type of improvement has also taken place in electron beam accelerators. K. H. Morganstern of Radiation Dynamics Inc. confidently states<sup>18</sup> that,

"Radiation costs is one of the few commodities that has gone down over this two decade span."

Table 1.1 clearly shows that irradiation is a preferred option for processing in terms of energy costs.

The oldest application for irradiation processing is in the upgrading of electrical insulators with the aim of improving reliability at elevated temperatures. The "memory effect",<sup>19</sup> observed in polyethylene, is widely used in the processing of films, pipes and numerous more sophisticated devices, and represents a large market, both in volume and in commercial value. Other applications are seen in the vulcanisation of sheet rubber and the curing of surface coatings and printing inks.<sup>16</sup>

Yearly world-wide production of radiation processed chemicals is approximately £250 million,<sup>20</sup> which represents less than 1% of present chemical production. Despite the advantages mentioned, it would appear that this proportion is a very small return for all the interest shown in this area. Although the process may be considered superior, the cost of the irradiation sources and equipment may be the reason for a reluctance to adopt such processes.

Table 1.1 Radiation Processing Costs compared with those involving Heat

Applications	Heat	Radiation
Crosslinking polyethylene on 600v - 4/0 wire	£0.019/Kg	£0.0088/Kg (15 Mrad)
Vulcanisation of sheet rubber	£0.05/Kg	£0.006/Kg (10 Mrad)
Curing reinforced polyester panels (1500 kg/hr)	£40/hr.	£9.60/hr
Curing Paint (energy input for same product throughput)	£7200/month (gas)	£1280/month (electricity)
Food preservation	£0.03/Kg	£0.0003 /Kg (0.5 Mrad)
Medical disposable sterilisation	£1.44/m <sup>3</sup>	£0.32/m <sup>3</sup> (2.5Mrad EB)

(exchange rate £1.00 = \$1.25

(Table adapted from Reference 18)

### 1.2.2 The Need for Radiation Resistant Polymers

The advent of the nuclear power reactor stimulated many investigations into the effects of irradiation on materials; particularly the structural metals for the core containment and ceramic insulators for control equipment. The need for radiation resistant polymers arises when there are weight and space limitations, for example in instrumentation and control apparatus.

#### 1.2.2.1 Normal Operation

The absorbed dose rate in the 'active zone' is in the region of  $10^{12}$  rad hr<sup>-1</sup> ( $10^6$  Mrad hr<sup>-1</sup>)<sup>21</sup> this automatically excludes the continuous use of polymers as possible materials of design. During normal operation the environment in the containment consists of X-rays and neutrons that escape through the concrete walls of the reactor core. The  $\gamma$ -ray energy spectrum is in the range of a few KeV to about 8 MeV depending on the type of reactor. With dose-rates in the range  $10 - 100^{22,23}$  rad h<sup>-1</sup> for an average rate of 50 rad h<sup>-1</sup> the integrated dose would be  $2 \times 10^7$  rads, over a period of 40 years.

#### 1.2.2.2 Accident Situation

A nuclear power generating station must be operated with a high "reliability", not only in the safe construction and operation of the core, but in the systems that use cables and other electrical equipment. Cables must keep their qualities for a guaranteed period of 40 years whilst in normal use. Incorporated in this guarantee, there must be a margin for the possibility of an accident situation. Class 1E<sup>24-26</sup> cables are employed in equipment that are responsible for emergency reactor shutdown.

If an interruption were to occur in the supply of coolant,

accidents of varying degrees could occur, resulting in the rupture of one or more of the fuel element containers to the extent that complete vaporisation of the core could take place. The release of fission products would occur and continue until the process is cooled by the emergency cooling system. The dose rate would vary with time, but the maximum is expected to reach a value of  $10^7 \text{ rad h}^{-1}$  with the added problem that high pressure and steam would be present at temperatures of  $150^\circ\text{C}$ .<sup>27</sup> During all this time, the emergency equipment must continue to be in operation, even though the integrated dose in this region, could be in the range of  $5 \times 10^8 \text{ rad}$ . In addition, the environment will consist of a continuous spray of chemical solutions, such as boric acid and sodium hydroxide. It is clear that in an accident situation extreme conditions would arise; the high temperatures and pressures, the corrosive chemicals, will combine with the  $\gamma$ -radiation to increase the damage to the polymeric materials present.

#### 1.2.2.3 Nuclear Plant Equipment incorporating Polymeric Materials

The equipment that is needed inside the containment is typical of that found in any large scale industrial complex. In addition, there is the equipment needed to provide emergency functions. A list of the typical equipment, with polymer applications is given in Table 1.2.

In all of these functions, polymeric materials are required. They may be in the form of fluids, elastomers, flexible plastics or rigid plastics. The development and production of seals for use in moderate radiation fields presents a most difficult problem, since a small amount of radiation damage to seals removes the 'sealing ability'. If radiation resistance was not a specific requirement then designers would have little problem in obtaining material for each function. However,



the choices available are somewhat limited, when reliability is essential, for service with nuclear reactors and similar installations.

Table 1.2 Plant Equipment with Polymer Applications

Electrical	Mechanical
Power cable	Gaskets
Control cable	O-rings
Instrumentation cable	Spacers
Motors	Sheaths
Switches	Seals
Relays	Motor mounts
Connectors	Flexible tubes
Valves	Protective coatings
Electrical enclosures	

#### 1.2.2.4 Further Applications of Radiation Resistant Polymers

Another use for radiation resistant polymers is in radiation processing facilities. In the radiation and sterilisation of medical supplies (where the maximum permitted dose is 2.5 Mrad), and food products, polymeric materials are required in many forms as packaging. Polyethylene and polyvinyl chloride may be used as sheeting, or formed into containers. In these instances, it is essential that the polymer be undamaged by the irradiation process. Regulations require  $10^5$  to  $10^7$  rad<sup>28-30</sup> to ensure complete sterilisation; it is expected that little or no change should be evident in the packaging material at such doses.

### 1.3 The Stability of Polymers to Radiation

#### 1.3.1 General Overview

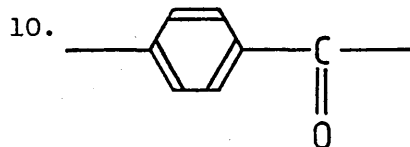
In 1951, Bopp and Sisman,<sup>31-32</sup> published the first comprehensive reports on the effects of radiation on plastics and elastomers, which, for a good many years remained a major source of information. Charlesby, in 1960, provided a second source of information with his book, 'Atomic Radiation and Polymers'.<sup>7</sup> Charlesby produced scientific data, whereas Bopp and Sisman produced engineering data, thus the two were complementary. In more recent years, many reviews have been published<sup>4,21,33,34,35</sup> and individual papers dealing with selected polymer systems now run into the hundreds. Helmann and Ross<sup>36</sup> of the Radiation Chemistry Data Centre, University of Notre Dame U.S.A. have revealed that their bibliographic data base currently contains 50,000 references covering radiation chemistry and photochemistry of polymers.

Bopp and Sisman<sup>32</sup> determined a ranking of the relative stabilities of various polymer structures (Table 1.3). They advised caution against taking the ranking as being absolutely precise, as the relative order may vary due to differences in the polymer specimens studied. Nevertheless over the years this list has proved to be most authoritative.

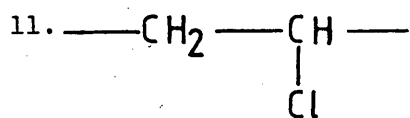
Classification of polymer behaviour, following  $\gamma$ -irradiation are subject to disagreement about the grouping of certain polymers. Table 1.4 indicates the predominant reaction that is found to take place; again care must be exercised, as with the Bopp and Sisman classification. The presence of additives and plasticizers or a change in the irradiation conditions may cause a shift of polymer from one group to another. The following general conclusions have been reached:

Table 1.3 Relative Stabilities of Polymer Structures

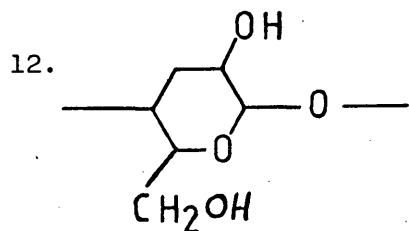
Structure	Occurrence/Behaviour
1. $\text{---CH}_2\text{---}\underset{\text{C}_6\text{H}_5}{\text{CH}}\text{---}$	Repeat unit - polystyrene, most stable of unfilled polymers tested.
2. $\text{---CH}_2\text{---}\underset{\text{C}_6\text{H}_5}{\text{N}}\text{---}$	Repeat unit - aniline formaldehyde.
3. $\text{---CH=CH---}$	In many elastomers, stability insensitive to unsaturation.
4. $\text{---CH}_2\text{---CH}_2\text{---}$	Repeat unit - polyethylene.
5. $\text{---}\underset{\text{O}}{\underset{\parallel}{\text{C}}}\text{---}\underset{\text{H}}{\underset{ }{\text{N}}}\text{---}$	Present in Nylon - stability as polyethylene.
6. $\text{---Si(CH}_3)_2\text{---O---}$	Repeat unit - silicone rubber, stability as most other elastomers.
7. $\text{---}\text{C}_6\text{H}_4\text{---CH}_2\text{---}$	Repeat unit - phenol formaldehyde polymer.
8. $\text{---CH}_2\text{---O---}$	Repeat unit - poly(allyl diglycol carbonate).
9. $\text{---CH}_2\text{---S---}$	Present in thiokol.



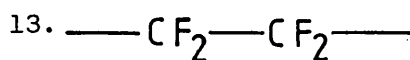
Present in Dacron.



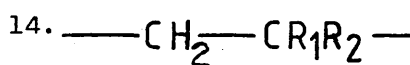
Repeat unit - poly(vinyl chloride).



Repeat unit - cellulose.



Repeat unit - polytetrafluoroethene



$R_1 = R_2 = \text{CH}_3$ , butyl rubber

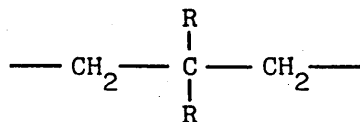
$R_1 = \text{CH}_3$ ,  $R_2 = \text{phenyl}$ , poly( $\alpha$ -methylstyrene).

Table 1.4 The Predominant Reaction observed for a selection  
of Irradiated Polymers

Crosslinking	Scission
Polyethylene	Polyisobutylene
Polypropylene	Poly(methyl acrylate)
Polystyrene	Poly- $\alpha$ - methylstyrene
Sulphonated polystyrene	Poly(vinylidene chloride)
Polyacrylates	Polytetrafluoroethylene
Polyacrylamide	Poly(ethylene terephthalate)
Poly(vinyl chloride) <sup>(a)</sup>	Cellulose
Polyamides	Poly(vinyl chloride) <sup>(a)</sup>
Polyesters	
Natural rubber	
Synthetic rubbers	
(except polyisobutylene)	
Polysiloxane	
Polyacrylonitrile	

(a) Note that poly(vinyl chloride) appears in both groups, since it has been observed to undergo crosslinking and scission by different authors.

- i) scission predominates in polymers which have the structure,



- ii) polymers that have a tendency to form monomers on pyrolysis, normally undergo scission during irradiation;<sup>2c</sup>
- iii) in branched chain hydrocarbons, scission appears to be predominate over crosslinking;
- iv) aromatic containing polymers show greater stability, in general, than aliphatics.

There is an abundance of detailed information on the radiation behaviour of polymers, but it is only necessary to consider the polymers and polymer systems of interest.

### 1.3.2 Polystyrene

From all the radiation studies undertaken, polystyrene is found to be one of the most radiation resistant polymers available.<sup>4b,6b,37,38.</sup> Parkinson and Keyser<sup>6b</sup> in their excellent review suggest possible reasons as to the stability of polystyrene. It is thought that this resistance is due to the protective action of the pendant aromatic rings. The radiation-induced processes responsible for this protection have not yet been conclusively delineated.

Large doses of  $\gamma$ -radiation result in crosslinking; an increase in the molecular weight of the species being detectable by gel permeation chromatography.<sup>39</sup> Simultaneous evolution of hydrogen increases with increased exposure to irradiation.<sup>40</sup> Shimuza<sup>40</sup> and Bowmer<sup>41</sup> et al have reported that elevation of the irradiation temperature, reduces the amount of crosslinking taking place, whilst

increasing the scission reaction, as would be anticipated. O'Donnell et al<sup>42</sup> found that an oxygen environment accelerates the scission reaction, with a marked decrease in crosslinking. This is contrary to what occurs when irradiation takes place in a vacuum. O'Donnell concludes that some of the polystyrene radicals, that would normally take part in crosslink formation, react with oxygen to form peroxides, which then decompose and cause degradation of the main chain. However polystyrene still emerges as a stable polymer as regards resistance to irradiation.

It is the aromatic stabilisation observed in polystyrene, that has caused interest in the utilisation of aromatic containing polymers in the field of radiation resistant materials.

### 1.3.3 Polysiloxanes

Silicones form a chemical group intermediate between organic polymers and inorganic glasses. They are unique in that they do not contain carbon in the main skeletal chain, however the side chains consist of groups such as methyl, phenyl or vinyl groups. The silicon-oxygen backbone<sup>43</sup> imparts an unusual high operating temperature, of up to 270 °C,<sup>33</sup> as well as flexibility at low temperatures (down to -70°C) along with resistance to hydrocarbon oils and corrosive chemical agents. Silicones have been studied in many investigations, with the conclusion that they are generally less resistant than most elastomers.<sup>4c, 6b, 33, 44, 45, 46.</sup> It was found that the irradiation of siloxanes resulted in a rapid hardening due to extensive crosslinking. The crosslinking reaction in siloxanes results in the evolution of hydrogen, methane and ethane. The reaction pathways leads to two radicals i.e.  $\equiv\text{Si}^\bullet$  and  $\equiv\text{SiCH}_2^\bullet$  which can give rise to three types of crosslinks.<sup>47</sup> The mole quantities of gas produced give some indication as to which crosslinks are produced.

Table 1.5 Possible Siloxane Crosslinks

Type of Crosslinks	Approximate Ratio
$\equiv\text{Si}—\text{Si}\equiv$	1
$\equiv\text{Si}—\text{CH}_2—\text{Si}\equiv$	2
$\equiv\text{Si}—\text{CH}_2—\text{CH}_2—\text{Si}\equiv$	0.5

Charlesby<sup>7</sup> reports that as the temperature of irradiation increases, the number of crosslinks formed are found to increase, this is in agreement with results from Fischer.<sup>48</sup> It was found that the samples irradiated at 200°C had twice the number of crosslinks, as samples irradiated at 40°C. Using electron beam as the source of irradiation, Okamura<sup>49</sup> found that the crosslinking efficiency was higher when irradiated in vacuum, than in air, but the difference is not as prominent as observed with polystyrene.

When Jenkins<sup>50</sup> irradiated polydimethylsiloxane, under a wide range of different atmospheres, he found that the crosslinking rate was the highest when in a vacuum, followed by helium, then nitrous oxide and finally an air atmosphere. When the temperature of irradiation was increased to 121°C, the crosslinking rates in vacuum and air atmospheres become almost equal.<sup>51</sup> It is evident that the temperature of irradiation and the conditions under which it takes place, are factors which affect the nature and extent of the 'net reaction' taking place.

To illustrate the wide difference between the behaviour of polydimethylsiloxane and polystyrene, it can be noted that it requires almost 100 times more energy to form a crosslink between chains of polystyrene than chains of polydimethylsiloxane.



### 1.3.3.1 Phenyl Substituents in Polydimethylsiloxane

The stability of polystyrene is due to the presence of the pendant phenyl group, acting in such a way as to dissipate the incident energy without bond rupture taking place. Substitution of aromatic groups, e.g. phenyl for methyl, in the polydimethylsiloxane structure, was found to impart resistance to  $\gamma$ -irradiation.<sup>7d,52,53</sup> Miller<sup>52</sup> showed that the position of the methyl group with respect to the aromatic substituent, has a marked effect on the radiation stability. Of the two side groups, the methyl group is the most susceptible to crosslink formation through bond rupture, of the three possible sites previously outlined. The methyl group receives the greatest protection when it is attached to the silicon to which the phenyl group is also attached. It was found that in phenylmethylsiloxane, crosslinking occurred through the aromatic as well as the methyl group.

The relative ease at which crosslinks are formed in a series of siloxane polymers are:-

— Si(Me) <sub>2</sub> — O —	20
— Si(Ø) (Me) — O —	2
— Si(Ø) <sub>2</sub> — O —	1

The overall radiation stability of a siloxane polymer may also be affected by the nature of the end-group, which may be a trimethylsilyl or dimethylphenylsilyl group. However, the contribution of the end-group, varies inversely with the average molecular weight. Thus, a large molecular weight polymer sample contains a very low percentage of end-groups, so the effect is somewhat reduced.

The presence of one or two phenyl groups results in the polymer being more resistant to crosslinking. When groups of increased

conjugation such as biphenyl and naphthyl, replace the pendent phenyl group; a greater stability is observed.<sup>52</sup> It appears that the degree of radiation protection is related to the extent of conjugation in the aromatic side chain.

#### 1.3.3.2 Dimethylsiloxane - Diphenylsiloxane Copolymers

Substitution of the methyl side groups, by phenyl confers an increased stability towards  $\gamma$ -radiation. An alternative method could be to incorporate blocks of diphenyl along the siloxane backbone chain. Warrick<sup>46,53</sup> found that the energy required to produce the same order of crosslinking in a dimethylsiloxane-diphenylsiloxane copolymer, was 20 times greater for a comparable dimethylsiloxane polymer. This was confirmed by Koike and Danno,<sup>54</sup> who reported that the efficiency of crosslink formation depends on the concentration of the phenyl group within the copolymer. They used calculations developed by Alexander and Charlesby<sup>55</sup> to determine the extent of the protective effect by the phenyl section. It was found that the protection by a single phenylsiloxane unit, extended over five or six monomer units of dimethylsiloxane. They compared these results with those of Alexander and Charlesby, whose work was based on the protective effect of styrene units in a isobutylene-styrene copolymer. There is a considerable difference in the protection offered by the phenyl group within a vinyl copolymer, compared to a siloxane copolymer situation. This difference is due to the number of phenyl groups within a monomer unit, and the structure of the backbone chain.

Irradiation of polydimethylsiloxane (PDMS) and polydimethylsiloxane-polydiphenylsiloxane (PDMS-PDPS) was carried out in the low temperature region. ( $-67 \rightarrow 196^\circ\text{C}$ ). Koike<sup>56</sup> found that whereas the crosslinking efficiency of PDMS below  $-100^\circ\text{C}$  was temperature independent

suggesting that crosslinking may be due to a non-radical process at this temperature, the copolymer was determined to be dependent on temperature, over the whole range studied. The difference in behaviour is thought to be because non-radical processes occur in the PDMS instance, whereas the copolymer undergoes crosslinking purely via a radical mechanism.

The extended protecting effect of phenylsiloxyl groups over 5-6 dimethylsiloxyl units, has been the subject of much disagreement,<sup>57</sup> but recent work by Delides<sup>58</sup> provides evidence for this protection.

#### 1.3.4 Radiation Behaviour of Copolymers

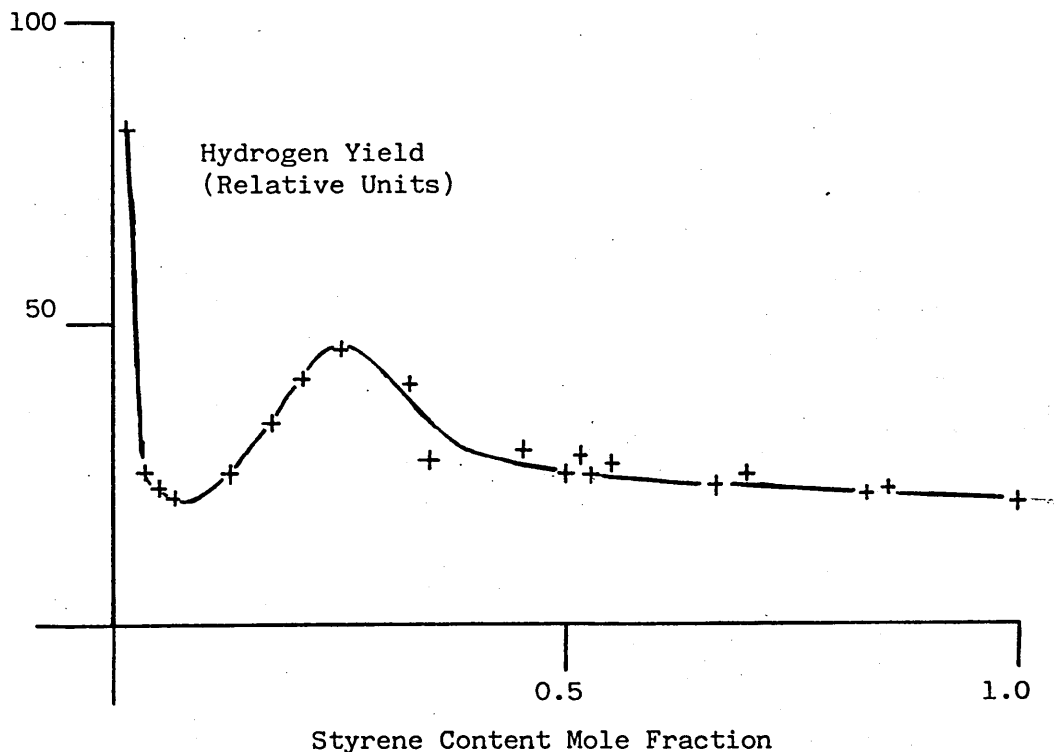
In order to obtain polymers of higher radiation stability, several studies on other copolymers containing phenyl groups have been carried out.

##### 1.3.4.1 Protection against Crosslinking

As early as 1954, Bopp and Sisman<sup>32</sup> studied the radiation effect of copolymers of styrene - butadiene, and styrene - acrylonitrile. Their initial observation was that the change in hardness of the copolymers was much less than for the pure polybutadiene and polyacrylonitrile. Witt<sup>59</sup> observed that styrene units not only absorb the radiation energy that is directly received, but are also capable of absorbing radiation energy from the neighbouring butadiene units, without undergoing any chemical change. In continuing this area of work, Basheer and Dole<sup>60,61</sup> found that radiation protection was greater when the styrene units were randomly dispersed along the polymer chain, than when it is in segregated units as in a block copolymer. It would appear that the transfer of energy from the butadiene to the styrene depends on the proximity of a butadiene unit to a styrene unit.

Maximum protection was observed in a styrene - acrylonitrile copolymer<sup>62</sup> when the styrene had a mole fraction of 0.05, (see Fig.1.1), this corresponds to one styrene unit/20 units of acrylonitrile.

*Fig 1.1 Irradiation of styrene-acrylonitrile copolymers at 31.7 MRad.*



With a decreased styrene content, 0.02 mole fraction, the protective effect is reduced, since the absorbed energy results in "damage" before it can be transferred to the protecting styrene units. These being sparingly dispersed within the siloxane polymer.

#### 1.3.4.2 Protection against Degradation

Methyl methacrylate is classified as undergoing degradation via main chain scission. When styrene - methyl methacrylate copolymers are irradiated at low doses,<sup>63</sup> the gas yields (e.g.  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $HCOOCH_3$  and  $CH_3OH$ ) indicated that styrene protected the methyl

methacrylate against main chain scission. This phenomenon was later investigated by Busfield, O'Donnell and Smith,<sup>64,65,66</sup> who agreed with the earlier observations, that the styrene units suppressed the emission of volatile products, which are characteristic of the degradation of methyl methacrylate.

In this particular type of system, the styrene is preventing scission of the main chain, whereas in polybutadiene crosslinks are prevented from forming between the main chain backbone.

#### 1.3.5 Effect of Additives

Certain additives which are incorporated into a polymer mixture, with the aim of gaining radiation protection, yet are not part of the polymer chain itself are termed "antirads". Antirads are effective against crosslinking, and scission, in the presence or absence of air.<sup>67</sup> Research into antirads, is based on the assumption that the polymer chain undergoes crosslinking through a radical mechanism. Compounds with a labile hydrogen, which after donation of this atom would form a stable radical, are the main compounds of interest. A reduction in crosslinking has been found, using aromatic amines, quinones, and aromatic hydroxyl, sulphur and nitrogen compounds.<sup>4c</sup>

Table 1.6 A selection of Antirads

N, N<sup>1</sup>-Dicyclohexyl-p-phenylenediamine

2-Naphthol

Phenyl Hydroquinone

1, 4-Naphthoquinone

Charlesby has extensively investigated the effect of antirads with polydimethylsiloxane.<sup>7e,68</sup> He found that although iodine may prevent crosslinking, its presence causes some degree of degradation. The behaviour of certain antirads has contributed to understanding of the mechanisms of crosslinking and degradation.

It is generally understood that the protective action is enhanced with increased concentration of antirad, up to the level of 1% w/w, but at this value, no more benefit is observed for further addition of antirad.

#### 1.4 Aim of this Work

At a recent Royal Society of Chemistry conference (Aston, April 1982), Sir Geoffrey Allen pointed out:

"for economic reasons, the emphasis in the future would be more on the modifications of polymers, than on the synthesis of new ones"<sup>69</sup>

This is how it would appear, when one considers the content of presently published work. There are the occasional new polymers reported, but the majority of developments tend to be modifications of existing polymers for specific applications. This concept encompasses the approach of this investigation.

The general objective of this proposal is to produce elastomers with precise, controlled structures and composition, to assess the performance in relation to absorbed dose, and thus to identify factors responsible for conferring radiation resistance. This could improve knowledge of the mechanisms of radiation protection and allow design of radiation resistant structures.

There is current interest at Central Electricity Generating Board in elastomers for use in nuclear engineering as gaskets and seals which are subject to radiation fields and elevated temperatures. Dow Corning are a major manufacturers of silicone elastomers for speciality requirements where high and low temperature properties and insulation characteristics are utilised e.g. gaskets, sealing strip, ducting, and cable insulation.

In general, polysiloxanes provide good thermal stability, however, they are below elastomers in radiation resistance. Despite much work it is still not clear how the following affects radiation resistance in polysiloxanes:

- i) Chemical structure
- ii) Additives

It is evident that the presence of a pendant aromatic group in polydimethylsiloxanes, or the presence of aromatic containing units in copolymers, increases the resistance to crosslinking. It is proposed that this study will investigate the possibility of obtaining a silicone elastomer or silicone blend having good radiation resistance, with retention of mechanical properties. The main area of interest will be the resistance to radiation of blends and block copolymers, in which an aromatic thermoplastic block forms a separate micro phase from the elastomeric silicone component.<sup>70</sup> The influence of this type of morphology upon radiation resistance has not been studied to date, although crystallinity and related morphological features have been investigated in some other cases.

Specifically, it is proposed that a range of polydimethylsiloxane/polystyrene blends are produced, along with a range of dimethylsiloxane-styrene block copolymers, which are prepared with a precise structure

and composition. This will be achieved by either anionic polymerisation or the condensation of preformed blocks. Variation of block sizes, relative proportions and distribution of either component should yield information on the extent to which energy can be transmitted from the dimethylsiloxane units to adjacent aromatic rings.

Full structural characterisation and appropriate physical and chemical properties will be determined for all polymers before and after irradiation. Of particular interest will be the determination of  $G(X)$ , or the yield of crosslinks per 100 eV of radiation energy absorbed, from gel measurements at different doses. From this investigation, information on the relation between chemical structure and radiation resistance should be obtained and further understanding of the effect of polymer morphology on radiation stability.



## CHAPTER 2

### POLYMER BLENDS

#### 2.1 Introduction

The incorporation of an aromatic component (i.e. polystyrene) within a polydimethylsiloxane elastomer, can be achieved in a number of ways. It can be brought about: (a) physically; (b) chemically or (c) by a combination of the two.

- (a) Physically - this requires the physical mixing or entanglement of the dissimilar polymer species to produce a material in which the polymer chains are interspersed to a degree which is dependent on the particular polymer system. The products of such a dispersion are generally known as 'polymer blends'.
- (b) Chemically - the range of chemical methods available include sequential polymerisation of two monomers, or condensation of two preformed polymer 'blocks'. Whatever procedure is adopted, the result is that a distinct chemical bond is formed between the two dissimilar species, giving a 'copolymer'.
- (c) Combination - a monomer can be physically mixed with a polymeric species, through the swelling of the polymer. This monomer can then be polymerised, to form an 'Inter-Penetrating Network' (I.P.N.). The end result is that the chains of the initial polymer have entangled about them a second polymer (i.e. the polymerised monomer), in a completely random network.

In this investigation the first two procedures have been used to study the effect of composition and morphology on the radiation behaviour of polysiloxane.

## 2.2 Polymer Blends

The concept of combining two or more different polymers to obtain a new material, was first realised in 1912.<sup>71</sup> It was much later, in 1948, that the first commercial blend was introduced by Dow Corning; this was a blend of polystyrene with 5% of a styrene/butadiene copolymer, giving a product with a very high impact resistance. It was this improvement of impact resistance, that was responsible for its attractiveness.

In recent years there has been many publications, books and conferences,<sup>72-76</sup> on the subject of polymer blends. Throughout their development, there has arisen some confusion over the meaning of certain terms used to describe the nature of blends. For example the word "compatible" in a general sense is not synonymous with "miscible". Since good mechanical properties can be obtained when two immiscible polymers are mixed together, the resulting product being a compatible blend.

Compatibility can best be described as being:

"how close a polymer blend approaches the ultimate state of molecular mixing".

The degree of homogeneity of two polymeric materials, is a description of the relative measure of the affinity of two dissimilar polymers for each other. The definition used by Yu<sup>77</sup> to describe a blend is:

"as a single entity of material containing within its physical boundary at least two thoroughly mixed polymers, which are not linked covalently".

### 2.2.1 Thermodynamics of Polymer Blends

To achieve the state of miscibility (i.e. complete homogeneity) of any mixture, whether it is a solution or a polymeric system, the free energy of mixing  $\Delta G_{\text{mix}}$  is the determining factor. This is defined as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (\text{Eqn.2.1})$$

where  $\Delta H_{\text{mix}}$  = enthalpy change on mixing;

$\Delta S_{\text{mix}}$  = entropy change on mixing.

If the free Energy ( $\Delta G_{\text{mix}}$ ) of a reaction or process is negative, then the process will proceed spontaneously. If  $\Delta G_{\text{mix}}$  is negative a true miscible mixture will form; however, if it is positive the two components will separate into two distinct phases. This thermodynamic analysis is in principle only applicable to equilibrium processes; but due to the restriction of large-scale molecular mobility, the mixing of two polymers should not strictly be considered as an equilibrium process. However this treatment which applies to solutions can be extended and used for the qualitative analysis of polymer blends.

If certain properties for two components are known, then predictions can be made as to whether two polymers are miscible. If the attraction between dissimilar species is greater than between those of the same, then the enthalpy of mixing will be negative. The mixing of any two components is also accompanied by an increase in entropy  $\Delta S > 0$ . The degree of change is much smaller for a polymer blend, than when a low molecular solution is considered. In very high molecular weight polymers the entropy change on mixing is essentially zero.

It follows then, that  $\Delta H_{\text{mix}}$  can be negative, zero or a small positive value, for  $\Delta G_{\text{mix}}$  to remain negative and result in a miscible mixture. Fig.2.1 shows three possible ways in which the free energy of mixing varies with composition.

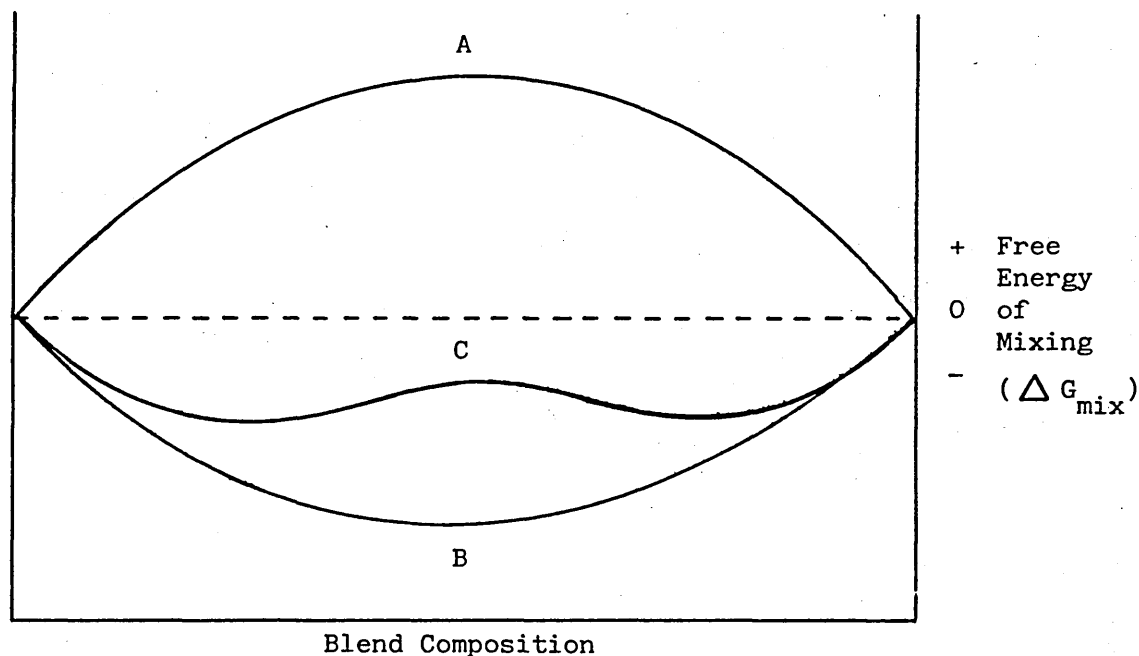


Fig.2.1 The Free Energy of Mixing of a 2-component system, which may be:-

- a) completely immiscible
- b) completely miscible
- c) partially miscible

The enthalpy of mixing, depends on the energy changes when two dissimilar species come in contact, and to an approximation, is independent of the molecular chain length.<sup>78</sup> This then allows the heat of mixing to be adequately estimated from the solubility parameters of the two polymeric species.

$$\Delta H_{\text{mix}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (\text{Eqn.2.2})$$

where  $V$  = total volume of the mixture

$\delta_1, \delta_2$  = solubility parameters of the two homopolymers.

$\phi_1, \phi_2$  = volume fraction of the two homopolymers.

The term  $\phi_1 \phi_2$  has a maximum value when  $\phi_1 = \phi_2$  , and in dilute mixtures  $\phi_1 \phi_2$  approaches  $\infty$  .

When  $\delta_1 = \delta_2$

$$\Delta H = 0,$$

and if  $\delta_1 \neq \delta_2$

the  $(\delta_1 - \delta_2)^2$  term is always positive.

Therefore it can be seen that  $\Delta H$  is always positive, with the result that the enthalpy term dominates the free-energy expression (eqn.2.1). With the entropy term essentially zero for high molecular weight polymers, the free-energy of mixing ( $\Delta G_{mix}$ ) is positive. This means that it is unlikely that a single homogeneous phase will form when two polymers are mixed.

Attempts to find miscible polymer pairs, by matching similar structures, or solubility parameters have proved rather unsuccessful. However, if certain specific interactions between polar groups along the polymer chain can take place, it is possible that the enthalpy becomes a negative value, and consequently the free energy of mixing ( $\Delta G_{mix}$ ) is negative, thus facilitating mixing.

These interactions, which could be due to dipole-dipole forces, allow selection of polymer pairs having chemical groups within, or attached to the chains, which on mixing yield an exothermic enthalpy ( $\Delta H_{mix}$ ) of mixing. Paul<sup>75a</sup> is of the opinion that miscible polymer pairs will be discovered, by selecting dissimilar structures, rather than by matching similar structures.

### 2.2.2 Classification and Properties of Polymer Blends

A limited number of miscible blends, can be classified by the presence of a common component.<sup>75b,76,79</sup> The most familiar example being that of polystyrene, and poly (2,6,-dimethyl-1, 4-phenylene oxide).<sup>80-83</sup> The reason for their miscibility is due to their almost

identical solubility products; in addition there may be some weak intermolecular interactions that contribute. These polymer blends give rise to a single phase morphology and as a result they are found to be transparent.

As previously mentioned, high molecular weight polymers are nearly always immiscible. This is seen, for example, in the polystyrene-polybutadiene, polysulphone-polydimethylsiloxane systems, where immiscibility causes separation to take place. Each separate component in the two phase morphological system, is usually quite large and there is poor interphase adhesion. As a result the blend has an opaque appearance, with poor mechanical properties.

Polymer blends may exhibit any of three possibilities for the effect of composition upon a mechanical property.

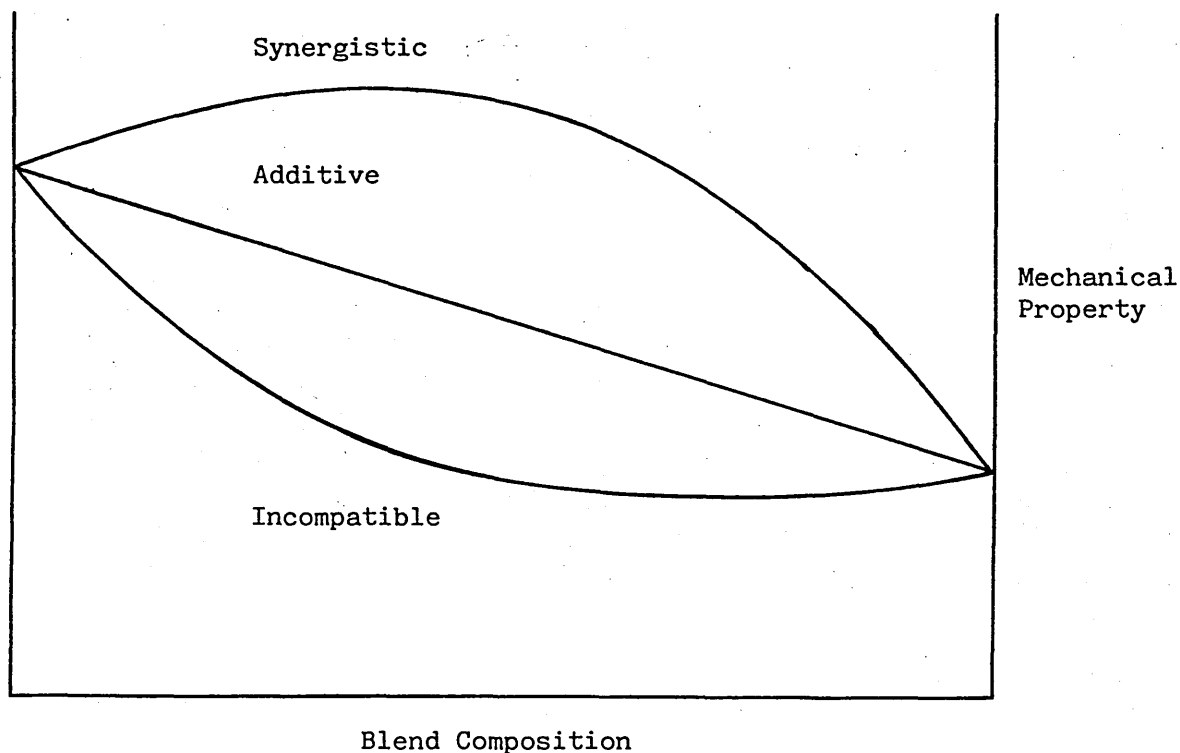


Fig.2.2 The possible effects of composition of Polymer Blend upon a mechanical property.

An additive effect occurs when the blend has a property which is a weighted average of that property for the pure homopolymer. This is seen where you consider the property of modulus. A blend gives an intermediate value for modulus which depends upon the percentage weight composition. Blending represents a less expensive route to materials of intermediate property values, rather than use of the more expensive block or graft copolymers.

When the rare situation arises that the property of the blend is larger than that for either polymer, a 'synergistic' effect is observed. Blends of polystyrene-poly (2,6,-dimethyl-1, 4-phenylene oxide), have the good thermal stability of poly (2,6,-dimethyl-1, 4-phenylene oxide) combined with the ease of processing of polystyrene. A blend can be obtained that is more easily processed, with slightly reduced thermal resistance, compared to pure poly (2,6,-dimethyl-1, 4 phenylene oxide). The synergistic effect is also observed in the modulus<sup>84</sup> and tensile strength<sup>85</sup> parameters.

In some polymer systems, it is found that properties such as strength and toughness exhibit a minimum at certain blend compositions. At this point the blend may have properties having values less than either of the homopolymers.<sup>75c</sup> This phenomena is due to poor interfacial adhesion between the two components, usually rendering the two polymers unsuitable for blending.

In the above discussion, only one property has been considered, but in many commercial application, the impetus for blending is to achieve an advantageous combination of properties. As with all new materials, the interest they attract is essentially due to their property - processing - cost performance.

This is the basis for the decision in this study to investigate the possibility of blending polystyrene and polydimethylsiloxane. A

combination of the good radiation resistance of polystyrene and the desirable thermal and mechanical properties of polydimethylsiloxane would give advantageous properties to a blend.

### 2.3 Blends involving Polystyrene and Polydimethylsiloxane

Polystyrene has been used in a number of polymer blends to obtain a completely miscible system, the second polymer being poly (phenylene-oxide) or its derivatives.<sup>76</sup> It is found that polystyrene exhibits partial miscibility with poly (vinyl methyl ether),<sup>86,87</sup> the polycarbonate of tetramethyl bisphenol - A,<sup>88</sup> and polymethyl phenyl siloxane.<sup>89,90</sup> Partial miscibility is taken as the appearance of the lower critical solution temperature<sup>75d</sup> (LCST). The LCST is the temperature at which an opaque two-phase blend system changes to a clear transparent material on cooling. On heating, the two phases separate to such an extent that a cloudy blend material is obtained. Paul and Barlow<sup>76</sup> see this as a clear indication that the blend originally consisted of a single homogenous phase at equilibrium.

A review of the literature, reveals very few reports of the blending of polydimethylsiloxane with other polymeric species. Blaga and Feldman<sup>91</sup> blended polyurethane with a number of polymers, including polydimethylsiloxane, in an investigation to determine the extent of miscibility. They found great difficulty in reaching definite conclusions regarding the partial miscibility of the blend systems. The morphology shows a two-phase heterogeneous mixture, whilst some aspects of the thermal properties indicated some degree of miscibility.

Thermodynamic considerations indicate that the blend comprising polydimethylsiloxane and polystyrene would be immiscible. Using equation 2.2 with the relevant solubility products (polydimethyl-



siloxane = 7.3; polystyrene = 9.1) gives too large an enthalpy of mixing. Galin and Rupprecht<sup>92</sup> devised a technique to determine the degree of miscibility, using polymer-polymer interaction parameters, of a siloxane-styrene block copolymer. In that particular study a series of siloxane/styrene blend of varying molecular weights were produced as a suitable comparison. They concluded that the blends behaved as separate macrophases, but made no further comment as to the degree of miscibility. Their experimental results would seem to reinforce the prediction that these two polymers are immiscible.

When Okazawa<sup>75b</sup> investigated the polystyrene-polydimethylsiloxane-ethyl acetate ternary system, they found that a narrow miscibility gap appeared, close to the cloud point curve of the corresponding binary polymer solvent system. This was observed with polydimethylsiloxane-polystyrene digomers (both approximately hexamer) at very low concentrations ( $< 4$  weight percent). This system is completely different to the proposed study where interest is in the preparation of a solid material rather than a polymer solution, but it does give some indication of the difficulty of obtaining a miscible blend of polystyrene and polydimethylsiloxane.

### 2.3.1 The Use of Compatibilizing Agents

Blends of immiscible polymers can be made more stable by the addition of a third component, which results in the formation of strong adhesive forces between the original components of the blend.<sup>93</sup> The excellent review by Rudin<sup>94</sup> gives a wide range of examples and explanations of this area of development.

In a study relevant to this work, Lu, Krause and Iskandar<sup>95</sup> investigated the effect of blending polystyrene with a styrene-dimethylsiloxane diblock copolymer. Primarily they were interested in

the glass transition temperatures ( $T_g$ ) of the polystyrene homopolymer and that of the polystyrene units contained with the block copolymer. It was found that  $T_g$  for the blended polystyrene was between the  $T_g$  of the pure polystyrene and that of the styrene units within the diblock copolymer. This phenomena was observed when the molecular weight of the homopolystyrene was both greater and smaller than that of the styrene block within the copolymer with which it was mixed. This is contrary to what was expected, in that when a homopolymer forms a separate phase in a mixture two  $T_g$  would be anticipated, those of the homopolymer and of the microphase.

### 2.3.2 Theoretical Prediction of the Miscibility of Polystyrene and Polydimethylsiloxane

A number of equations can be used to determine polymer-polymer miscibility, providing the solubility parameters and molecular weights are known. In this case a mathematical treatment of polymer miscibility, devised by Sonja Krause<sup>75a</sup> has been applied to the polydimethylsiloxane and polystyrene used in this study.

#### a) Calculation of the Solubility Parameter for each Polymer

The polymers of interest, polystyrene and polydimethylsiloxane, have solubility parameters 9.1 and 7.3 respectively. Solubility parameters for any new polymer system can be calculated from Group Molar Attraction Constants.

$$\delta = \frac{\sum F}{M}$$

Eqn. 2.3

where

$\delta$  = Solubility Parameter

$\rho$  = Density of the polymer at the temperature of interest.

$\sum F$  = Sum of the Group Molar Attraction Constants.

$M$  = Molecular Weight of the repeat group in the polymer.

b) Calculation of the Interaction Parameter

The interaction parameter between molecules of comparable size can be expressed in the following terms.

$$X_{AB} = \frac{(V_r)}{RT} (\delta_A - \delta_B)^2$$

Eqn. 2.4

where

$X_{AB}$  = Interaction Parameter between two polymers A and B.

$T$  = Temperature/K (298K)

$R$  = Gas Constant (1.987 cal deg mol<sup>-1</sup>)

$V_r$  = Reference Volume/cm<sup>3</sup> mol<sup>-1</sup> (taken to be 100 cm<sup>3</sup> mol<sup>-1</sup>).

Equation 2.4 becomes

$$X_{AB} = \frac{(\delta_A - \delta_B)^2}{6}$$

Eqn. 2.5

substitution of solubility parameter values

$$X_{AB} = \frac{(9.1 - 7.3)^2}{6}$$

$$X_{AB} = 0.54$$

- c) Calculation to determine the critical conditions necessary for miscibility (at all compositions).

It is necessary to know the approximate molecular weight of the polymers, in order to predict if they will be miscible.

The critical condition is:

$$(X_{AB})_{cr} = \frac{1}{2} \left[ \frac{1}{X_A^{1/2}} + \frac{1}{X_B^{1/2}} \right]^2 \quad \text{Eqn. 2.6}$$

where

$X_A, X_B$  = degree of polymerisation

(In this case

$$X_A = \frac{100,000}{104} = 961$$

$$X_B = \frac{350,000}{73} = 4795$$

substitution in Eqn. 2.6

$$\begin{aligned} (X_{AB})_{cr} &= \frac{1}{2} \left[ \frac{1}{4795^{1/2}} + \frac{1}{961^{1/2}} \right]^2 \\ &= 1.0904 \times 10^{-3} \end{aligned}$$

The theoretically determined interaction parameter,  $(X_{AB})$  is greater than the interaction parameter  $((X_{AB})_{cr})$  derived from molecular weights, by a considerable amount, indicating that the polymer blends of interest are likely to be immiscible at all compositions.

To obtain a miscible blend with components of the same molecular weight as the siloxane and polystyrene the difference in the solubility parameter would need to be less than 0.080.

(This value has been obtained in the following way

$$\text{For } (X_{AB})_{cr} \approx X_{AB}$$

$$1.1 \times 10^{-3} \approx \frac{(\delta_A - \delta_B)^2}{6}$$

$$\delta_A - \delta_B \approx \sqrt{6.6 \times 10^{-3}}$$

$$\delta_A - \delta_B \approx 0.081$$

Thus the blends of interest would likely be immiscible due to the wide differences in the solubility parameters and molecular weights of the polymer components. However, in this study interest lay in the effect of the polystyrene, as a separate microphase, on the radiation behaviour of polydimethylsiloxane, whether this is obtained in blending or block copolymerisation of the components.

#### 2.4 Preparation of Polystyrene/Polydimethylsiloxane Blends

#### 2.4.1 Reagents

Polystyrene was purchased from British Drug Houses,  $\bar{M}_n$  Psty. 100,000. It was purified by dissolution in tetrahydrofuran (THF) followed by precipitation into stirred methanol. A typical stock solution of polystyrene prepared in THF would contain  $200 \text{ gdm}^{-3}$ .

Polydimethylsiloxane was supplied by Dow Corning (vinyl free)  $\bar{M}_n$  PDMS 253,300  $\bar{M}_w$  674,800. A typical stock solution of  $200 \text{ gdm}^{-3}$  was prepared in THF.

Tetrahydrofuran was purchased from Fluka, then distilled with potassium metal to remove the stabiliser and any moisture that may be present.

#### 2.4.2 Mixing

Each of the stock solutions underwent thorough stirring prior to use to ensure a complete dissolution of the homopolymers. For the additions of the two polymers, a measuring cylinder was used for the higher percentage blends (15-50%), with a pipette being used for the addition of small volumes of polymer solution, each being washed with THF after the additions to remove any residual polymer. The blend was mixed by use of a stirrer in a reaction vessel for 20 minutes. This time was chosen as the 'standard mixing time', a longer mixing time did not visually reveal any decrease in opacity. Prolonged stirring, with the shearing motion of the blade, has the danger of causing bond scission of the polymer chains.

#### 2.4.3 Casting

Experimentation involved the casting of polymer films of varying thickness. In this approach a thin film of cellulose was stretched taut over a 6" diameter embroidery ring, upon which was placed a glass annulus with a precision ground edge (Fig. 2.3).

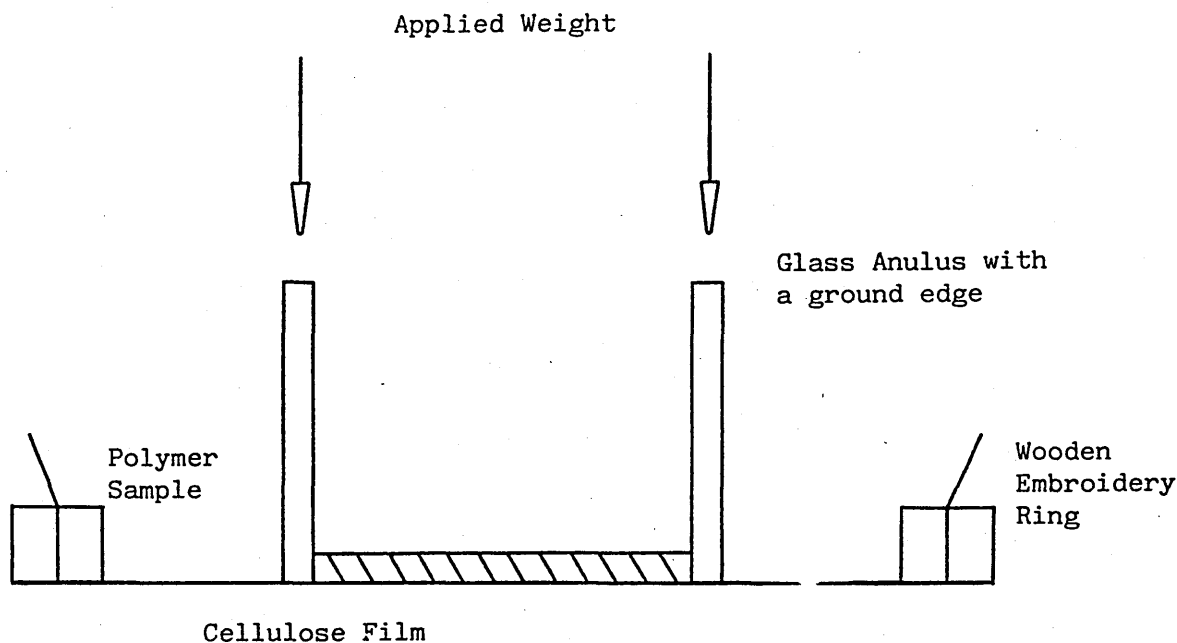


Fig.2.3 Apparatus used to prepare films of Polymer Blends

The solvent evaporated very slowly from the casting solution, over a period of 24 hours, to leave a film containing some residual THF. However it was found that phase separation took place in these thin polymer films, and this was quite noticeable at  $> 15$  w/w percent polystyrene when small spheres could be visibly observed. With increasing polystyrene content, gross separation of the components was observed. Then the two separate phases consisted of a bottom rubbery layer, predominantly siloxane (95% w/w), with a rigid upper layer of polystyrene (95% w/w). Clearly the slow evaporation of the THF allows the polymer components whilst in the fluid state to separate from the unlike species and associate together leading to phase separation.

#### 2.4.4 Use of Freeze-Dryer

The casting method allowed separation due to the slow removal of solvent. Rapid removal of solvent might be expected to minimise this problem. A freeze-dryer was designed in thick walled glass (fig. 2.4) to accommodate four individual vessels containing blend mixtures.

The thoroughly mixed blends were connected to the freeze-dryer, via the glass connecting arms. Careful manipulation of the vacuum allowed the solvent to be removed in approximately 20 minutes, after which overnight drying at 55°C in a vacuum oven ensured full removal of solvent. A range of blends of varying composition from 1 w/w percent to 50 w/w percent polystyrene were prepared using this procedure.

#### 2.4.5 Composition of Blends

The percentage composition of the blends was confirmed using infrared spectroscopy. The analysis was carried out using 2 cm diameter potassium bromide discs (these being transparent to infrared radiation from 2 to 25  $\mu$ m wavelength). A thin film sampling technique was used to allow an adequate amount of material to be deposited on the plate but allowing sufficient transmission of radiation to be registered by the detector.

The specific bonds of interest were at 560  $\text{cm}^{-1}$  and 1260  $\text{cm}^{-1}$  for polystyrene and polydimethylsiloxane respectively. By using a standard "mapping" procedure, base lines were drawn across the points 470 - 600  $\text{cm}^{-1}$  and 1210 - 1320  $\text{cm}^{-1}$  allowing the maximum peak heights to be measured.



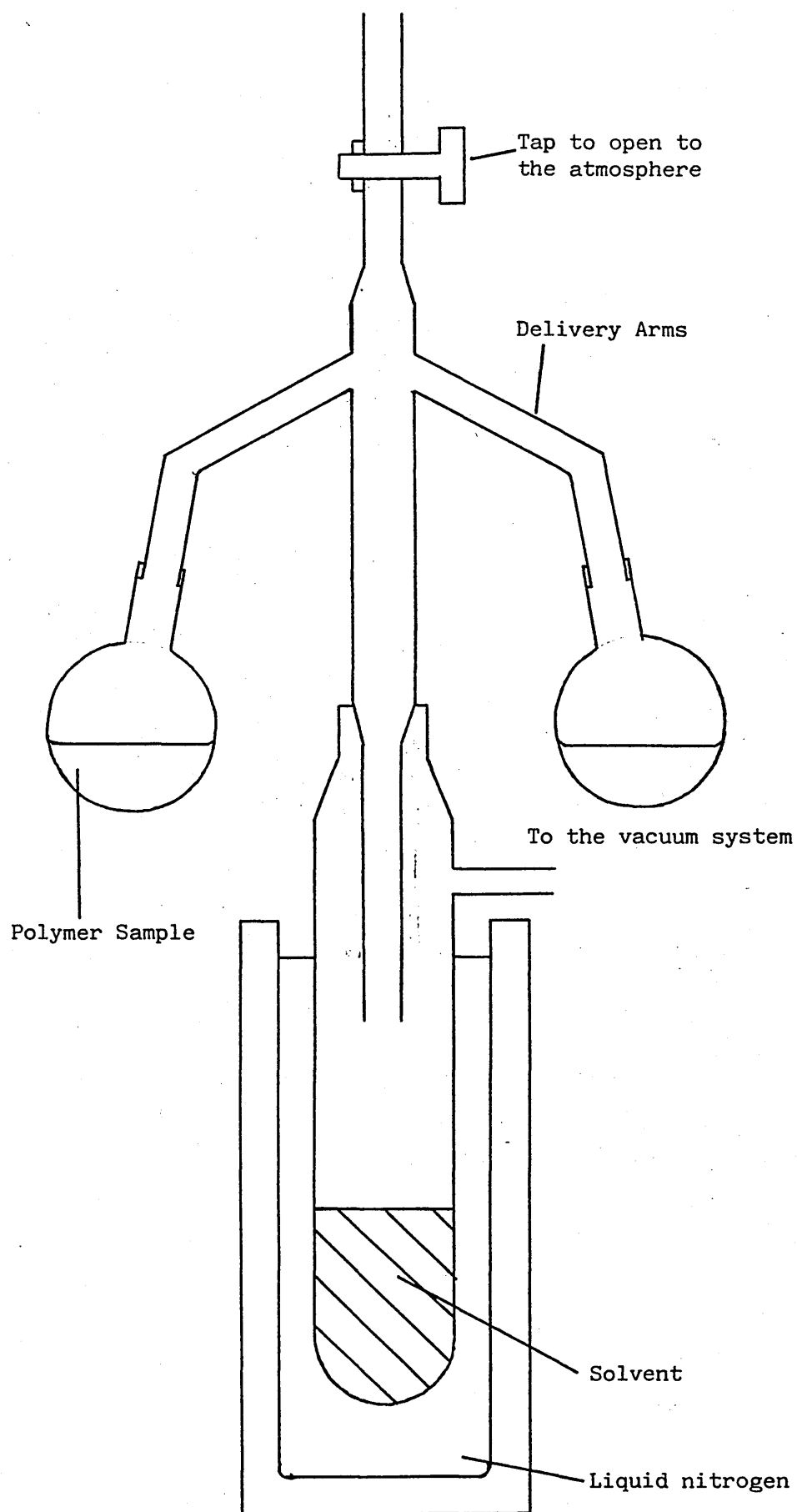


Fig.2.4 Freeze-Dryer

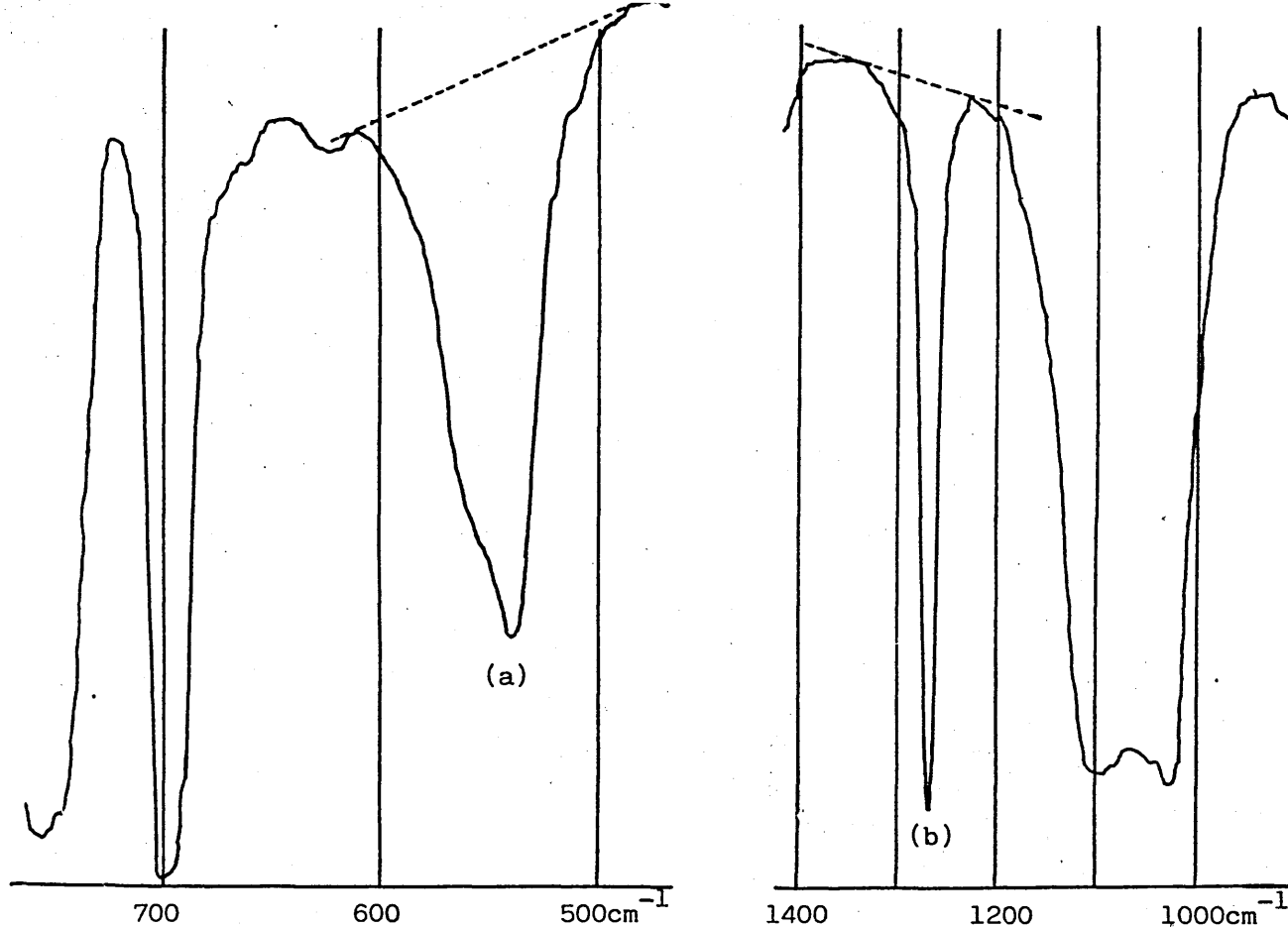


Fig. 2.5 Peaks (a) Corresponding to Polystyrene component.

(b) Corresponding to Polydimethylsiloxane component.

Errors arose from the measurement of peak heights via the mapping technique, and the thickness of the pen lines in the recording of the spectra. As was expected the precision limits increased with diminishing band intensity. Among the problems encountered were difficulties in obtaining well resolved peaks, from samples with small amounts of one component, in this case extra layers of samples were deposited to give discernible peaks. No investigation of the effect of film thickness was carried out, although repeat samples gave results in close agreement.

Table 2.1 Infrared Data for the Blend Samples

Sample % Polystyrene ± 1.0	Absorbance		Absorbance Ratio Psty/Pdms	Error +/-	% Precision Limit
	Polystyrene ± 0.50	Pdms. ± 0.50			
2	6.0	95.0	0.063	0.005	0.079
3	5.0	69.5	0.072	0.008	0.111
5	5.6	71.5	0.078	0.008	0.100
17	11.5	66.5	0.173	0.006	0.035
25	14.0	60.5	0.231	0.01	0.043
50	26.0	50.0	0.520	0.015	0.029
75	56.5	20.0	2.825	0.093	0.033

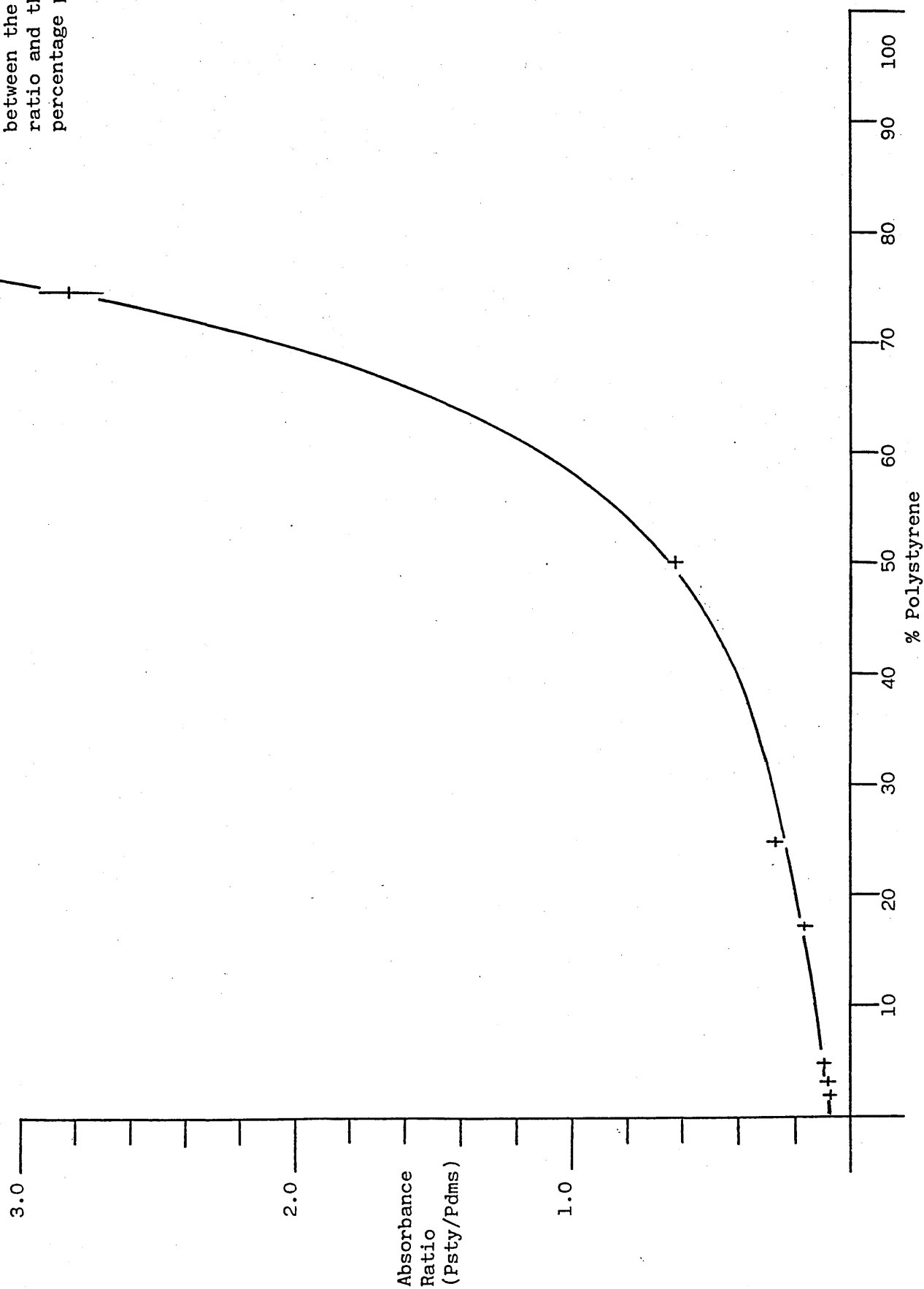
The results are illustrated in Fig. 2.6 and Fig. 2.7.

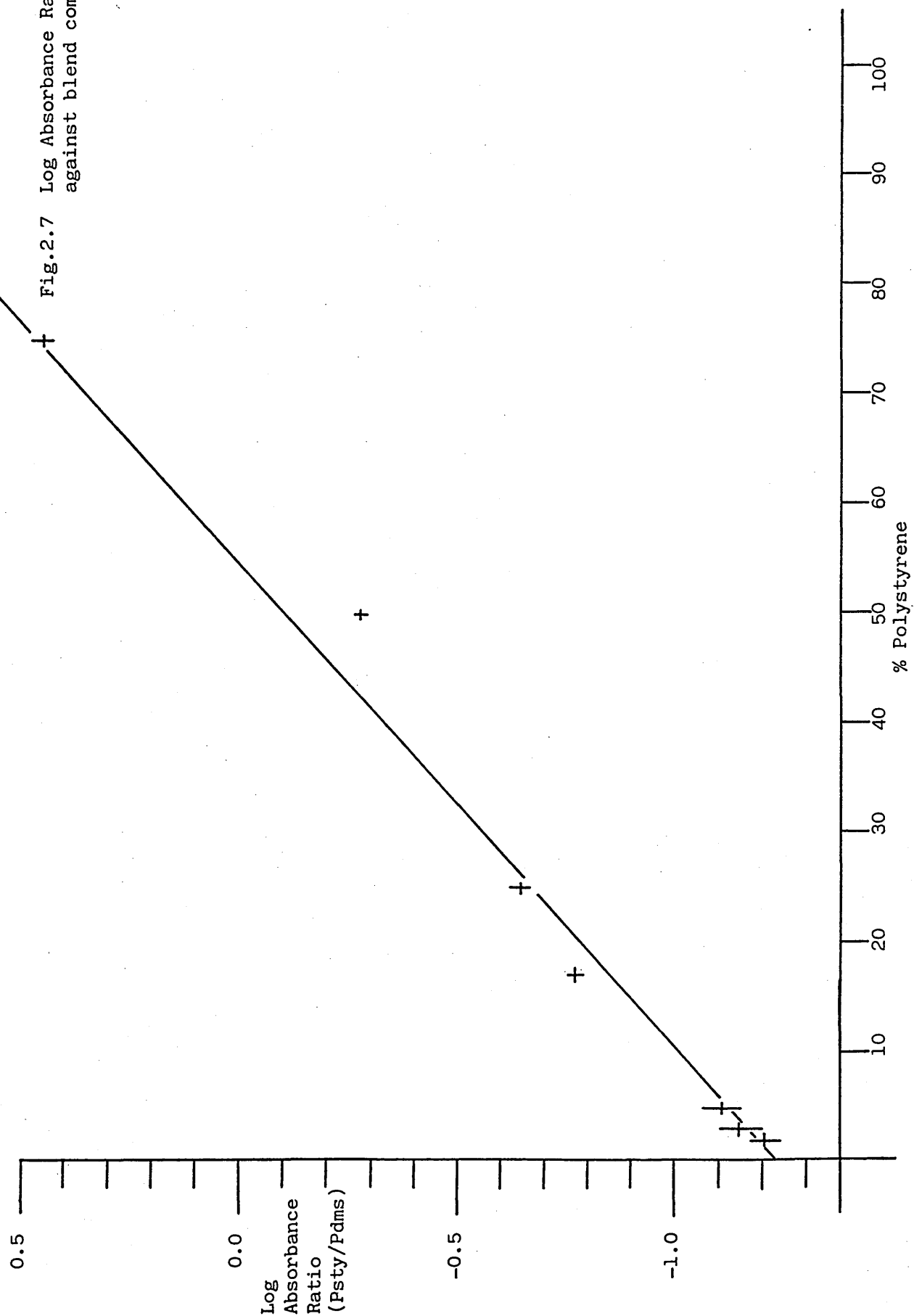
From the results it is clear that the band ratio is a precise method of analysis for the blends, although the errors make it very difficult to analyse samples containing less than 2 w/w percent of either of the components. A possible improvement to this technique would be to use a method for the cryogenic grinding of the polymer with potassium bromide to produce an intimate mixture for production of a KBr disc.

## 2.5 The Criteria for Miscibility

The preparation of a miscible blend, by the mixing of two polymer materials, usually results in an optically clear material. The optical clarity of a blend, has been used to determine whether a material is miscible or immiscible. However under special circumstances, films made from blends of immiscible polymers are found to be optically clear, in that they are so thin that light encounters only one of the two phases.<sup>98</sup> Optically clear samples have also been

Fig.2.6 The relationship  
between the absorbance  
ratio and the weight  
percentage polystyrene





obtained when the difference between the refractive indices of the two components is less than 0.01.<sup>99</sup> This particular method for determining whether a blend is miscible gives uncertain results, with no definite conclusions, hence this method has been ruled out in this study.

The most unambiguous criterion of polymer miscibility is the detection of a single glass transition at a temperature intermediate between those corresponding to the two component polymers. This implies that within the limits of detection, the blend is molecularly homogeneous. At the other extreme, blends of immiscible polymers separate into distinct phases, which exhibit glass transitions identical in temperature and width to those of the unblended components.

#### 2.5.1 Thermal Analysis - Experimental

All the blend samples were analysed using a Mettler 30 Differential Scanning Calorimeter (DSC), coupled with a TA microprocessor. The temperature axis of the calorimeter was calibrated from 35°C to 450°C using an indium-lead-zinc alloy (melting point 156.6, 327.4, 419.5°C respectively). The samples, after having been accurately weighed, were compacted into the base of the sample holder, to cover the whole of the base surface and to ensure good thermal contact. It is essential that the thermocouple situated directly underneath the sample holder, accurately records the temperature of the polymer material. Having been placed within the head of the "oven", the sample and reference is quenched very rapidly to a predetermined temperature. In this instance the heating process commenced at -175°C at 10°C min<sup>-1</sup>, under an air atmosphere. The data obtained during the screening was stored in the TA microprocessor and could be reproduced as a thermogram. (Fig.2.8). A selected portion of the scan can be expanded on the printer-plotter.

On passing through the glass transition temperature ( $T_g$ ) there is a discontinuous increase in the heat capacity of the polymer. The transition due to the siloxane is clearly observed in Fig.2.9. An expanded section of this temperature area is seen in Fig.2.10. Regression lines are computed before and after the transition. The intersection of the first regression line with the inflexional tangent, as well as the mid point of the inflexional tangent are determined.

The area of the peaks, both endothermic and exothermic, were reproduced on an expanded scale (Fig.2.11) and the precise temperature of the transition obtained. The microprocessor determines the area of the peaks, after construction of a standard baseline.

## 2.5.2 Thermal Analysis - Results and Discussion

### 2.5.2.1 $T_g$ for Polydimethylsiloxane

The method used for determination of  $T_g$  has been described, however the range over which the transition takes place can also be determined. This "range" is seen in Fig. 2.12.

Fig. 2.12 The Glass Transition of Polydimethylsiloxane.

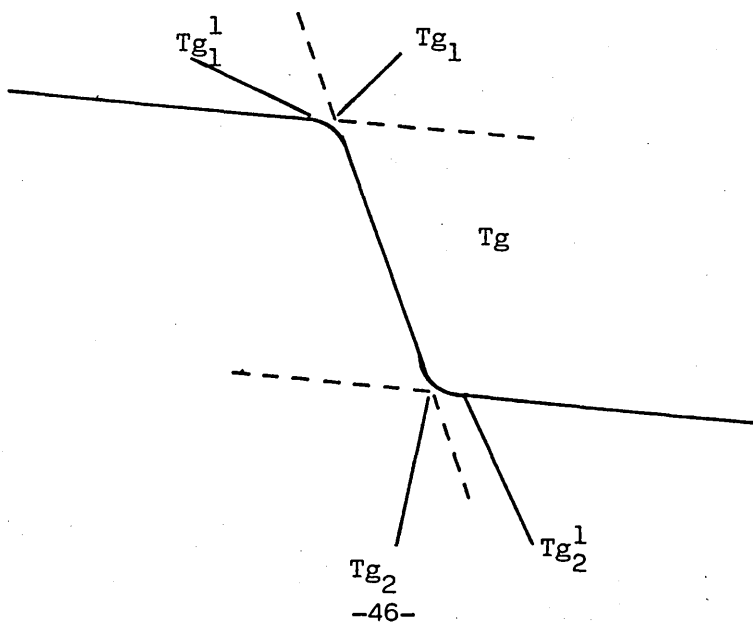


Fig.2.8 Thermogram of a Polystyrene  
polydimethylsiloxane Blend

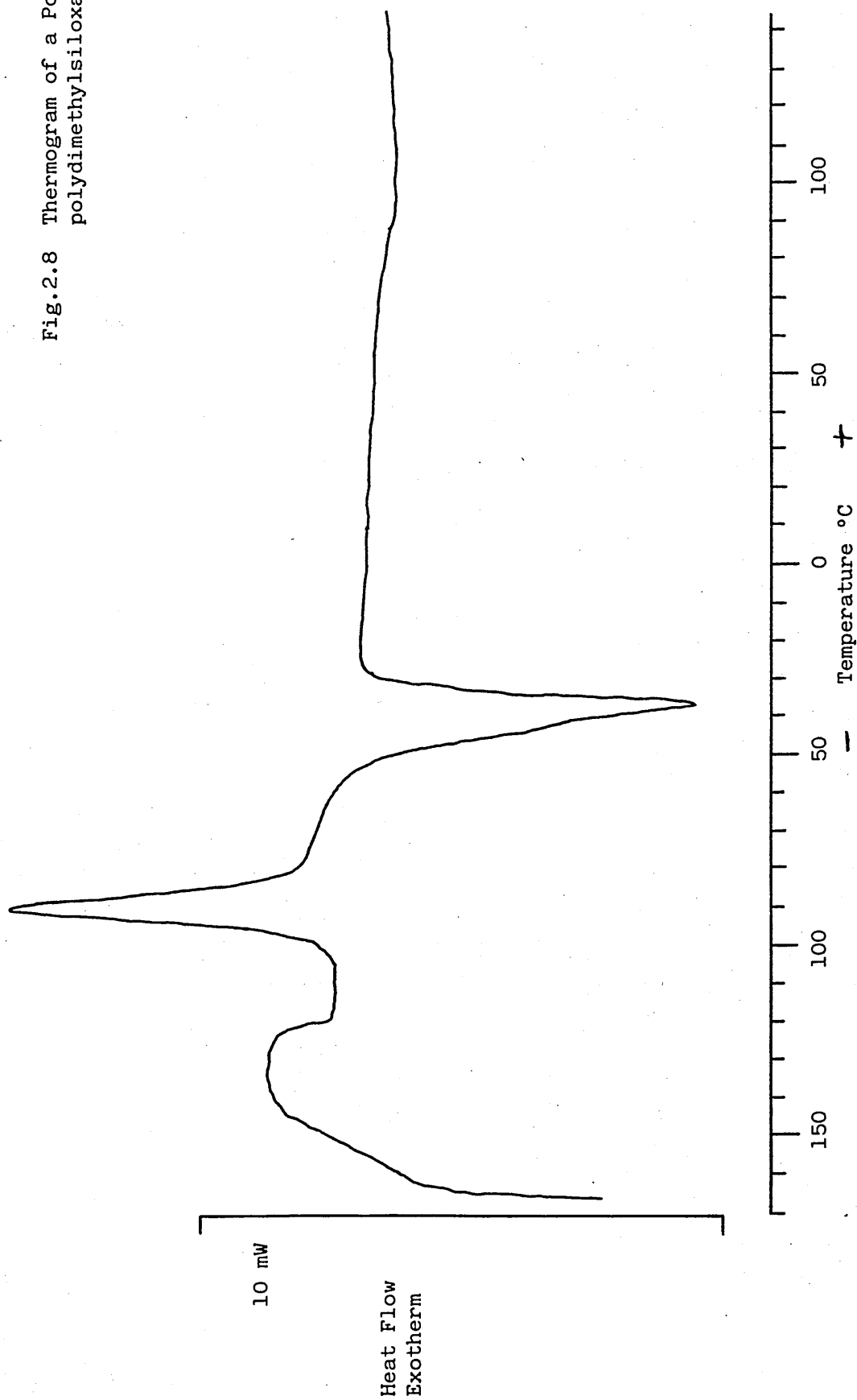




Fig.2.9 Thermogram of Polydimethylsiloxa

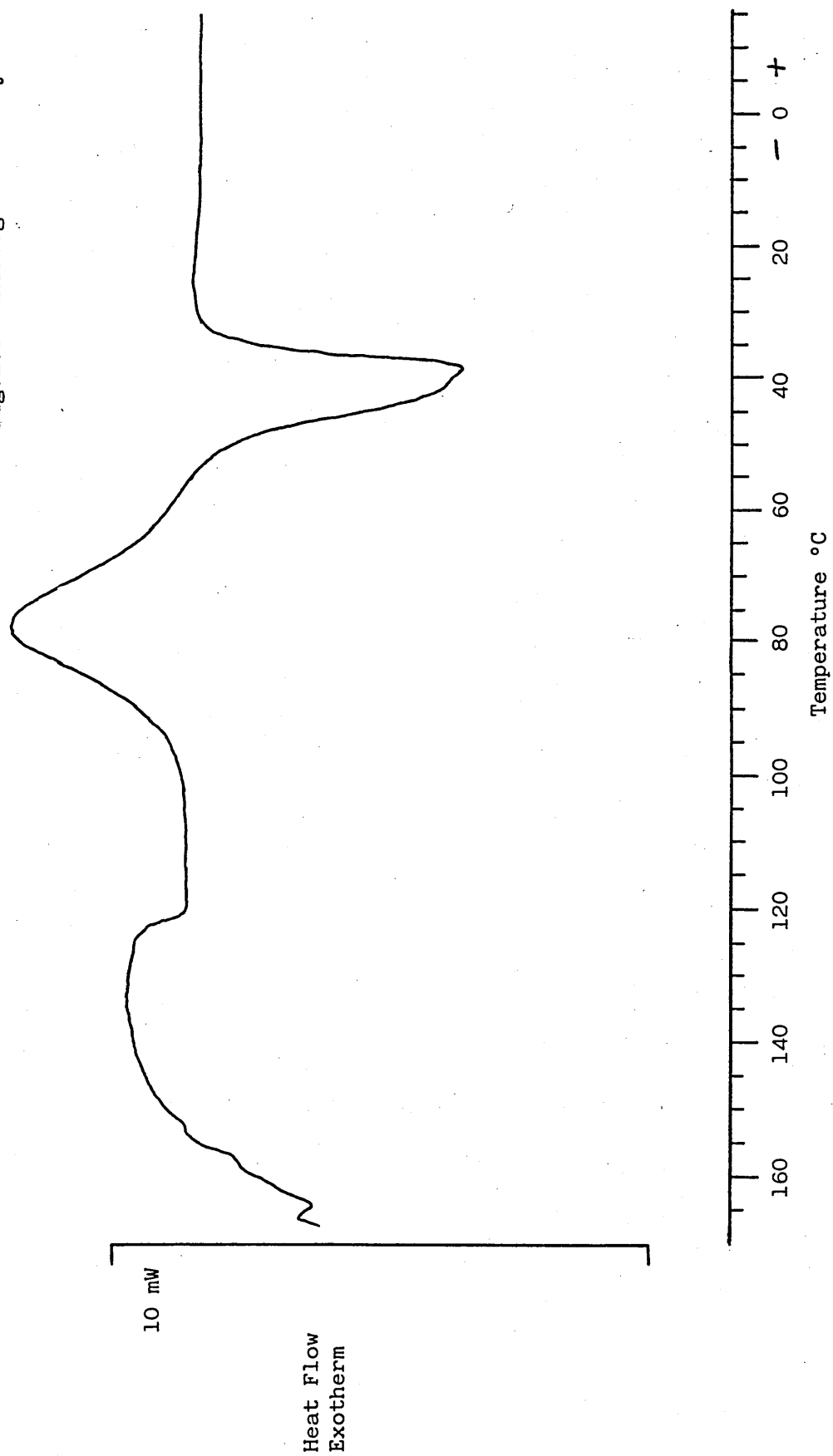


Fig.2.10 Expanded region of the thermogram illustrating the siloxane glass transition.

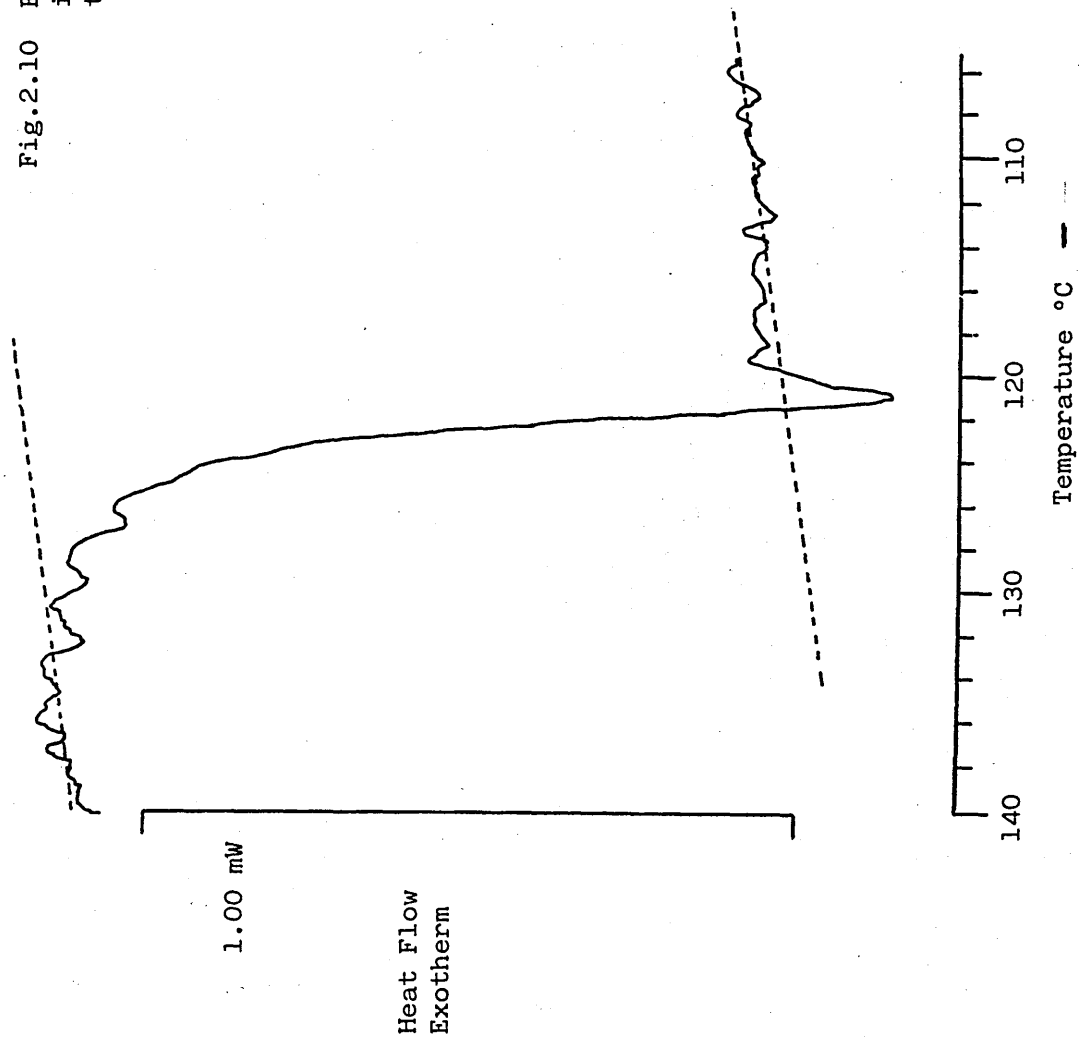
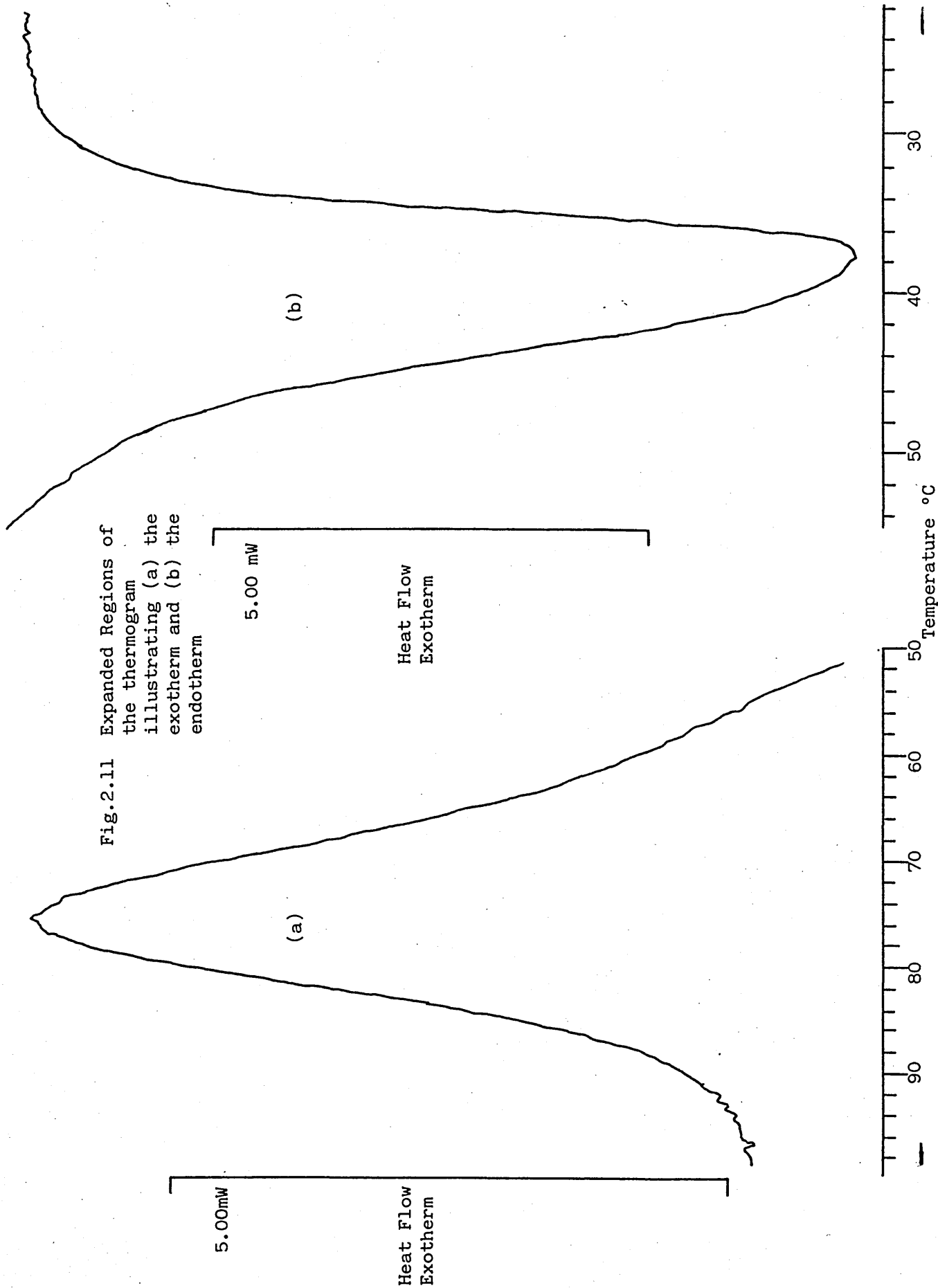


Fig.2.11 Expanded Regions of  
the thermogram  
illustrating (a) the  
exotherm and (b) the  
endotherm



The "range" can be taken as either

$$\Delta T_g = T_{g2} - T_{g1}$$

or

$$\Delta T_g^1 = T_{g2}^1 - T_{g1}^1$$

The latter value,  $\Delta T_g^1$ , would seem to be a more reasonable definition for the range as shown in Fig. 2.12, but it can be rather subjective. Therefore, the alternative value,  $\Delta T_g$ , would seem to be a more suitable value.

The data relating to  $T_g$  of the pure polydimethylsiloxane is given in Table 2.2.

Table 2.2 Data relating to the Glass Transition of  
the pure polydimethylsiloxane.

Mass m.g.	$T_g$ °C	$T_{g1}$ °C	$T_{g2}$ °C	$\Delta T_g$ °C	$\Delta C_p$ mw/weight
18.14	123.21	-123.5	-119.6	3.9	0.0694
18.14	123.37	-124.0	-119.4	4.6	0.0752
7.68	123.72	-125.2	-122.2	3.0	0.0587

(Heating rate  $10^\circ\text{C min}^{-1}$ )

$T_g$  for the pure polydimethylsiloxane was found to be  $-123.4 \pm 0.3^\circ\text{C}$ . This is in excellent agreement with values found in the literature.<sup>100,101.</sup> Cowie<sup>102</sup> used the same heating rate ( $10^\circ\text{C min}^{-1}$ ) to obtain a  $T_g$  of  $-124^\circ\text{C}$

Data associated with the various blends analysed are given in Table 2.3.  $T_g$  for the polydimethylsiloxane in the blends shows no apparent trend with increasing polystyrene content. A mean value of  $-122.5 \pm 0.3^\circ\text{C}$  was obtained. This is lower than the value for pure polydimethylsiloxane, by a difference of  $1^\circ\text{C}$ . The fact that all the thermograms came from the same instrument, and were determined consecutively as a batch, with some samples repeatedly determined, leads to the conclusion that this is a significant difference in  $T_g$ .

Measurement of the temperature range over which the glass transition ( $T_{g2} - T_{g1}$ ) takes place shows that it increases from an average of  $3.75^\circ\text{C}$  with pure polydimethylsiloxane to  $4.66^\circ\text{C}$ , the mean value for the blends analysed.

The change in the heat capacity also is found to be different between the pure polydimethylsiloxane and the blends. If the height between the intersections  $T_{g2}$  and  $T_{g1}$  is taken to be the change in the heat capacity ( $\Delta C_p$ ) the average value is  $0.067 \pm 0.008$  for the pure polydimethylsiloxane. The  $\Delta C_p$  values for the blends are given in Table 2.3, but these are corrected for the composition and given in Table 2.4.

The change in heat capacity ( $\Delta C_p$ ) appears to be higher in the blends than the mean value obtained from the pure polydimethylsiloxane.

Elevation of the  $T_g$ , the 25% increased broadening in the transition, and the slightly higher heat capacity values ( $\Delta C_p$ ), are all indicative of some interaction occurring at the molecular level.

When two polymers separate into distinct phases,  $T_{g1}$  and its range, is identical to those of the unblended components. Where partial mixing between the components takes place,  $T_g$  of each individual component may be shifted.<sup>103,104</sup> Broadening of the transition has also been observed in blends of partial miscibility.<sup>75e,105</sup>

Table 2.3 Data Associated with the Glass Transition  
of Pdms in Blends.

Sample % Polystyrene	Weight mg	Tg °C	Tg <sub>1</sub> °C	Tg <sub>2</sub> °C	Δ Tg °C
2%	19.58	-122.47	-124.3	-119.5	4.8
		-122.31	-124.8	-119.4	5.4
3%	18.895	-122.46	-124.8	-119.6	5.2
		-122.62	-124.4	-119.5	4.9
5%	19.72	-122.78	-124.5	-119.8	4.2
		-122.62	-123.7	-120	3.7
7%	18.785	-122.73	-124.8	-119.8	5
10%	18.05	-122.52	-125.1	-119.8	5.3
		-122.84	-124.2	-120.2	4
		-122.40	-124.4	-119.5	4.9
15%	19.77	-122.76	-124.2	-119.8	4.4
20%	19.97	-122.59	-124.8	-119.8	5
		-122.50	-124.4	-120.0	4.4
30%	16.58	-122.52	-124.0	-120.0	4
50%	13.68	-122.01	-124.2	-119.2	5

The results for T<sub>g</sub> of the polydimethylsiloxane indicates that the siloxane in the blend, has within its phase some mixing of a second component i.e. polystyrene. This assertion is made, even with knowledge of the theoretical predications for total immiscibility which was given earlier, since it is apparent that some degree of interaction has taken place. It is possible that the interaction is limited to the localised area near the surface of the two components, giving rise to "different regions" within the siloxane boundary. Another explanation is that there is a small number of polystyrene molecules entwined with those of the siloxane. This would give a siloxane component whose transition from a glossy material to that of a rubbery nature, is somewhat restricted, therefore takes place over a wider temperature range, and at a slightly higher temperature.

Table 2.4 Experimental and "Corrected" values for the change in the heat capacity, of the glass transition of polydimethylsiloxane.

Sample Percent Polystyrene	Mean Heat Capacity $\Delta C_p$ (mw/weight)	Corrected Heat Capacity $\Delta C_p$
2	0.0768	0.0783
3	0.07675	0.0819
5	0.0733	0.0691
7	0.0726	0.0781
10	0.0685	0.0733
15	0.0719	0.0846
20	0.656	0.0854
30	0.0488	0.0697
50	0.0422	0.0844

#### 2.5.2.2. Tg for Polystyrene

The presence of the benzene ring attached to the hydrocarbon backbone chain restricts rotation about the C—C bond, which results in an increase in Tg. The —Si—O— bond is quoted<sup>107</sup> as being one of the most flexible backbone chains, giving rise to a very low Tg (−123.5°C), whereas the more rigid backbone of polystyrene gives a Tg of 100°C.

Homopolystyrene was screened over the temperature range 30–150°C, at the same heating rate as for polydimethylsiloxane, and the results are given in Table 2.5.

Table 2.5 Data relating to the Glass Transition  
of the homopolystyrene.

Sample	Mass	Tg °C	Tg <sub>2</sub> °C	Tg <sub>1</sub> °C	ΔTg °C	Heat Capacity
1	17.13	99.90	104.2	97	7.2	0.8837
2	17.13	99.73	104.2	96.2	8.0	0.8895
3	8.89	101.20	104.3	98.6	5.7	0.2965



Table 2.6 Data associated with the Glass Transition

of Polystyrene in the Blends

% Polystyrene in Blend	Weight mg	T <sub>g</sub> °C	T <sub>g2</sub> °C	T <sub>g1</sub> °C	Δ T <sub>g</sub> °C
3	18.895	Not detectable			
5	19.72	Not detectable			
7	18.785	100.05	Not detectable		
10	18.05	99.92	105.5	94.5	11.0
20	19.97	83.97	97	80	17
30	16.58	86.08	97.8	82	15.8
50	13.68	89.70	103.5	89	14.5

The experimental value was determined to be  $100.3^{\circ}\text{C} \pm 0.9^{\circ}\text{C}$ , which is in good agreement with polystyrene of similar molecular weight determined at a similar heating rate.<sup>92,108,109.</sup> The transition takes place over a wider temperature range ( $7.5^{\circ}\text{C}$ ), than for the polydimethylsiloxane. This behaviour was found also in work by Krause et al<sup>110</sup> where the temperature range for polystyrene was found to be  $6^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , with that for polydimethylsiloxane as  $2^{\circ}\text{C}$ .

The change in heat capacity ( $\Delta C_p$ ) in polystyrene is much less than that for polydimethylsiloxane, which makes it very difficult to obtain  $T_g$  in blends of low polystyrene content. The limit of detection of this method of determination is found to be around 7% w/w polystyrene. Table 2.6 gives results for  $T_g$  of polystyrene in the blends. The corrected heat capacity change ( $\Delta C_p$ ) gives values (Table 2.7) slightly different to those in homopolystyrene.

$T_g$  is very clearly depressed upon incorporation of the siloxane, and broadening of the transition ( $\Delta T_g$ ) is found to occur. This again indicates that some interaction between the two components is taking place.

Table 2.7 The change in Heat Capacity of Polystyrene in Polydimethylsiloxane-Polystyrene blends

% Polystyrene in Blend	Heat Capacity $\Delta C_p$	Corrected Heat Capacity $\Delta C_p$
20	0.1965	0.0492
30	0.2196	0.0441
50	0.2832	0.0414

### 2.5.2.3 Exotherm of Polydimethylsiloxane

A large sharp exotherm caused by the crystallisation of polydimethylsiloxane commenced at  $-102^{\circ}\text{C}$  with a maximum occurring at  $-78^{\circ}\text{C}$  (mean of 5 replicates). Table 2.8 lists the temperature of the exotherm peak for the pure polydimethylsiloxane, and the polydimethylsiloxane component in the blend.

Table 2.8 The temperature at which the Cold Crystallisation in Polydimethylsiloxane takes place.

Sample % Polystyrene	Exotherm Temperature $^{\circ}\text{C}$
0	-78
2	-92.3
3	-90.2
5	-86.3
7	-90.5
10	-90.2
15	-85.5
20	-90.6
30	-87.8
50	-89.3

The presence at this peak indicates that during the cooling process, part of siloxane remains uncrystallized in the amorphous state. During the heating process these amorphous regions undergo alignment, giving rise to 'cold crystallisation'. The slower the cooling rate, the greater is the initial crystallisation, thus there would be less

amorphous siloxane available for cold crystallisation on the heating cycle. Helmer and Polmanteer<sup>111</sup> studied the effect of the quenching rate upon supercooling of polydimethylsiloxane. They reported that supercooling was observed when the cooling rate was higher than  $1.6^{\circ}\text{C Sec}^{-1}$  ( $96^{\circ}\text{C min}^{-1}$ ). At this cooling rate, no exotherm peak, i.e. no cold crystallisation was observed.

The minimum temperature required for cold crystallisation seems to be related to  $T_g$ . Boyer<sup>112</sup> established the following empirical relationship:

$$T_c (^{\circ}\text{C}) = 32.5 + 1.125 T_g (^{\circ}\text{C})$$

Substitution of the experimentally determined transition values ( $T_g$ ) of  $-123.5^{\circ}\text{C}$ , into this equation predicts the minimum crystallisation temperature to be  $101.6^{\circ}\text{C}$ . This predicted value is in very good agreement with that obtained by our experimentation.

The presence of polystyrene has a profound effect on the temperature of the cold crystallisation peak, however it does not appear to be composition related. The cold crystallisation temperature is similar over the composition range, with a mean value of  $-89.5^{\circ}\text{C} \pm 5^{\circ}\text{C}$ . This scatter could be due to the slight variations in the cooling rate, which can dramatically affect the cold crystallisation temperature.

However the temperature at which cold crystallisation takes place has been reduced from  $-78^{\circ}\text{C}$  to  $-89^{\circ}\text{C}$ . Lee et al<sup>100</sup> established that as the heating rate of the calorimeter increases, cold crystallisation takes place at a higher temperature. They concluded that this could shed some light on crystal imperfections, in that the lower the temperature at which cold crystallisation takes place, the less perfect will be the resultant crystals. Possibly in this case the polystyrene has hindered crystal formation in the siloxane, resulting in imperfect

crystals, as seen by a lower crystallisation temperature. This supports the earlier conclusions that a certain degree of mixing of the two components has taken place, which prevents the formation of siloxane crystals similar to those in the pure polydimethylsiloxane.

#### 2.5.2.4 Endotherm of Polydimethylsiloxane

The melting endotherm ( $T_m$ ) commenced at  $-64^\circ\text{C}$ , with a maximum occurring at about  $-39.5^\circ\text{C}$ , and melting completed at  $-24^\circ\text{C}$  (Fig.2.11b). The melting endotherm was broader than the cold crystallisation exotherm, and two peaks are clearly observed. The literature cites examples of multiple melting peaks, which are fairly common for crystalline polymers. These two peaks are probably due to the presence of two crystalline forms.<sup>111</sup> This is seen particularly when an external strain is applied to polydimethylsiloxane<sup>113</sup> when a crystal form is observed which is not present in an unstretched sample. This is further substantiated by Lee<sup>100</sup> who has concluded that the size and position of the melting peaks are related to the amount of cold crystallisation and the reorganisation of metastable crystals after partial melting before the final melting.

The data for the melting endotherm are given in Table 2.9. The melting endotherm of polydimethylsiloxane in the blends is found to be  $-38.70 \pm 1.3^\circ\text{C}$ , which is marginally higher than the  $-39.5^\circ\text{C}$  in pure polydimethylsiloxane. This difference is very small, and it is difficult to conclude that it is a significant difference.

The enthalpy of melting reveals interesting results (Table 2.9). A plot of the enthalpy of melting against percent composition (Fig.2.13) is a straight line. If extrapolated it intersects the x axis at 100% polystyrene. It would appear that an additive relationship exists between the enthalpy of fusion and the composition of the blend. This could prove to be a useful method to determine the composition of unknown blends of these two components.

Fig.2.13 The relationship between the enthalpy of the endotherm peak and the percentage composition of the blend.

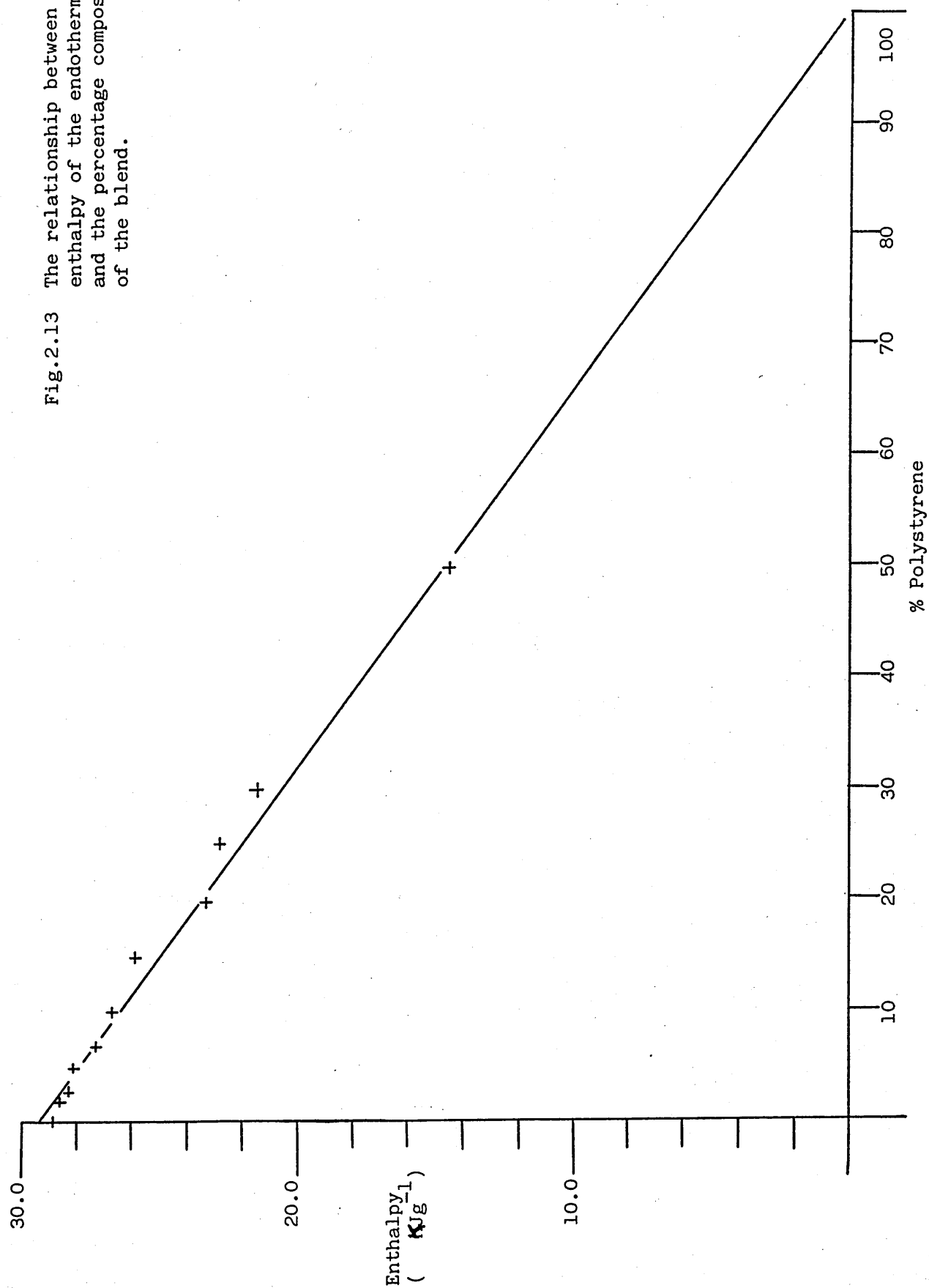


Table 2.9 The Temperature and Enthalpy of the  
Endotherm of Polydimethylsiloxane

Sample % Polystyrene	Endotherm Temperature °C	Enthalpy of Endotherm KJ/g
0	-39.5	28.09
2	-39.0	28.72
3	-38.9	29.44
5	-39.1	28.23
7	-38.8	27.45
10	-39.0	26.82
15	-39.1	25.86
20	-38.9	23.37
30	-38.60	21.47
50	-37.4	14.60

POLYSTYRENE - POLYDIMETHYLSILOXANE BLOCK COPOLYMERS

3.1 Introduction

The foundations of organosilicon chemistry were established by Kipping during the period 1899-1944, although the first reports of the existence of organosilicon compounds was from Dumas in 1840.<sup>114</sup> The resinous material that was frequently encountered by Kipping was regarded as an annoyance, of little or no interest. It was left to the large American companies, Corning Glass, G.E.C. and latterly Dow Corning, to develop this 'resinous material' into a valuable specialist product. Polysiloxanes are now important polymeric materials having valuable properties.

The current literature of silicone chemistry is very extensive, and it is beyond the scope of this thesis to discuss it in detail. There is an excellent book by Eaborn<sup>115</sup> and comprehensive reviews by Saunders,<sup>114</sup> Lewis,<sup>116</sup> Beuchner<sup>117</sup> and Warrick et al,<sup>118</sup> which deal with this area in depth. In this chapter, approaches to block copolymers of polystyrene and polydimethylsiloxane are discussed. References to relevant aspects of organosilicon chemistry will be introduced as necessary to this discussion.

3.1.1 Ionic Polymerisation Methods

Cyclic siloxanes are found to form low molecular oligomers (Fig.3.1) by the action of potassium hydroxide or other alkali metal hydroxides at elevated temperatures.<sup>119,120.</sup>



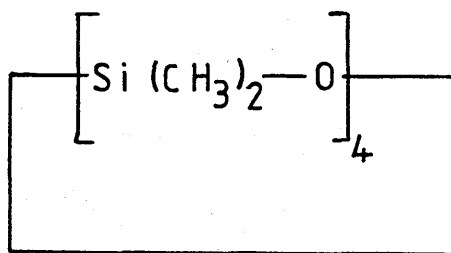
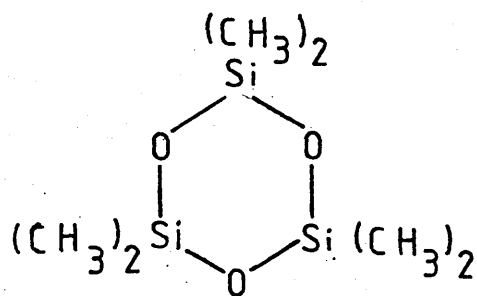
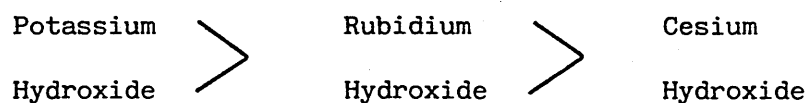
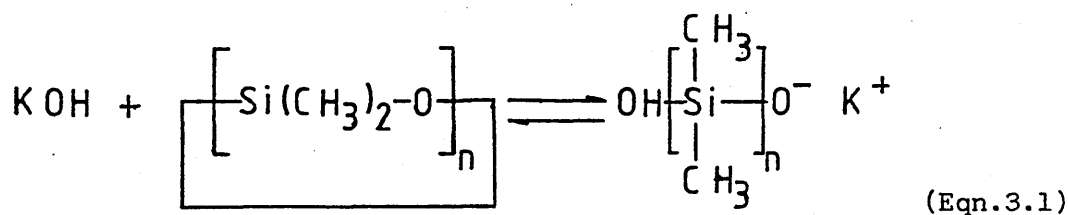


Fig.3.1 Cyclic Siloxanes: (a) Hexamethylcyclotrisiloxane  
(b) Octamethylcyclotetrasiloxane

The reactivity of the alkali metal hydroxides with cyclic siloxanes increases in the order:

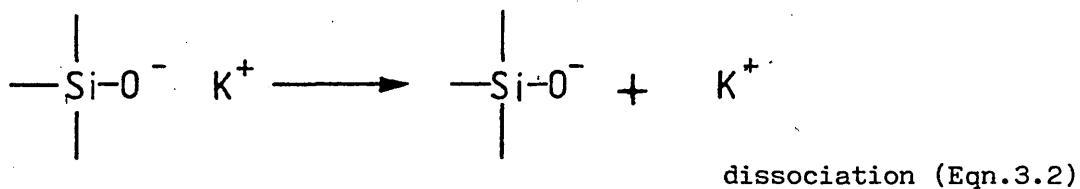


Grubb and Osthoff<sup>120</sup> showed that polymerisation proceeds via the following route:

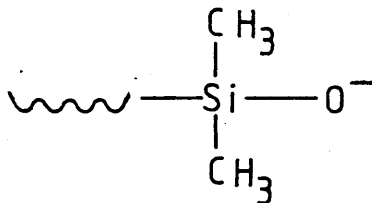


—————→ equilibrium displaced

then



The active species responsible for propagation being the silonate ion i.e.



The hydroxide catalyst is found to effect the rate constant of the polymerisation reaction and the overall molecular weight of the polymer. Cleavage of the silicon - oxygen bond can also be achieved by the catalytic action of sulphuric acid, with production of high molecular weight polysiloxanes.<sup>121,122.</sup>

In this type of reaction, there is no control over the distribution of the molecular weights in the polymer, the only effective control is that the concentration of the catalyst determines the average molecular weight. The final gum would consist of high and low molecular weight linear chains, along with cyclic oligomers. The latter include hexamethylcyclotrisiloxane ( $D_3$ ), octamethylcyclotetrasiloxane ( $D_4$ ) and higher cyclics in decreasing smaller amounts. In one of the industrial preparations of silicones, the ionic method is used, with the reaction being 'terminated' by the addition of a vinylsilane compound. This gives a certain degree of control over the average molecular weight and dictates the nature of the end-groups.

If a well defined silicone polymer is desired, the obvious synthetic route to use is anionic polymerisation with organometallic initiators. The important feature of this process is the consecutive addition of monomer through a reactive carbonion until either the reactivity of the species or the supply of monomer diminishes. The continuation of the reaction, in the absence of terminating agents, brought about use of the term, "living polymerisation" for this process.

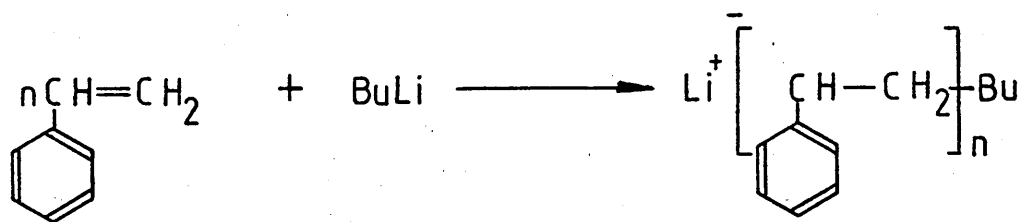
In order to produce a polymer with as narrow a molecular weight distribution as possible, the initiator must be of such activity that the rate of initiation is very much faster than the rate of propagation. This allows each of the initiated oligomers to propagate at the same rate, so that the chain length of all the growing chains increases simultaneously with time. The other feature required for this study is strict control over the composition of the components in copolymers which the anionic polymerisation route provides.

The successful use of this technique demands very pure reagents, solvents and rigorous experimental conditions. The initiator is easily deactivated by water and other species, which necessitates the use of high vacuum<sup>123</sup> or similar techniques. Further, we were primarily interested in block copolymers, with well defined and predetermined structures, so it was necessary that the active polymer first formed, should efficiently initiate the polymerisation of the second component.<sup>124-127</sup> Detailed discussion of the mechanistic and kinetic aspects of anionic polymerisation can be found in the book by Szwarc<sup>128</sup> and the review by Bywater.<sup>129</sup>

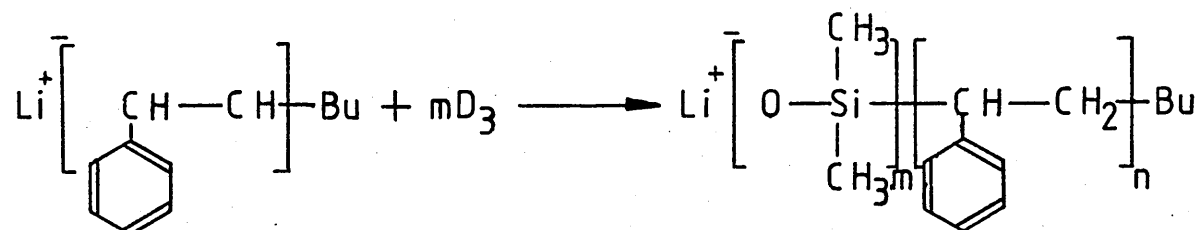
Despite the difficulties with this technique, many new polymers and copolymers have been synthesised, with the first reported synthesis of a siloxane containing block copolymer of controlled structure being reported in 1969.<sup>130</sup>

The synthesis of poly(dimethylsiloxane - b - styrene) has been achieved by the following two methods:

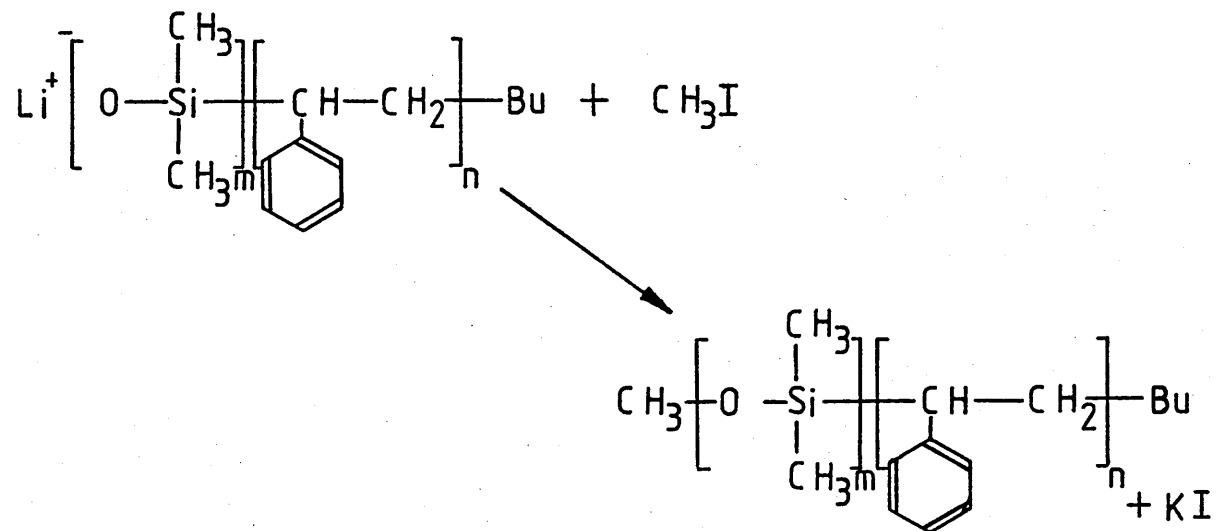
- a) polymerisation using a monofunctional initiator, such as butyl lithium,<sup>131-133</sup> to produce an A—B block copolymer; (Eqn.3.3)



Initiation/Propagation

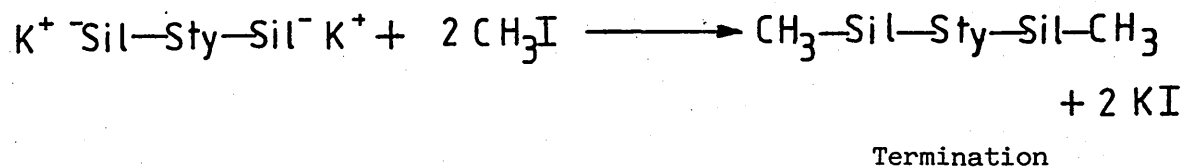
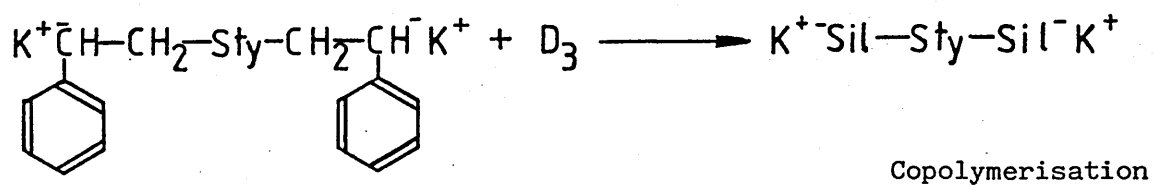
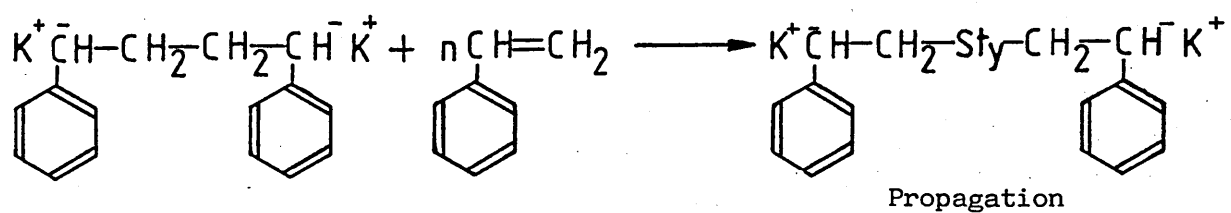
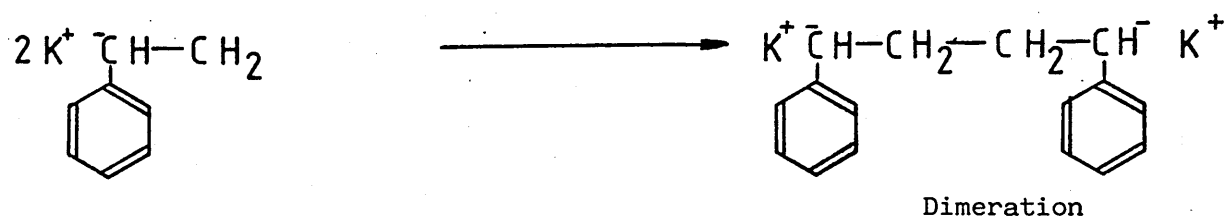
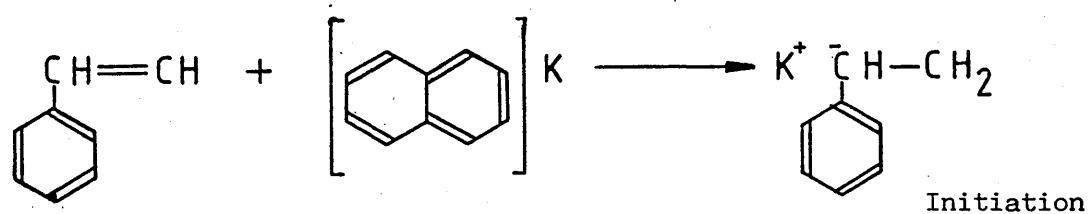


Copolymerisation



Termination

Equation 3.3 Copolymerisation of styrene and Hexamethylcyclotrisiloxane using a monofunctional initiator



Equation 3.4 Copolymerisation involving a bifunctional initiator.

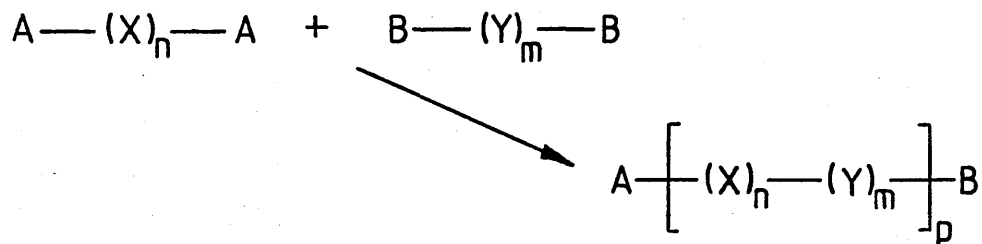
b) polymerisation using a bifunctional initiator, such as metallic naphthalene or metallic biphenyl<sup>134-139</sup> to produce an A—B—A block copolymer. (Eqn.3.4)

A copolymer of polydimethylsiloxane and polystyrene contains within the same molecular chain two segments which can independently show the extremes in properties and characteristics of each homopolymer. It is proposed in this study that an increase in the radiation resistance of silicones would be brought about by the presence of the polystyrene segment (as discussed in section 1.4).

In this work two routes to such block copolymers were investigated using both octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane as starting materials.

### 3.1.2 Polymers via Condensation Methods

Condensation polymerisation occurs by the stepwise repetition of simple condensation reactions. Each of the comonomers have reactive end groups which are capable of reaction to form high polymers via a random series of steps by which the polymer chain increases in molecular weight. This is illustrated for the formation of block copolymers by:



Polydimethylsiloxane has been used extensively as a component in di -, tri - and multiblock copolymers, in combination with a wide range of polymers as the second block.<sup>70,140</sup> The systems forming the second block were chosen to enhance certain physical and mechanical properties of the polysiloxane. For example, the thermal stability of the polymer backbone was found to be increased with polysilarylene<sup>141,142</sup> or polysulphone<sup>143,144</sup> as the second component.

It was the intention in this study to incorporate polystyrene with polydimethylsiloxane, via a condensation procedure, thus to facilitate such a reaction the following combinations of end groups are possible.

<u>Polydimethylsiloxane end group</u>	<u>Polystyrene end group</u>
i) $\equiv\text{Si} - \text{Cl}$	"Living" $\text{Na}^+$ polystyryl anions <sup>145</sup>
ii) $\equiv\text{Si} - \text{Cl}$	$\text{HO} - \text{Siloxane} - \text{Polystyrene}$ <sup>146,147</sup>
iii) $\equiv\text{Si} - \text{H}$	$\text{CH}_2 = \text{CH} - \text{Polystyrene}$ <sup>148,151</sup>
iv) $\equiv\text{Si} - \text{OH}$	$(\text{Me})_2\text{N} - \text{Si} - \text{Polystyrene}$ <sup>152,153</sup>

A scheme based on reaction (iv) was investigated as a route to a polydimethylsiloxane - polysiloxane block copolymers. A hydroxyl-terminated polystyrene can be produced by the termination of "living" polystyrylanions with acetaldehyde,<sup>154</sup> ethylene oxide,<sup>155</sup> or dimethyl-dichlorosilane, and subsequent hydrolysis to give the desired product. The hydroxyl-terminated block can be coupled with a preformed amine-terminated polysiloxane.

## 3.2 Experimental

### 3.2.1 Polymerisation involving Octamethylcyclotetrasiloxane

#### Reagents

Octamethylcyclotetrasiloxane ( $D_4$ ) - Dow Corning plc supplied batches of mixed liquid cyclic siloxanes, comprising, typically:

1.7% hexamethylcyclotrisiloxane ( $D_3$ );  
64% octamethylcyclotetrasiloxane ( $D_4$ );  
30% decamethylcyclopentasiloxane ( $D_5$ )  
with small amounts of higher cyclic oligomers.

By successive use of a spinning band distillation column, substantially pure  $D_4$  was obtained ( $>98\%$   $D_4$ , by gas liquid chromatography).

Metallic Naphthalene ( $M^+ = Li, \text{ or } K$ ) - These bifunctional initiators were prepared by the method described by Sorenson and Campbell.<sup>156</sup> The metal (3.55g Li,K) was finely divided to reveal a freshly cut surface; it was then stirred in dry tetrahydrofuran ( $100\text{ cm}^3$ ), under nitrogen, with re-sublimed naphthalene (30g). A dark green initiator mixture was produced within 30 minutes, which was stored under nitrogen and could be removed via a septum seal when needed. A measured sample ( $3\text{ cm}^3$ ) was quenched in methanol ( $25\text{ cm}^3$ ) and titrated with standard hydrochloric acid, using methyl orange as indicator, to determine the molarity of the initiator present ( $0.062\text{ mol dm}^{-3}$ ).

Styrene - This monomer was washed with dilute sodium hydroxide to remove the inhibitor, separated, then double - distilled from a calcium hydride - THF suspension.



Tetrahydrofuran - Purchased from Fluka, then distilled with potassium metal to remove the stabiliser and any moisture that may be present.

#### Procedure A

The difunctional initiator  $M^+$  naphthalene was used in a procedure adapted from work carried out by Bajaj.<sup>139</sup> Octamethylcyclotetrasiloxane (16g) and THF ( $15 \text{ cm}^3$ ) were introduced to a flame-dried vessel purged with nitrogen (via a septum using a glass syringe). A portion ( $0.7 \text{ cm}^3$ ) of the initiator from the "stock initiator solution" ( $0.062 \text{ mol dm}^{-3}$ ) was added to the vessel which was placed in a water bath and maintained at a temperature of  $50^\circ\text{C}$  for 6-8 hours. The reaction was then terminated by the addition of methyl iodide ( $0.5 \text{ cm}^3$ ).

Yield - 10.38g of liquid polymer.

Infrared Spectrum (Fig.3.2) :  $3000 (\text{C}_{\text{sp}^3}\text{H}_{\text{str}})$ ;  $1265 (\text{Si-CH}_3)$ ;  
1100-1030 doublet,  
 $810 (\text{Si-O-Si})\text{cm}^{-1}$

#### Procedure B

Tetrahydrofuran ( $15 \text{ cm}^3$ ) was introduced to a flame-dried vessel, purged with nitrogen, along with styrene ( $1.0 \text{ cm}^3$ ). A portion ( $0.7 \text{ cm}^3$ ) of the initiator from the "stock initiator solution" ( $0.062 \text{ mol dm}^{-3}$ ) was added to the vessel and after 5 minutes, octamethylcyclotetrasiloxane (15g) was also added, the temperature maintained at  $50^\circ\text{C}$  for 6-8 hours. The reaction was terminated by the addition of methyl iodide ( $0.5 \text{ cm}^3$ ).

Yield - 10.54g of an opaque liquid polymer.

Infrared Spectrum (Fig.3.3) :  $3100 (\text{C}_{\text{sp}^2}\text{H}_{\text{str}})$ ;  $3000 (\text{C}_{\text{sp}^3}\text{H}_{\text{str}})$ ;  
 $1610, 1505 (\text{C}=\text{C})$ ;  $1460, 1430 (\text{C}_{\text{sp}^3}\text{H}_{\text{b}})$ ;

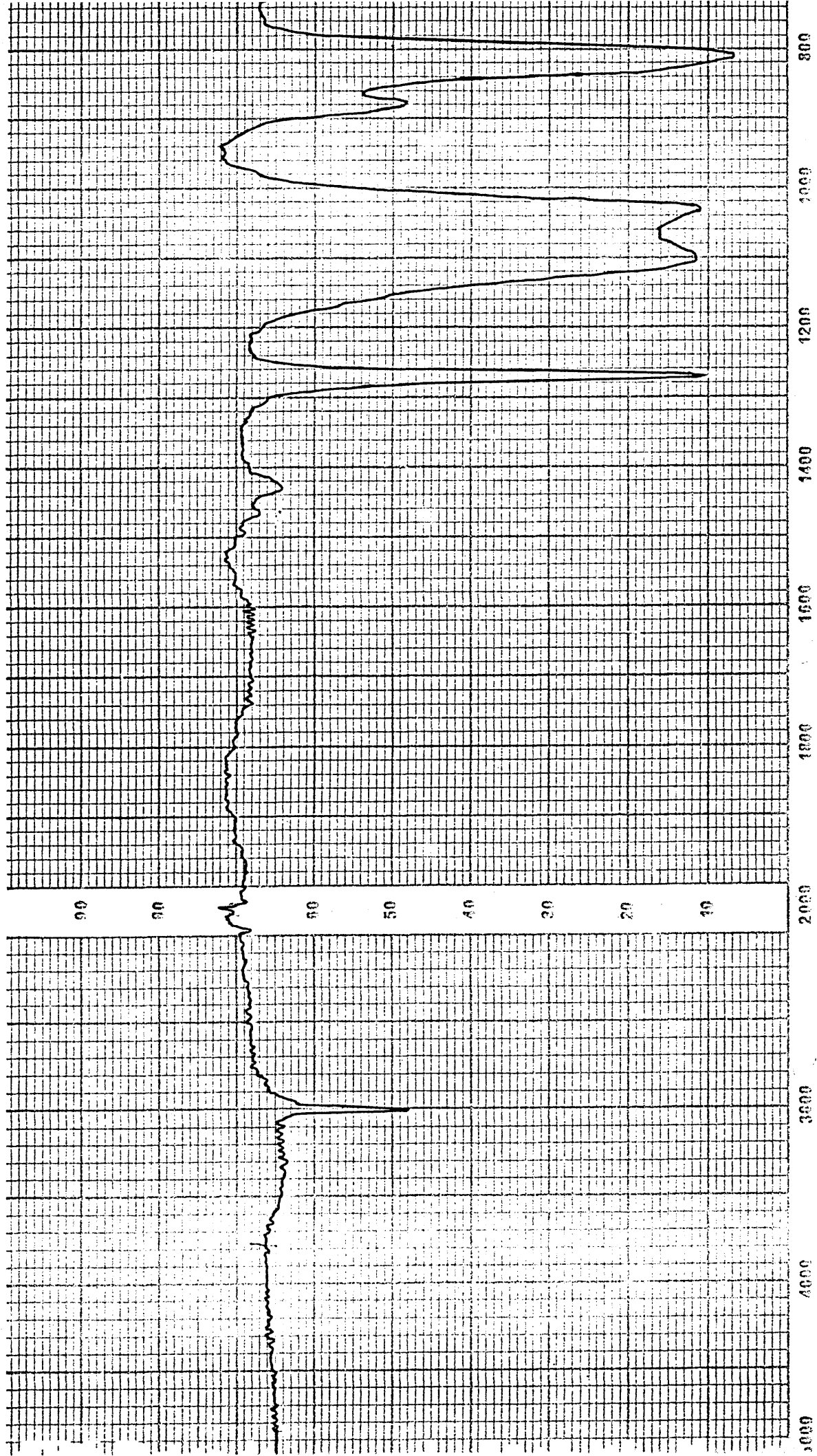


Fig.3.2 IR Spectra of a sample of polydimethylsiloxane.

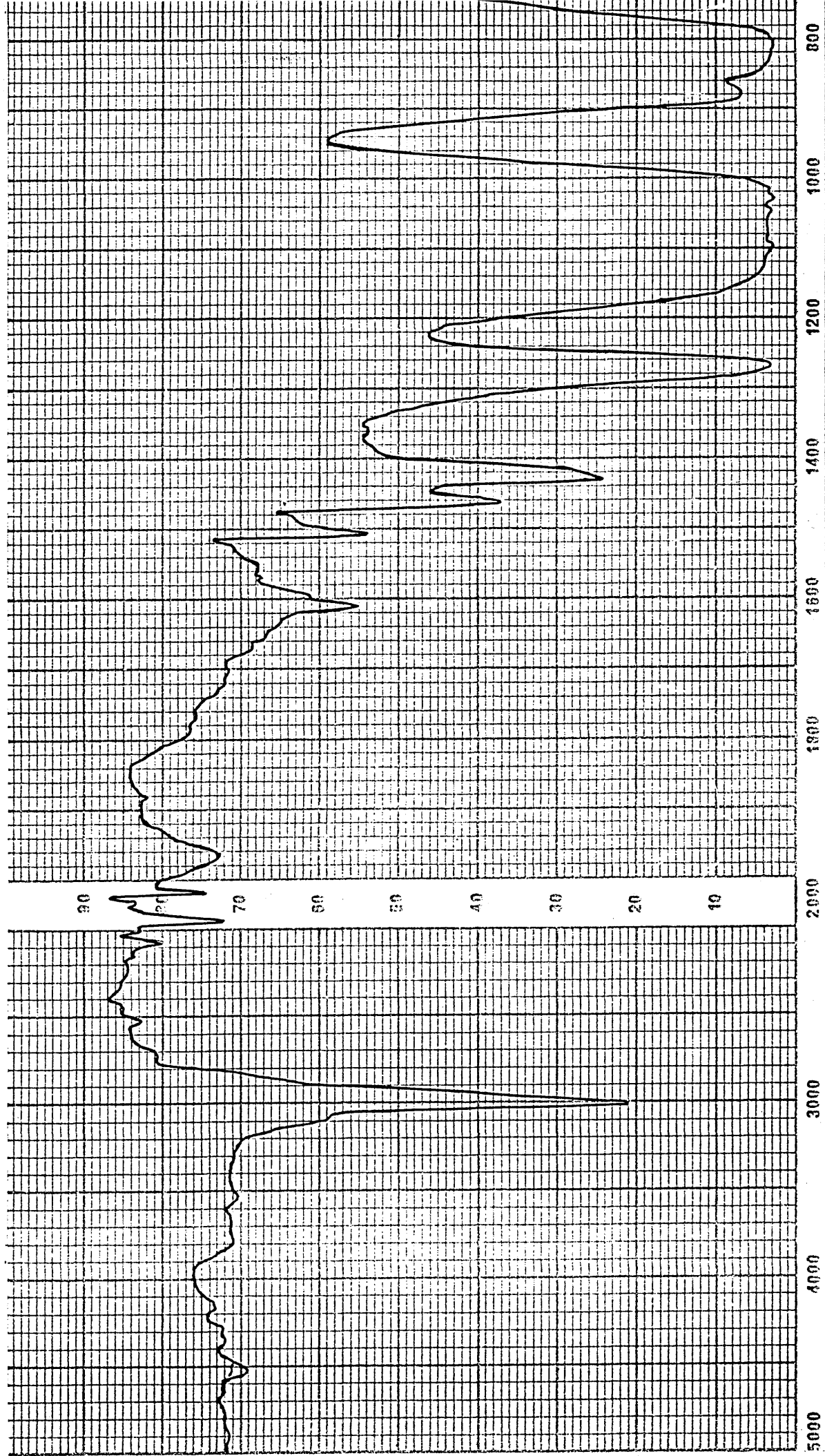


Fig.3.3 IR Spectra of a sample of polydimethylsiloxane - Polystyrene Block Copolymer

1270 (Si-C); 1140-1020

800 (Si-O-Si); 700 (Si-C<sub>vib</sub>)cm<sup>-1</sup>.

A full correlation is given in Table 3.2.

### 3.2.2. Preparation of Hexamethylcyclotrisiloxane (D<sub>3</sub>)

#### Reagents

Siloxane - Supplied as mixed cyclics by Dow Corning plc.

Potassium Hydroxide - Purchased from Aldrich in pellet form and used as a powder.

#### Procedure

Preliminary work investigated the polymerisation of 10g of mixed cyclics, using 1% w/w potassium hydroxide, in an evacuated glass tube. The tube was placed in a fluidised sand-bed at 300-380°C, the temperature monitored using a chromel-alumel thermocouple, after opening, the gum was removed and distilled under vacuum to obtain a number of liquid fractions, which were analysed by gas liquid chromatography. The results of these experiments are given in Table 3.1.

Table 3.1 Gas Liquid Chromatography Analysis of the Degradation of Polydimethylsiloxane prepared from Mixed Cyclics

Component	Starting Material %	300°C %	340°C %
Hexamethylsiloxane	4.3		
D <sub>3</sub>	1.7	15.7	20.8
D <sub>4</sub>	64	28.3	44.2
D <sub>5</sub>	30	28.0	30.6
D <sub>6</sub>	N.D <sup>a</sup>	23.0	N.D

(a) Not detectable

For larger scale reactions a glass reaction vessel was designed (Fig.3.4) in thick walled glass. The cyclic mixture ( $150\text{ cm}^3$  containing 1% w/w potassium hydroxide) was degassed, sealed and heated to  $300^\circ\text{C}$  in a fluidised sand-bed. After 19 hours at this temperature an explosion occurred. A second reaction using the same quantities was heated at  $350^\circ\text{C}$  for 8 hours. The vessel was cooled in liquid nitrogen before opening, but during the opening of the tube, an explosion occurred. Further studies of this kind were abandoned for safety reasons.

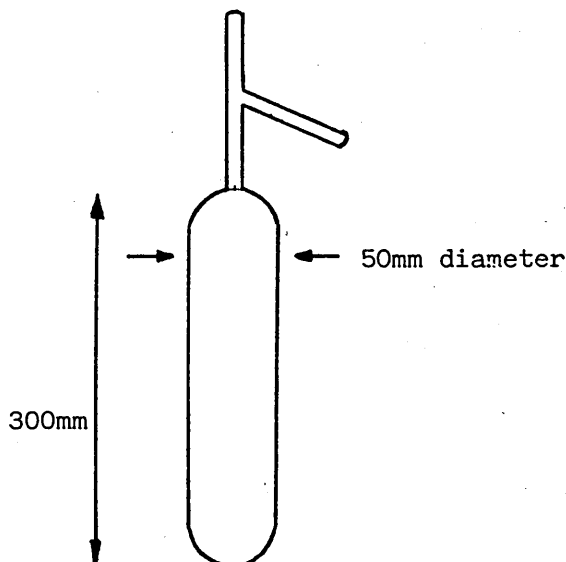


Fig.3.4 Reaction vessel

### 3.2.3 Copolymerisation using Hexamethylcyclotrisiloxane

#### Reagents

Hexamethylcyclotrisiloxane - Supplied by Dow Corning plc, also purchased from Field Chemicals, and resublimed as required.

Tetrahydrofuran - Section 3.2.1

Styrene - Section 3.2.1

Butyl Lithium - Purchased from Aldrich Chemical Co. as a 1.58M solution in hexane.

### Procedure

Purified styrene ( $4.8 \text{ cm}^3$ ) in dry tetrahydrofuran ( $16 \text{ cm}^3$ ) was initiated using butyl lithium, ( $0.30 \text{ cm}^3$  1.44M) at  $-40$  to  $-30^\circ\text{C}$ . Polymerisation of the styrene occurred and stirring was continued for 15-20 minutes (Equation 3.3). The characteristic crimson-red colour (indicative of "living" styryl anions) was present, until a tetrahydrofuran solution ( $26 \text{ cm}^3$ ) of hexamethylcyclotrisiloxane (10.13g) was added; the red colour perished for 2-3 minutes fading to a yellow colour, which faded with time. The vessel was placed in a water bath at  $60^\circ\text{C}$ , and after 6 hours polymer was precipitated by pouring the mixture into vigorously stirred cold methanol, vacuum dried at  $50^\circ\text{C}$  overnight, and characterised, using infrared and nuclear magnetic resonance spectroscopy.

Yield - 85%

Infrared Spectrum (Fig.3.5, Table 3.2)

A nuclear magnetic resonance spectrum (Fig.3.6, Table 3.3) was obtained with tetramethylsiloxane (TMS) as an external standard. The composition of the block copolymer can be calculated from the integrated peak areas.

The molecular weight distribution of some of the copolymers was investigated by the characterisation service of Rubber and Plastics Research Association. Four analytical columns containing Styragel with porosities  $10^6$ ,  $10^5$ ,  $10^4$  and  $10^3 \text{ \AA}$  were used with tetrachloroethylene as solvent at  $80^\circ\text{C}$  and a flow rate of  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . Refractive index and infrared (9.45 microns) detectors were used and calibration of the columns was with polystyrene standards.

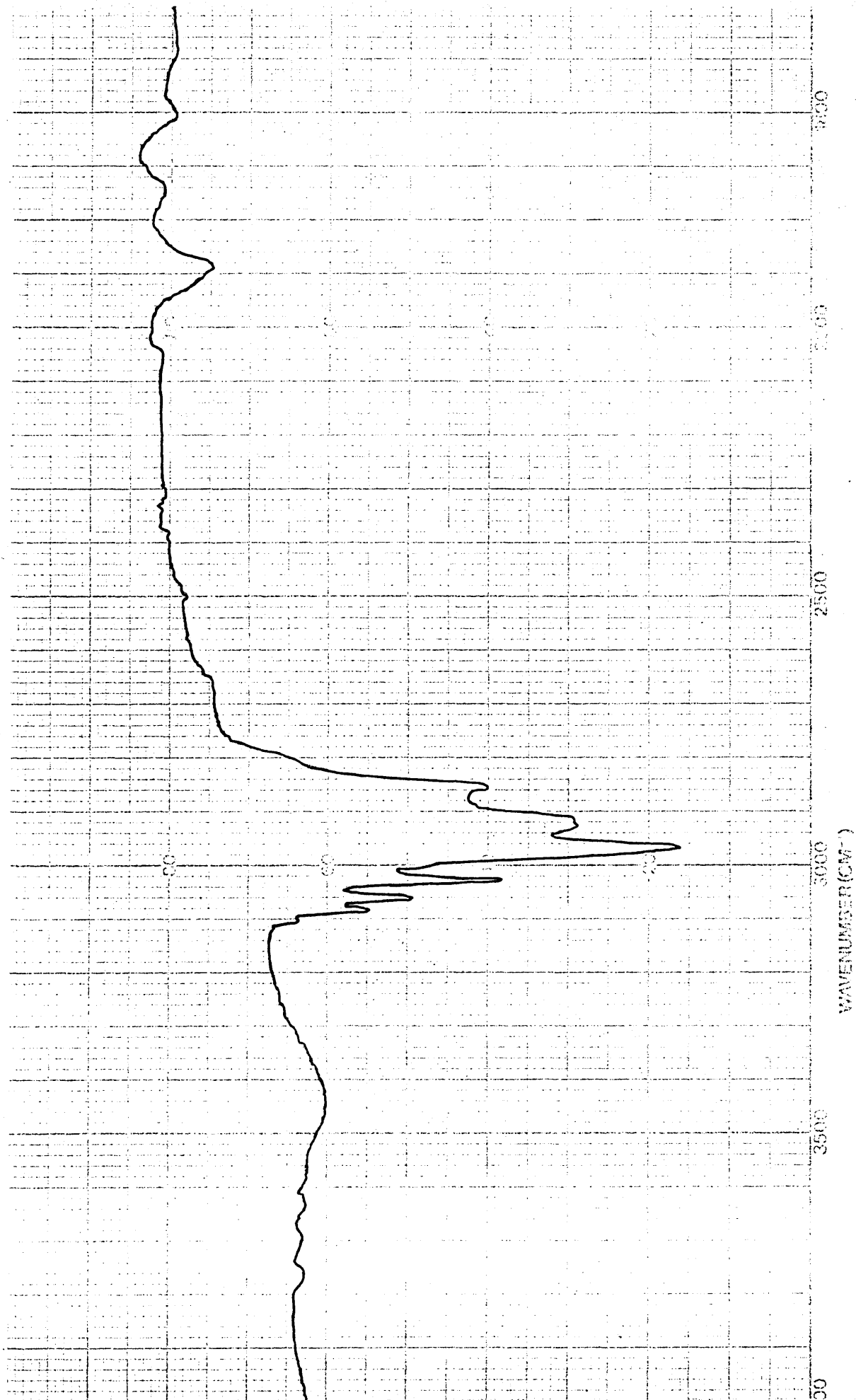


Fig.3.5a IR Spectra of a polystyrene-polydimethylsiloxane block copolymer

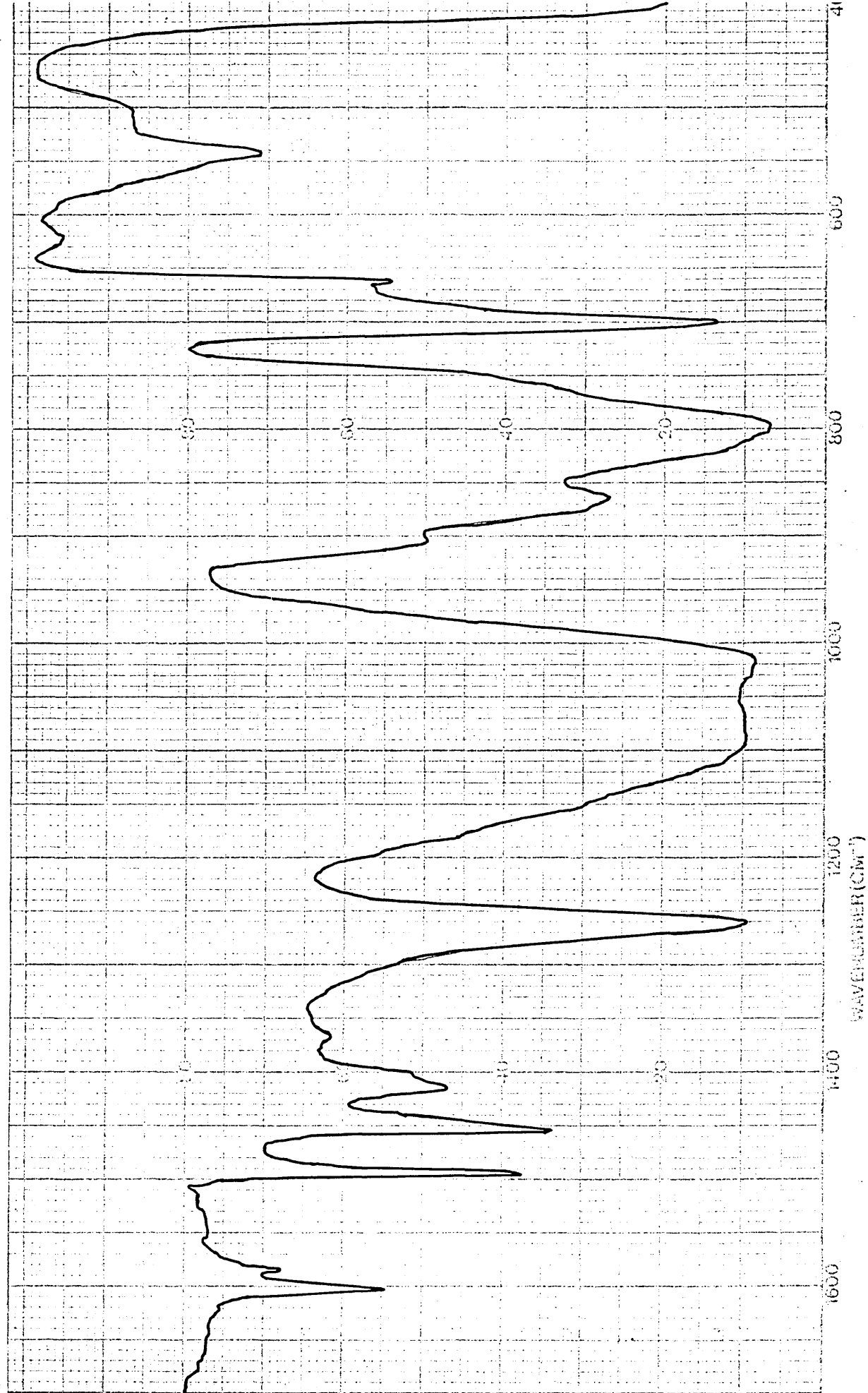


Fig.3.5b IR Spectra of a polystyrene-polydimethylsiloxane block copolymer



Fig.3.6 NMR Spectra for a polystyrene-  
polydimethylsiloxane block copolymer

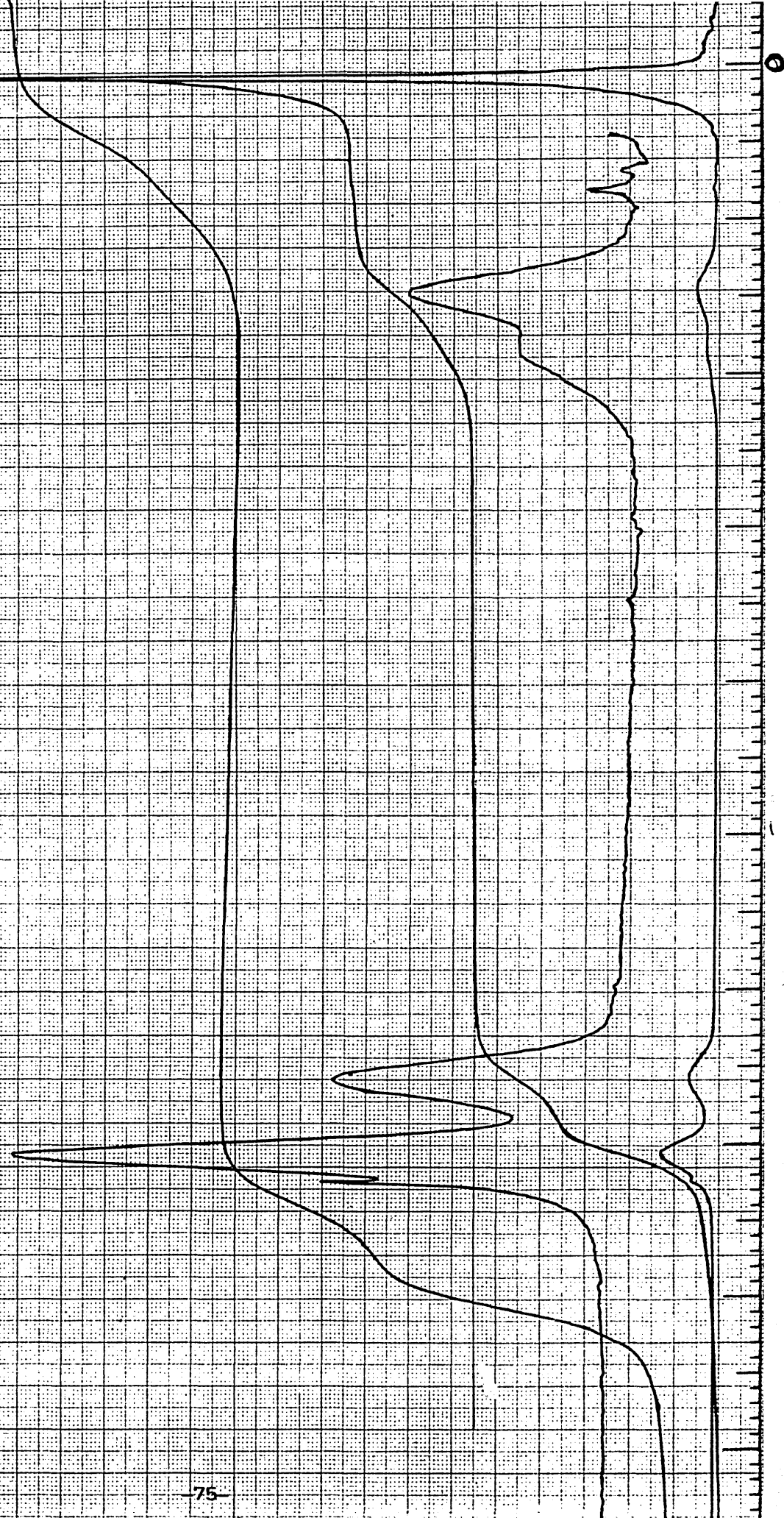


Table 3.2 Infrared Spectrum of Polydimethylsiloxane -

Polystyrene Copolymer

Peak $\text{cm}^{-1}$	Interpretation	Polymer Unit	
3080 3060 3030	$\text{C}_{\text{sp}^2} - \text{H}_{\text{str}}$	aromatic	styrene
2960 2920	$\text{C}_{\text{sp}^3} - \text{H}_{\text{str}}$	aliphatic	siloxane
2850	$\text{C}_{\text{sp}^3} - \text{H}_{\text{str}}$	aliphatic	styrene
1605 1495	In plane bending vibrational motion	aromatic	styrene
1455	$\text{C}_{\text{sp}^3} - \text{H}_{\text{b}}$	aliphatic	siloxane
1265	$\text{Si} - \text{CH}_3$	"	siloxane
1010-1110	$\text{Si} - \text{O} - \text{Si}$	"	siloxane
800	$\text{Si} - \text{O}$	"	siloxane
700	$\text{Si} - \text{CH}_3$ vibrational	"	siloxane
540	$\text{C}_{\text{sp}^2} \text{H}_{\text{b}}$	"	styrene

Table 3.3 NMR Correlation for Polydimethylsiloxane -

Polystyrene Copolymer

Chemical Shift $\delta/\text{ppm}$	Identification
0.1	$\text{Si} - (\text{CH}_3)_2$
1.50	Methylene (styrene)
1.80	Methine (styrene)
6.60	Ortho 'H' (styrene)
7.06	Meta and para 'Hs' (styrene)

Table 3.4 GPC Characteristics of Siloxane - Styrene Copolymers

Sample	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
Pss 23	25,300	62,300	2.47
Pss 25	19,200	42,800	2.23

Thermal Analysis: Differential Scanning Calorimetry data is given in Table 3.5 and Fig.3.7.

Table 3.5 DSC data of Siloxane - Styrene Copolymers

Sample	Siloxane				Styrene			
	Tg °C	Tg <sub>2</sub> °C	Tg <sub>1</sub> °C	ΔTg °C	Tg °C	Tg <sub>2</sub> °C	Tg <sub>1</sub> °C	ΔTg °C
Pss 23	-122.4	-118.8	-125.5	6.7	104.3	107.8	100	7.8
Pss 25	-122.5	-119	-126.2	7.2	98.7	103.8	96.5	7.3

#### 3.2.4 Preparation of Hydroxyl-terminated Polystyrene

##### Reagents

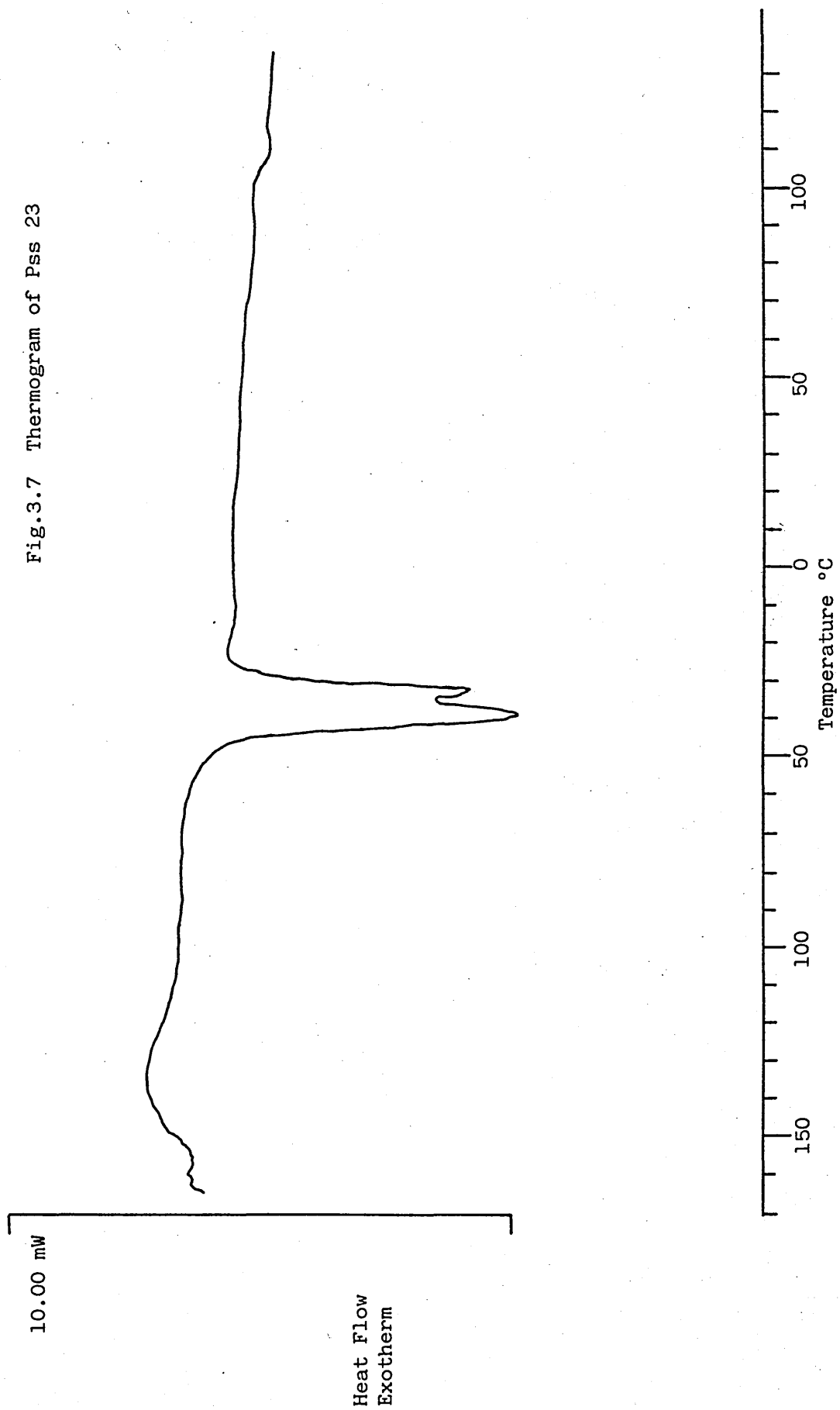
Styrene - Section 3.2.1

Tetrahydrofuran - Section 3.2.1

Butyl Lithium - Section 3.2.1

Dimethyldichlorosilane - Purchased from Aldrich Chemical Co. and distilled prior to use.

Fig.3.7 Thermogram of Pss 23



### Procedure

Styrene monomer ( $20 \text{ cm}^3$ ) was added, along with tetrahydrofuran ( $50 \text{ cm}^3$ ) to a flamed, nitrogen - purged, reaction vessel and placed in a carbon dioxide/acetone bath at  $-40$  to  $-30^\circ\text{C}$ . Butyl lithium ( $0.9 \text{ cm}^3$ ,  $1.53\text{M}$ ) was added and, after 1 hour, the polymerisation was terminated by the addition of distilled dimethyldichlorosilane ( $1.0 \text{ cm}^3$ ); polymer being obtained by precipitation into vigorously stirred cold methanol. The product was dried in a vacuum oven overnight at  $50^\circ\text{C}$ .

Yield - 98%

Infrared Spectrum:  $3200-3600$  (O-H);  $3080$ ,  $3060$ ,  $3020$  ( $\text{C}_{\text{sp}2}\text{H}_{\text{str}}$ ); (Fig.3.8)  
 $2920$  ( $\text{C}_{\text{sp}3}\text{H}_{\text{str}}$ );  $2840$  ( $\text{C}_{\text{sp}2}\text{H}_{\text{str}}$ );  $1600$ ,  $1480$  ( $\text{C} = \text{C}$ );  $1450$  ( $\text{C}_{\text{sp}3}\text{H}_b$ );  $1250$  (Si-C);  $1060$ ,  $1020$ ,  $905$  ( $\text{C}_{\text{sp}2}\text{H}$ );  $810$  (Si-C);  $760$ ,  $700$  ( $\text{C}_{\text{sp}2}\text{H}$ )  $\text{cm}^{-1}$ .

Nuclear Magnetic Resonance Spectrum data is given in Table 3.6.

Table 3.6 NMR Data for Hydroxyl Terminated Polystyrene

Chemical Shift S/ppm	Identification	Peak Height m.m.
0.15	Si - $(\text{CH}_3)_2$	2
1.52	Methylene (styrene)	58
1.88	Methine (styrene)	
6.62	Ortho 'H' (styrene)	99.5
7.15	Meta and Para 'H' (styrene)	
8.10	May be due to 'H' in the terminal OH group	Very small

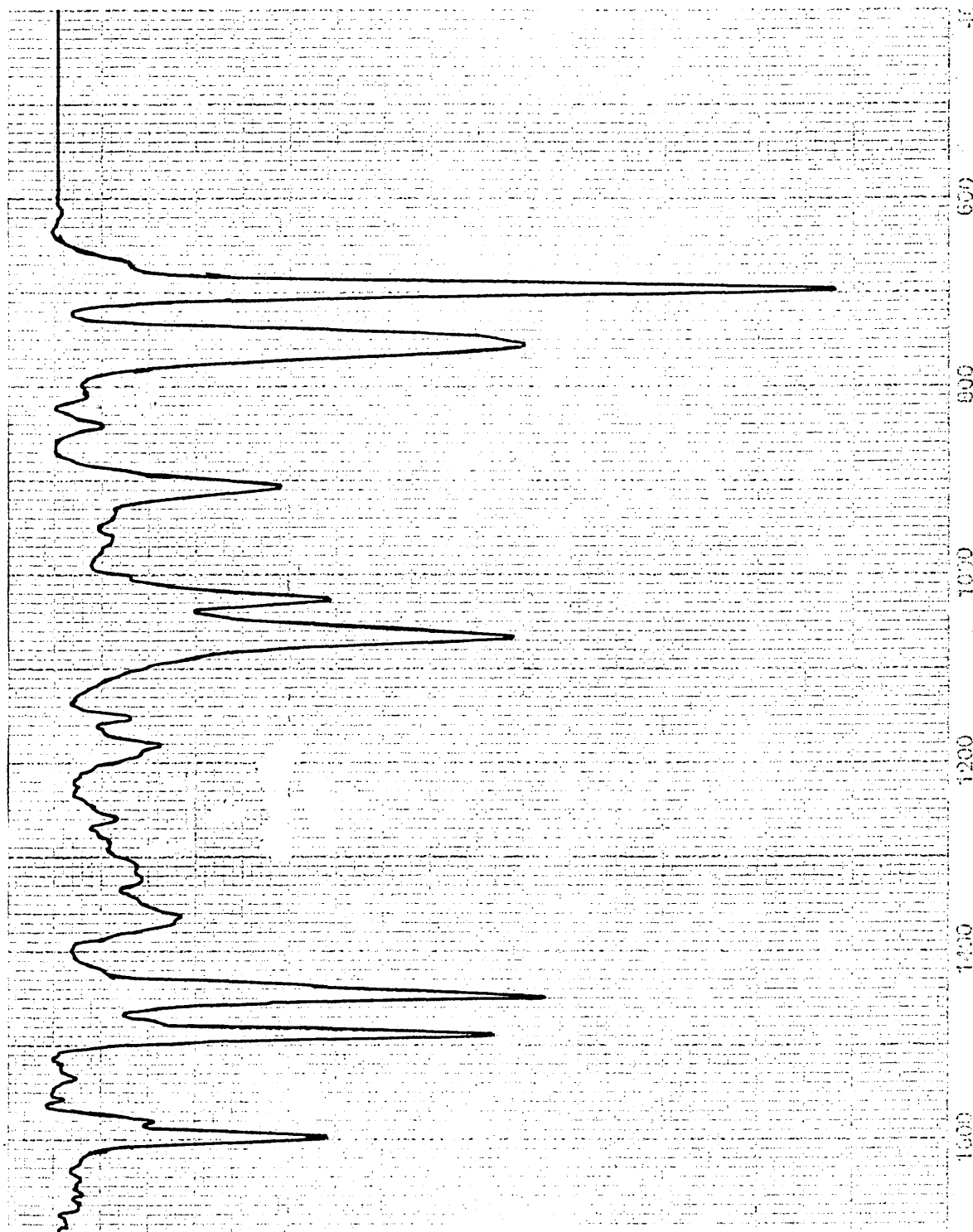


Fig.3.8 IR Spectra of Hydroxyl Terminated Polystyrene

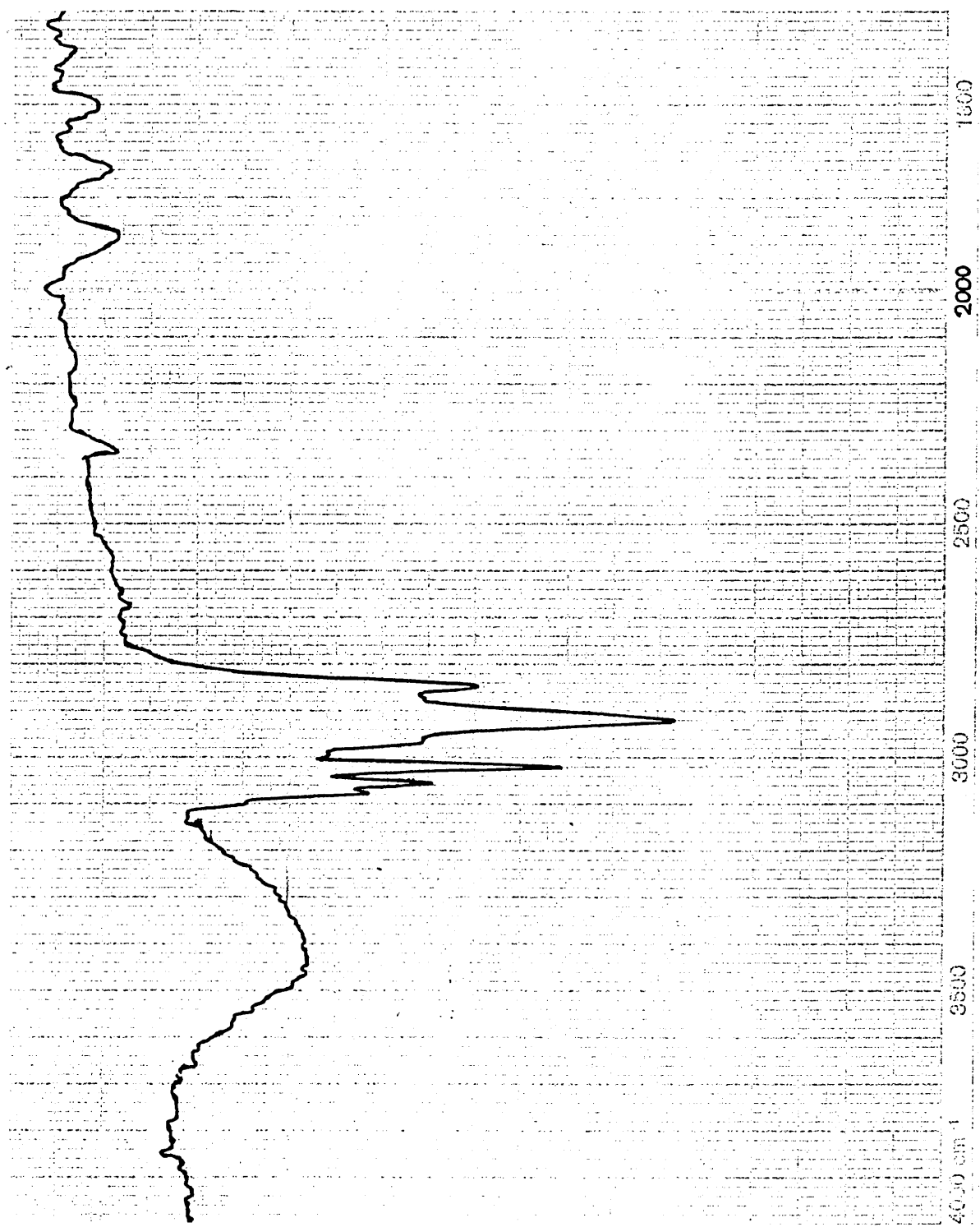
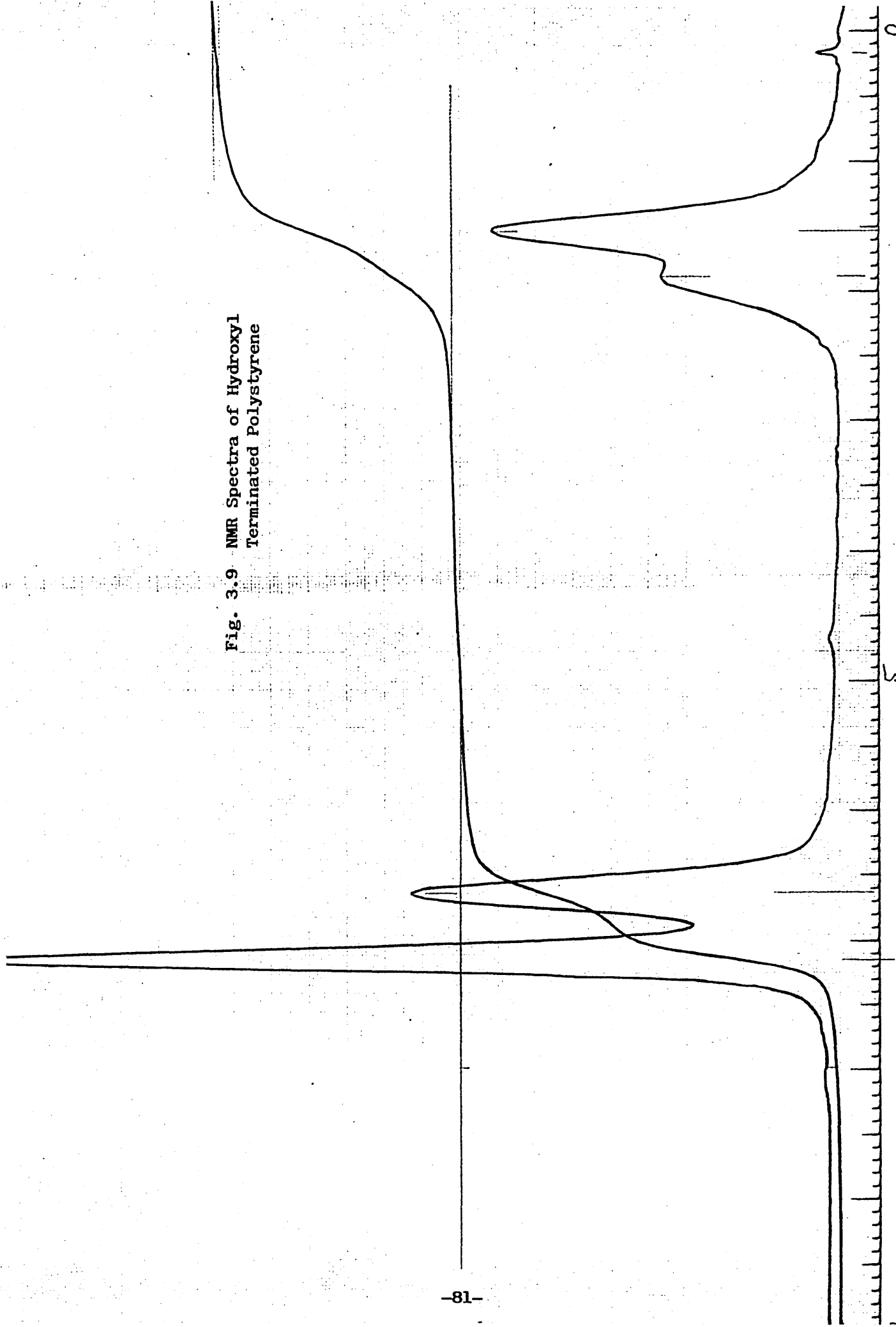


Fig.3.8 IR Spectra of Hydroxyl Terminated Polystyrene

Fig. 3.9 NMR Spectra of Hydroxyl  
Terminated Polystyrene





GPC : GPC determinations were carried out by RAPRA, of all the hydroxyl terminated polystyrenes (Table 3.7).

Table 3.7 GPC Data for Hydroxyl Terminated Polystyrene

Sample	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
Pss 9	12,851	29,700	2.31
Pss 10	7,100	33,800	4.76
Pss 11	11,900	31,500	2.65

Thermal Analysis: DSC data is given in Table 3.8

Table 3.8 Thermal data associated with the hydroxyl terminated Polystyrene

Sample	$T_g^{\circ}\text{C}$	$T_{g1}^{\circ}\text{C}$	$T_{g2}^{\circ}\text{C}$	$\Delta T_g^{\circ}\text{C}$	$T_g^{**\circ}\text{C}$	$T_{g1}^{**\circ}\text{C}$	$T_{g2}^{**\circ}\text{C}$	$\Delta T_g^{**\circ}\text{C}$
Pss 9	82.87	85	79	6	101.4	104	97	7
Pss 10	90.7	95	89.5	8.5	108.5	113	105	8

### 3.2.5 Preparation of Amine-Terminated Polysiloxane

#### Reagents

Hydroxyl Terminated Siloxane - Three samples of preformed siloxane blocks were supplied by Dow Corning plc of molecular weight 800, 2000 and 50,000.

Dimethyldichlorosilane - Purchased from BDH and distilled prior to use.

Benzene - Purchased from BDH (Analar grade).

Ether - Purchased from BDH and double dried with sodium wire.

Anhydrous Dimethylamine - Purchased from BDH and the ampoule opened as required.

#### Procedure

Three samples of hydroxy-terminated polysiloxanes of molecular weights 800, 2000 and 50,000 were supplied by Dow Corning. The chosen sample (40g) was added to a mixture of refluxing dimethyldichlorosilane ( $100\text{ cm}^3$ ) in benzene ( $50\text{ cm}^3$ ) over a period of one hour, under a nitrogen atmosphere. After refluxing for a further two hours the solvent and unreacted chlorosilane were removed by rotary evaporation.

Anhydrous ether ( $130\text{ cm}^3$ ) was cooled to  $-5^\circ\text{C}$  in a three-necked flask and anhydrous dimethylamine ( $20\text{ cm}^3$ ) was added, under a slight nitrogen pressure. The chloro-terminated polysiloxane (34g) was added dropwise, whilst maintaining the temperature at  $0^\circ\text{C}$ . After the addition, the mixture was refluxed for a further 1 hour, then the hydrochloride salts were removed by filtration under a nitrogen atmosphere, in a glove box. The ether solvent was removed by rotary evaporation and the amine-terminated prepolymer was stored under nitrogen.

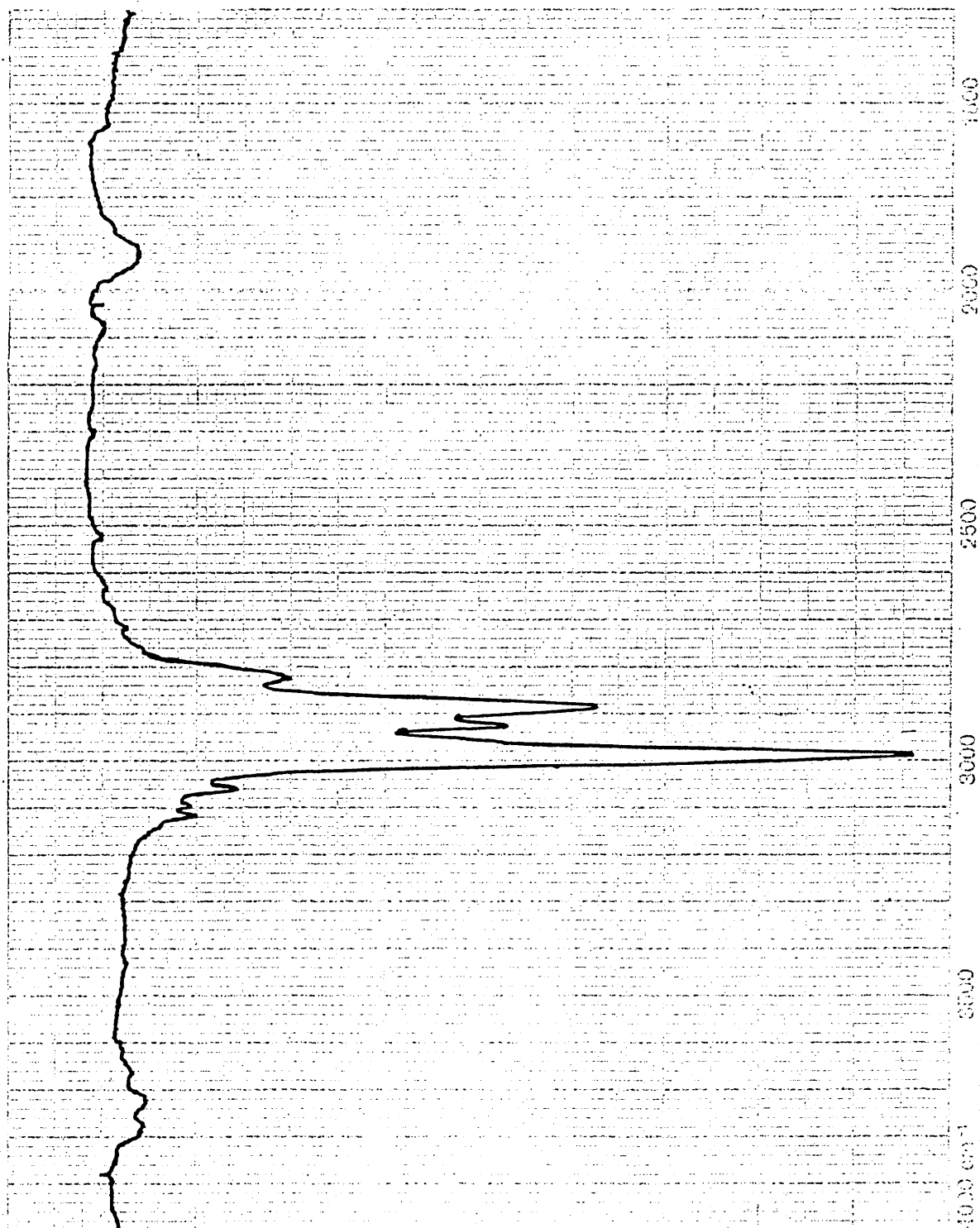


Fig.3.10 IR Spectra of Amine-Terminated Polydimethylsiloxane

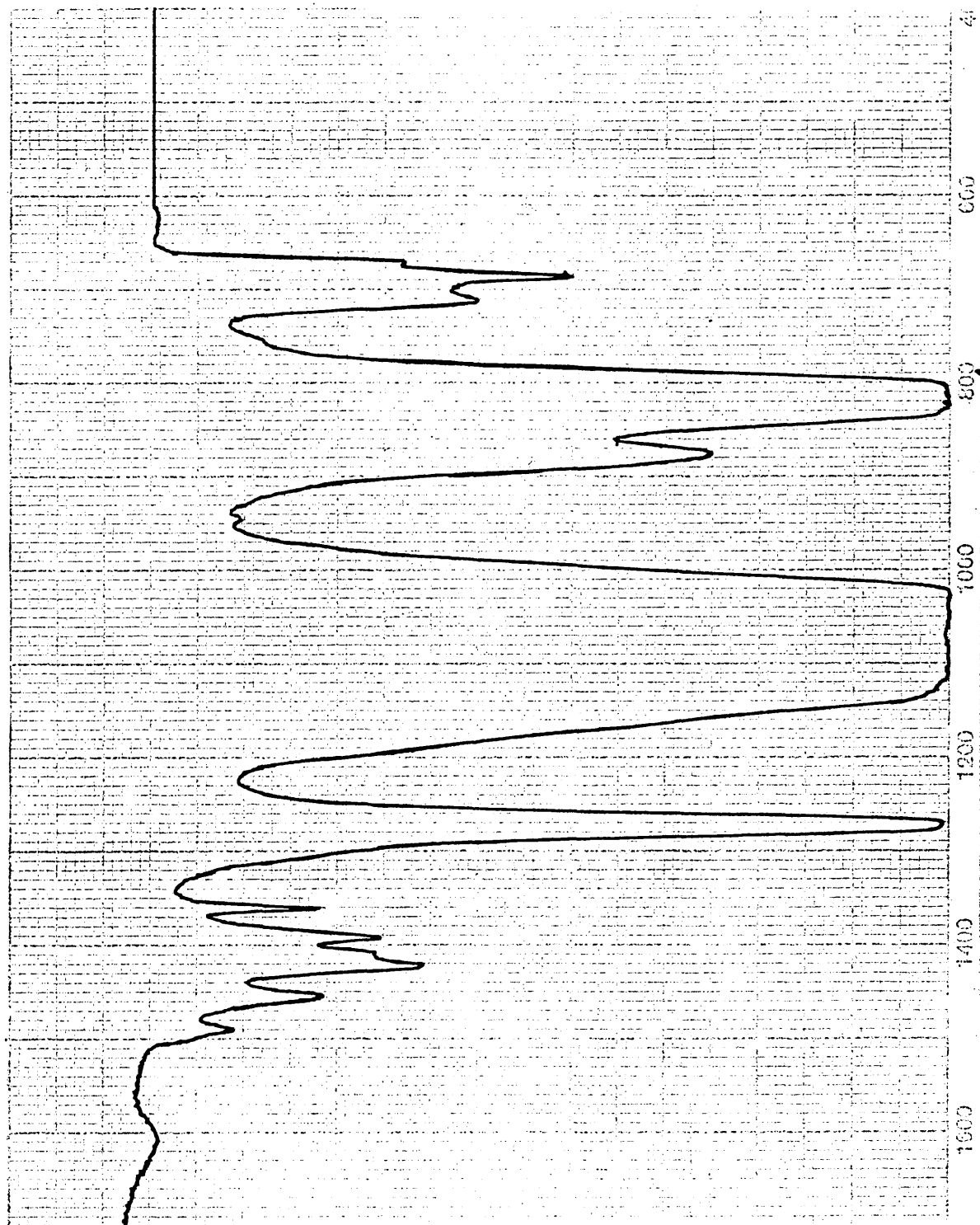


Fig.3.10 IR Spectra of Amine-Terminated Polydimethylsiloxane

Yield - 85%

### Infrared Spectra

Chloroterminated Siloxane: 2980, 2930, 1270 (Si-CH<sub>3</sub>);  
1100-1020 doublet, 800 (Si-O-Si);  
530, 465 (Si-Cl)cm<sup>-1</sup>.

Amine-terminated Siloxane: 2980, 2920, 1265 (Si-CH<sub>3</sub>); 2820  
(Fig.3.10)  
(N-CH<sub>3</sub>); 1100-1010 doublet, 800  
(Si-O-Si)cm<sup>-1</sup>.

### 3.2.6 Preparation of N, N-dimethylaminodimethylsilane

#### Reagents

Ether - Purchased from BDH and double dried with sodium wire.

Anhydrous Dimethylamine - Purchased from BDH and the ampoule opened  
as required.

Dimethyldichlorosilane - Purchased from BDH and distilled prior to  
use.

#### Procedure

Ether (50 cm<sup>3</sup>) was placed in a 2-neck flask (250 cm<sup>3</sup>) with the  
temperature maintained at -20°C. Anhydrous dimethylamine (10g) and the  
dimethyldichlorosilane (7g) were added via a septum seal. The amine  
hydrochloride salts which precipitated were filtered off at room  
temperature in a glove box. Intense white fumes developed on exposure  
of the solution from which after removal of ether by rotary evaporation  
to air, a clear liquid was obtained.

Infrared Spectrum: 3000, 2900 (C<sub>sp3</sub>-H<sub>str</sub>); 2820 (N-CH<sub>3</sub>);  
1270 (Si-CH<sub>3</sub>); 1000 (Si-N); 810 (Si-CH<sub>3</sub>) cm<sup>-1</sup>.

### 3.2.7 Copolymerisation of the Hydroxyl-terminated

#### Polystyrene and Amine-terminated Polysiloxane

##### Reagents

Amine-terminated polysiloxane - Preformed blocks, prepared in previous experiments of molecular weight 2000 and 50,000 (5.35g dissolved in 100 cm<sup>3</sup> toluene)

Hydroxyl-terminated polystyrene - Preformed blocks. (4.40g dissolved in 100 cm<sup>3</sup> toluene).

Toluene - Purchased from BDH (Analar Grade).

##### Procedure

Hydroxyl-terminated polystyrene (4.40g ) was placed in a 2-neck 500 cm<sup>3</sup> flask and dissolved in toluene (25 cm<sup>3</sup>) along with a major portion of the toluene solution of the amino terminated polysiloxane (45 cm<sup>3</sup>). After refluxing for 1 hour at 130°C under nitrogen, sequential additions of the remaining polysiloxane solution (6 x 4 cm<sup>3</sup>) were carried out over a 3 hour period. After refluxing for a further 1 hour, the pale opaque yellow mixture was poured into vigorously stirred methanol to precipitate the polymer. The product was filtered and dried in a vacuum oven overnight at 60°C.

Yield - 81%

Infrared Spectrum: 3080, 3060, 3020 ( $\text{C}_{\text{sp}^2}\text{H}_{\text{str}}$ ); 2960, 2920 ( $\text{Si-CH}_3$ );  
(Fig.3.11) 1600, 1495 ( $\text{C=C}$ ); 1450 ( $\text{C}_{\text{sp}^2}\text{H}$ ); 1265 ( $\text{Si-CH}_3$ );  
1120-1010 doublet ( $\text{Si-O-Si}$ ); 800 ( $\text{Si-O}$ );  
700, 540 ( $\text{C}_{\text{sp}^2}\text{H}$ )cm<sup>-1</sup>

Nuclear Magnetic Resonance data is given in Fig. 3.12 and Table 3.9.

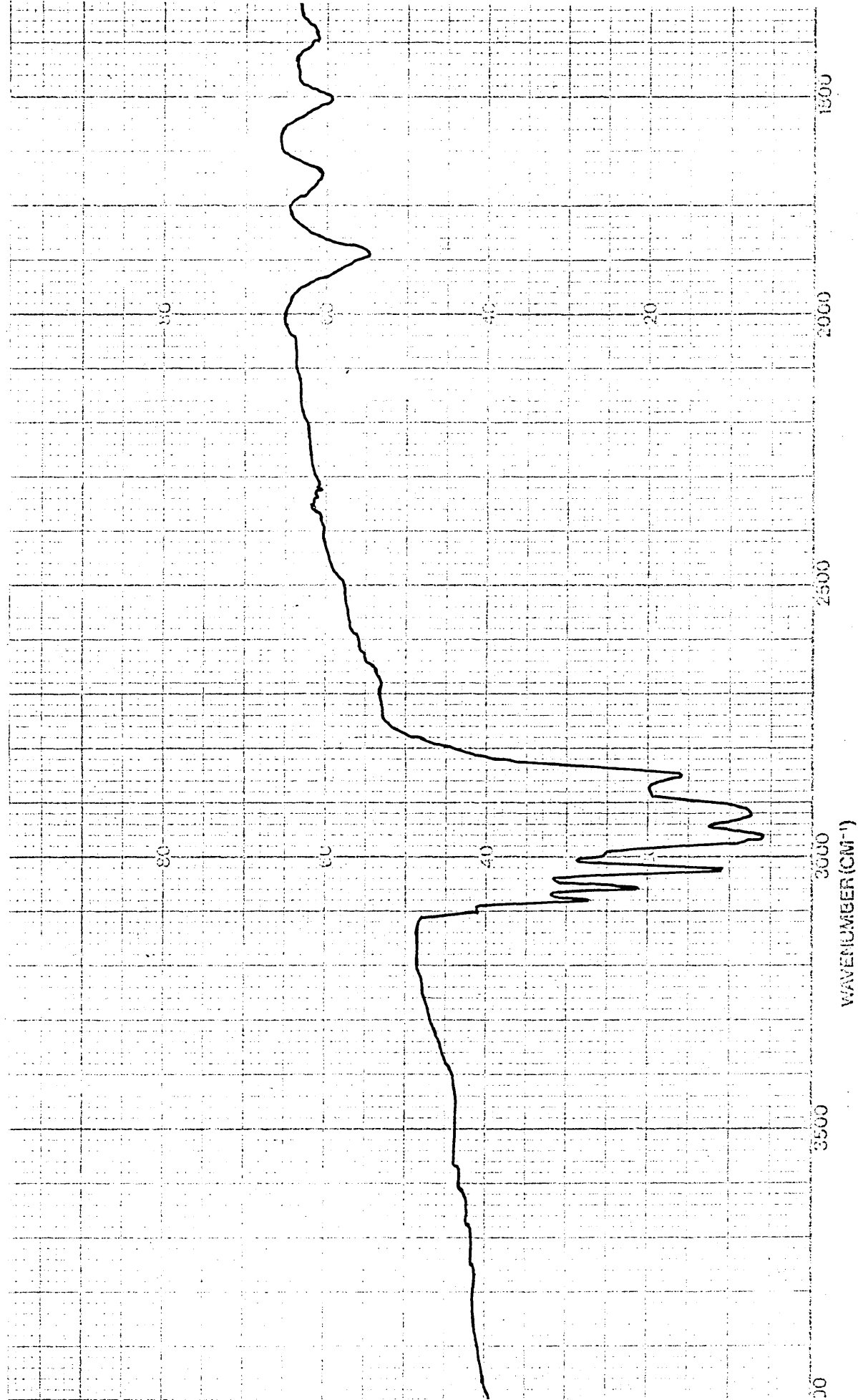


Fig.3.11 IR Spectra of a Polystyrene-Polydimethylsiloxane block copolymer.

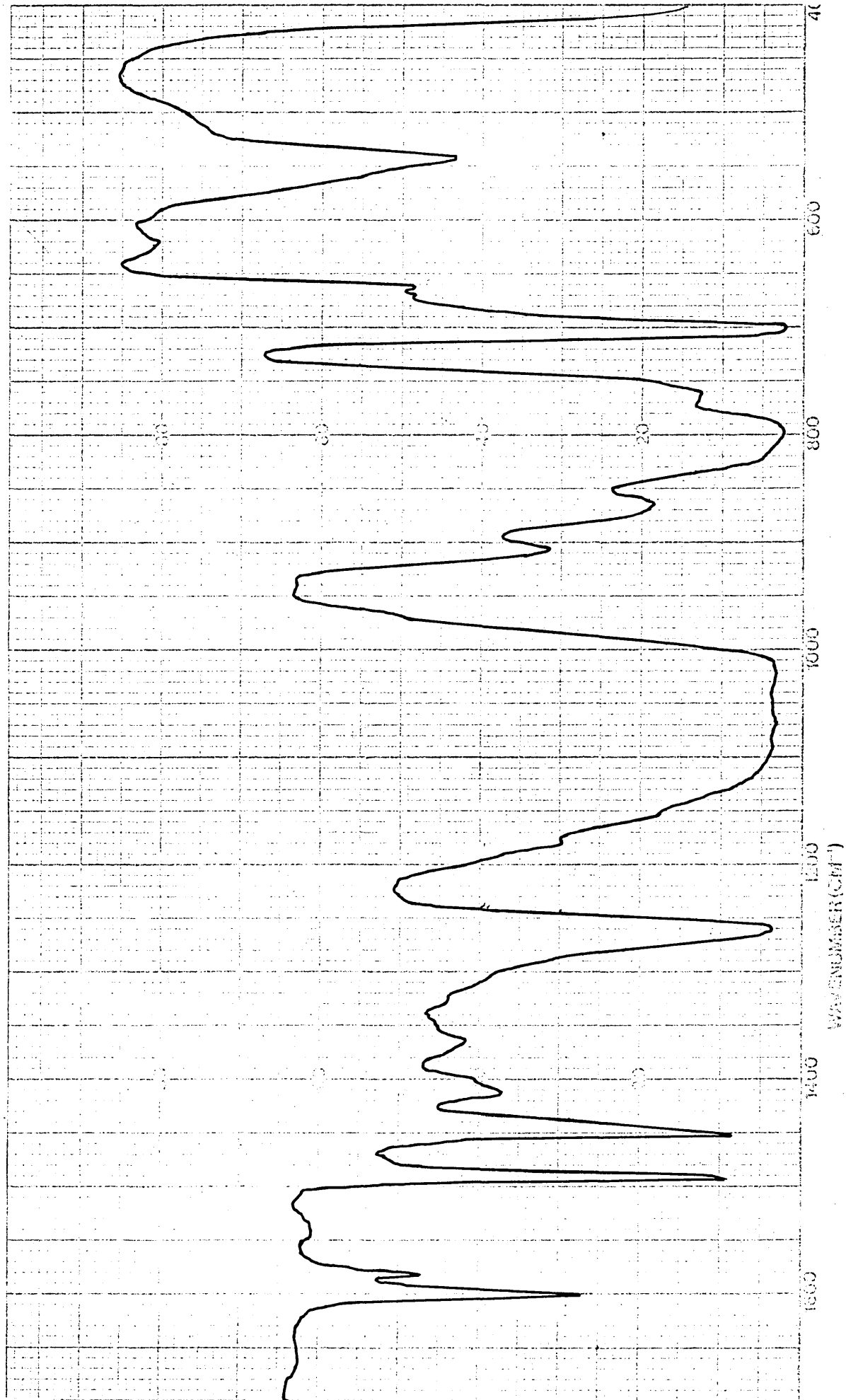




Fig.3.12 NMR Spectra of a Polystyrene-  
Polydimethylsiloxane block copolymer.

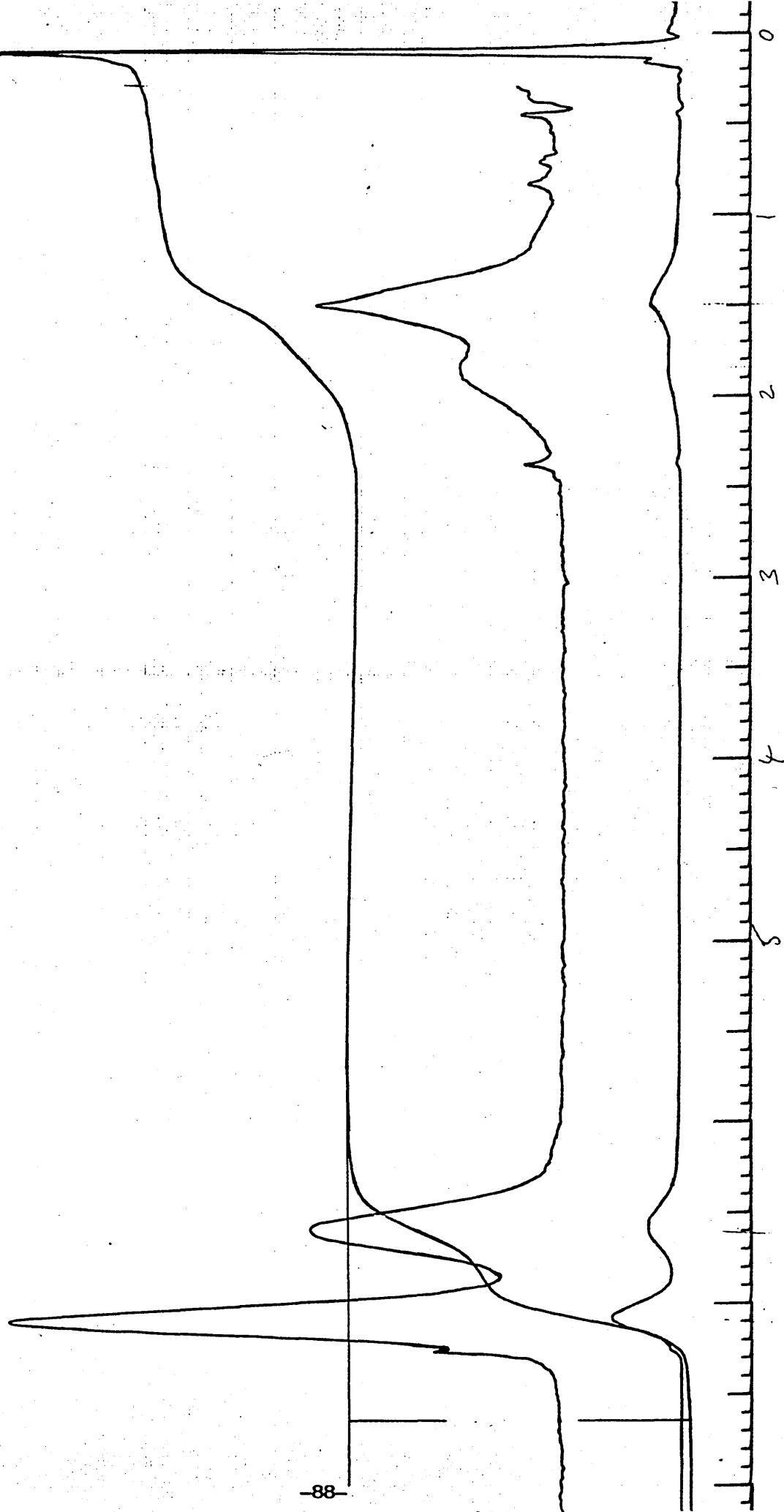


Table 3.9 NMR data for Siloxane-Styrene Copolymers

Sample	Yield %	% Siloxane	Chemical Shift ( $\delta$ ppm)			
			Pdms	Phenyl	Methine	Methylene
9.1	81	43.8	0.10	7.10, 6.62	1.85	1.50
10.1	74	50.7	0.08	7.08, 6.58	1.80	1.48
10.2	46	56.4	0.08	7.08, 6.60	1.82	1.48

GPC : GPC data from RAPRA is given in Table 3.10

Table 3.10 GPC data for Siloxane-Styrene Copolymers

Sample	$\bar{M}_n$	Mw	Dispersity
10.1	11,070	28,450	2.57
10.2	14,300	40,700	2.85

Thermal Analysis:

Differential Scanning Calorimetry data is given in Table 3.11

illustrated in Fig. 3.13.

Fig.3.13 Thermogram of sample Pss 10.1

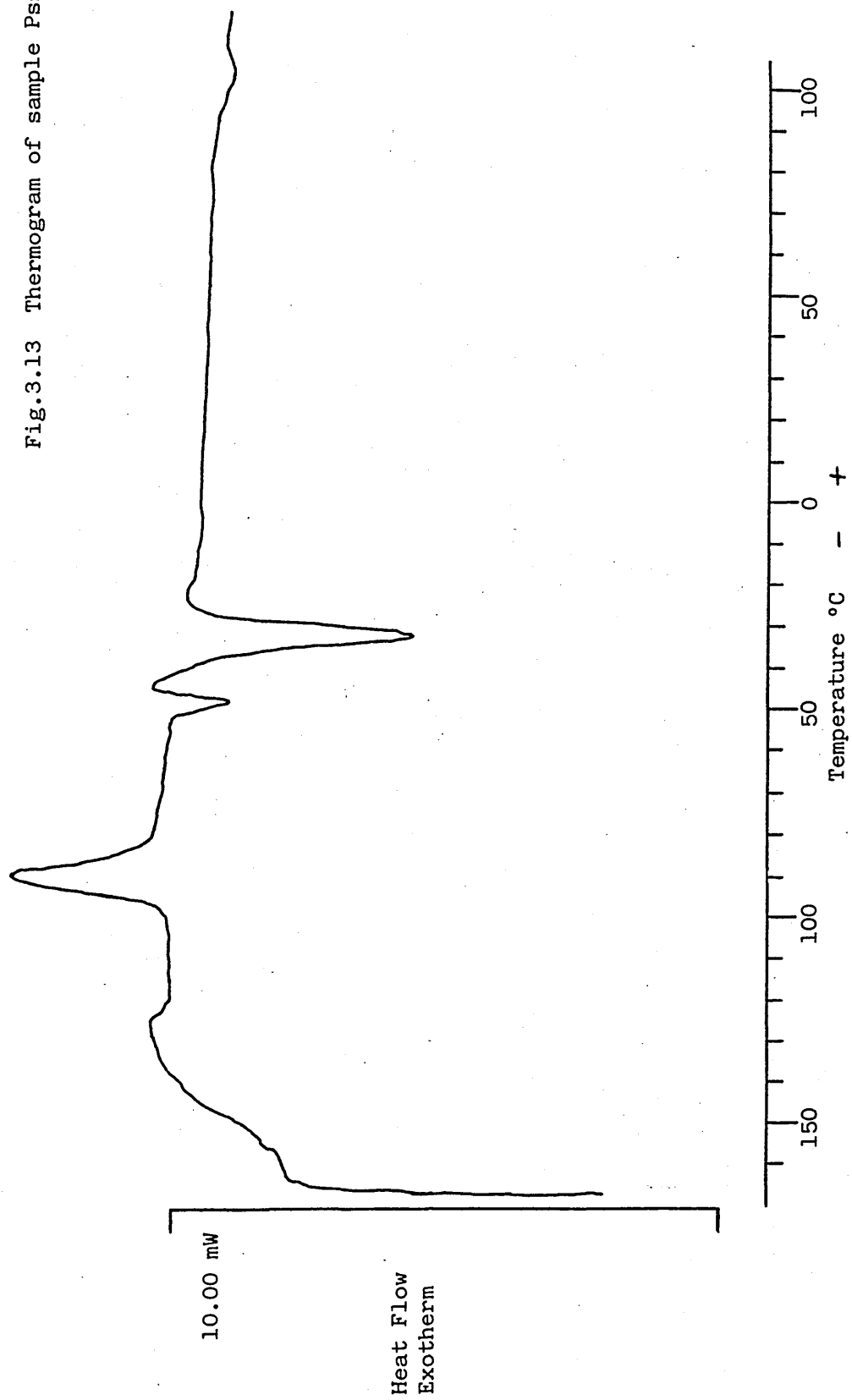


Table 3.11 Thermal data associated with Siloxane-Styrene Copolymers

(a) Siloxane

Sample	Glass Transition				Exotherm °C	Endotherm (1) °C	Endotherm (2) °C
	T <sub>g</sub> °C	T <sub>g1</sub> °C	T <sub>g2</sub> °C	ΔT <sub>g</sub> °C			
Pss 9.1	-122.76	-127	-119	8	-94	-39 (small)	-44.5
Pss 10.1	-123.3	-126	-122	4	-88.5	-33	-48 (small)
Pss 10.2	-122.5	-125.5	-119	5	-94	-34	-43 (small)

(b) Styrene

Sample	Glass Transition			
	T <sub>g</sub> °C	T <sub>g1</sub> °C	T <sub>g2</sub> °C	ΔT <sub>g</sub> °C
Pss 9.1	66.07	72.5	59	13.5
Pss 10.1	96.78	103	92	11.0
Pss 10.2	97.88	105	93	12.0

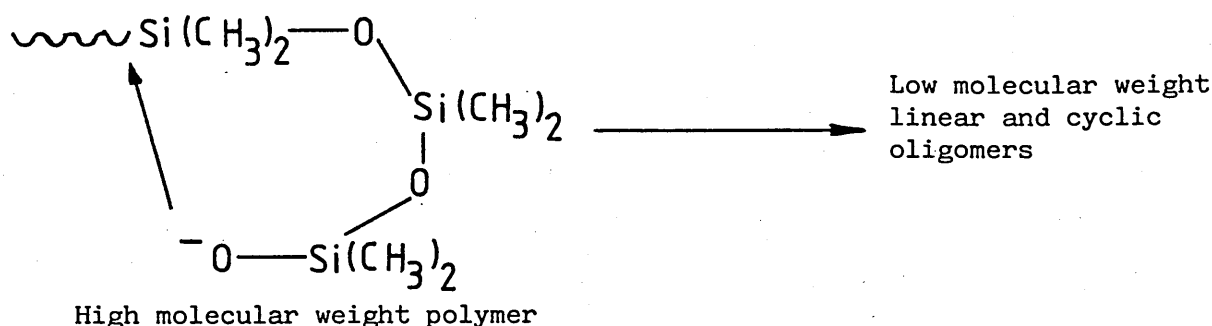
### 3.3 Results and Discussion

#### 3.3.1 Polymerisation involving Octamethylcyclotetrasiloxane

Styrene was initiated by potassium naphthalene, to produce "living styryl anions" with their characteristic crimson-red colour. On addition of octamethylcyclotetrasiloxane the crimson-red colour disappeared to leave a pale yellow mixture. The end product being a liquid polymer.

Polymerisation was not observed at all with lithium naphthalene, however using the potassium derivative a liquid siloxane polymer was clearly produced. Morton<sup>157</sup> has reported that on initiation with potassium naphthalene, "siloxane equilibration" is found to take place. Minoura<sup>135</sup> further investigated this phenomena and found that the tetramer ( $D_4$ ) was polymerised using a variety of initiators but that the polymerised high molecular weight silicone undergoes degradation to low molecular weight chains and oligomers when potassium naphthalene is used. The effect of the 'counter-ion' on the molecular weight and polydispersity was investigated by Bajaj.<sup>139</sup> Broadening of molecular weight distribution was observed in the presence of a sodium cation, compared to that with a lithium species. The lithium ion-pair is the least reactive of the two.

It would appear that the potassium-ion pair is very reactive, and the "living" potassium silonate species reacts with the already formed polymer chains resulting in a redistribution of the average molecular weight of the chains. There is also a shift towards the formation of cyclic siloxanes.



### Eqn.3.5 Equilibration Reaction.

A strong initiator is required to polymerise the tetramer ( $D_4$ ), such as potassium naphthalene, however this results in equilibration. To avoid this, this problem requires that the rate of propagation be faster than the equilibration reaction. This can be achieved using a less reactive ion-pair. Octamethylcyclotetrasiloxane is a relatively stable molecule, on the other hand hexamethylcyclotrisiloxane is quite the reverse.

### 3.3.2 Preparation of Hexamethylcyclotrisiloxane

In Scotts classical work<sup>158</sup> on the equilibria between linear and cyclic polysiloxanes, hexamethylcyclotrisiloxane was found to be under considerable ring strain. The normal Si - O - Si bond angle in a methyl siloxane, is  $160^\circ \pm 15^\circ$ , and the angle O - Si - O is  $109^\circ 28'$ ; the formation of the trimer requires that these angles be distorted. Crystallographic studies have found a planar ring structure for the trimer, which must exhibit strain within the ring. Thus the initiation of this monomer requires a less reactive initiator, and subsequently results in a decreased amount of equilibration.

The highly reactive nature of hexamethylcyclotrisiloxane does not favour its formation compared to the more stable tetramer. Hexamethylcyclotrisiloxane was present in the available mixed cyclics (supplied

by Dow Corning plc) in amounts less than 2%. Successive distillation was an impractical source of monomer, thus a synthetic route was investigated.

Numerous studies have been conducted into the distribution of cyclic monomers. Jacobson and Stockmayer<sup>159</sup> considered the statistical distribution of cyclics in a purely theoretical manner. They proposed that the weight distribution of the macrocyclic constituents at equilibrium was shown to be a monotonically decreasing function of molecular size. Full experimental results by Brown and Slusarczuk<sup>160</sup> have been compared to the Jacobson and Stockmayer's theory, where cyclic dimethylsiloxanes over the range  $x = 4$  to  $x = 200$  has been measured by chromatographic methods.

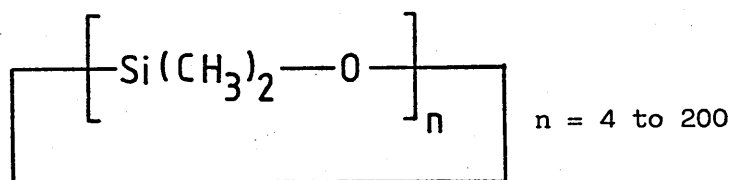
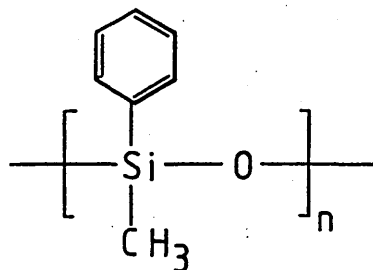


Fig.3.14 Cyclic Structures.

A linear relationship<sup>161</sup> between log molar cyclicisation constant ( $K_n$ ) and ring size was observed for the larger rings; this apparently represents the first experimental verification of the Jacobson-Stockmayer cyclicisation theory. There are experimental deviations of  $K_n$  at small ring values, which is attributed to a non-random distribution<sup>160</sup> of end-to-end segment distances. Brown and Slusarczuk<sup>160</sup> suggested a tentative  $K_n$  value for hexamethylcyclotrisiloxane of the same order as found for a siloxane ring of approximately 30 units, indicating the difficulty of forming the trimer in an equilibrium situation. Each of the investigations by Carmichael<sup>162,163</sup> found hexamethylcyclotrisiloxane

to be of such a low percentage concentration that it is termed "not detectable" in equilibrium studies. The tetramer was the starting cyclic unit for these experiments.

The action of potassium hydroxide<sup>164</sup> or sulphuric acid at high temperatures on high molecular weight polydimethylsiloxane, (300°C and above) causes depolymerisation, resulting in high yields of low molecular weight cyclics. Patnode<sup>121</sup> using acid, and Thomas<sup>165</sup> using base, agree that the trimer (44%) was the most abundant product with decreasing proportions of tetramer (24%), pentamer (9%), Hexamer (11%) and higher oligomers. The degradation of polymethyl phenyl siloxanes<sup>166</sup> (Fig.3.15) in work by Ostrovskii has been analysed by mass spectroscopy,



(Cyclic Oligomers	n = 3	Trimethyltriphenylcyclotrisiloxane
	n = 4	Tetramethyltetraphenylcyclotetrasiloxane)

Fig.3.15 Polymethylphenylsiloxane

and it is found that the rate of formation of tetramethyltetraphenylcyclotetrasiloxane ( $D_4^1$ ) is greater than those of trimethyltriphenylcyclotrisiloxane ( $D_3^1$ ) up to 180-200°C. After this point the trimer formation rate increases until approximately 260°C, where the trimer rate is greater than the tetramer.

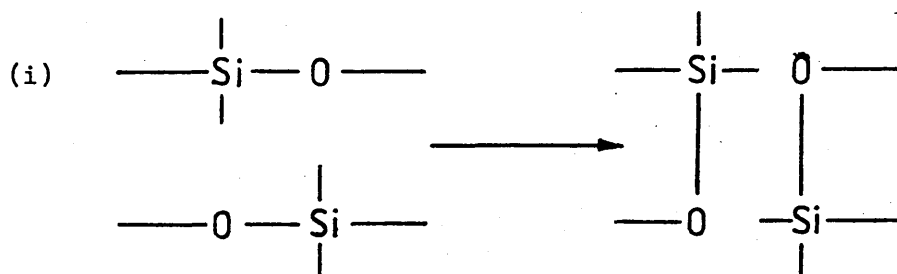
The conditions are clearly very different from those of the equilibrium studies. We know from previous discussions that polydimethylsiloxane can be obtained by the polymerisation of cyclic



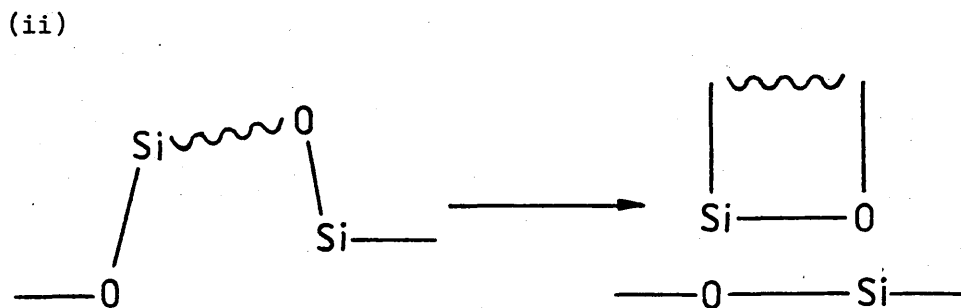
oligomers by alkali metal hydroxides, thus it was decided to investigate the possibility of obtaining hexamethylcyclotrisiloxane by the thermal depolymerisation/degradation of the polymerised gum.

It was expected, and this is seen in Table 3.1 that at higher temperatures the percentage composition of the trimer, would be increased. It is difficult to readily explain the change in composition of the oligomers, before and after the thermal rearrangement, since there are a number of complex reactions taking place.<sup>167</sup>

(A) Siloxane bond interchange, between chains.

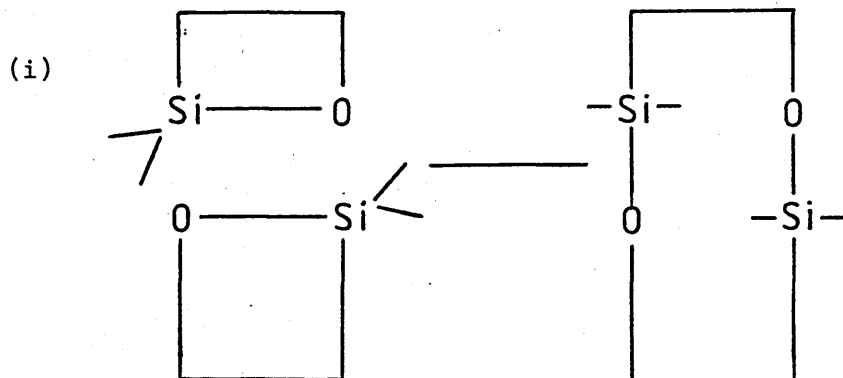


Equation 3.6a Resulting in a broadening of the molecular weight distribution.

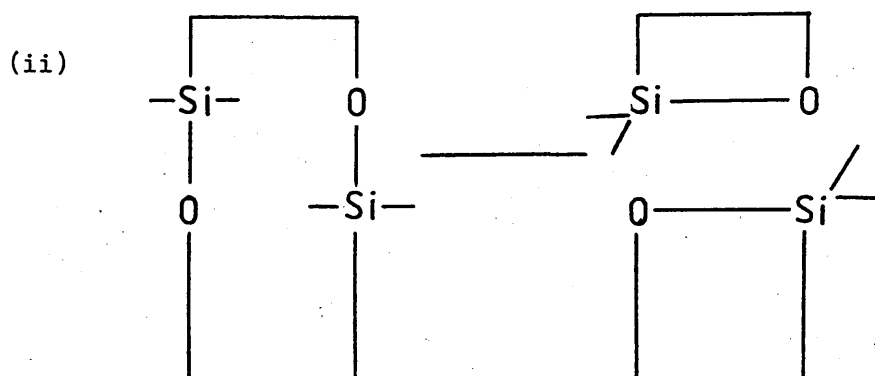


Equation 3.6b Giving a wide range of cyclic oligomers, the size of the ring being determined by the number of siloxane units between the sites of bond interchange.

(B) Siloxane bond interchange, involving cyclics.

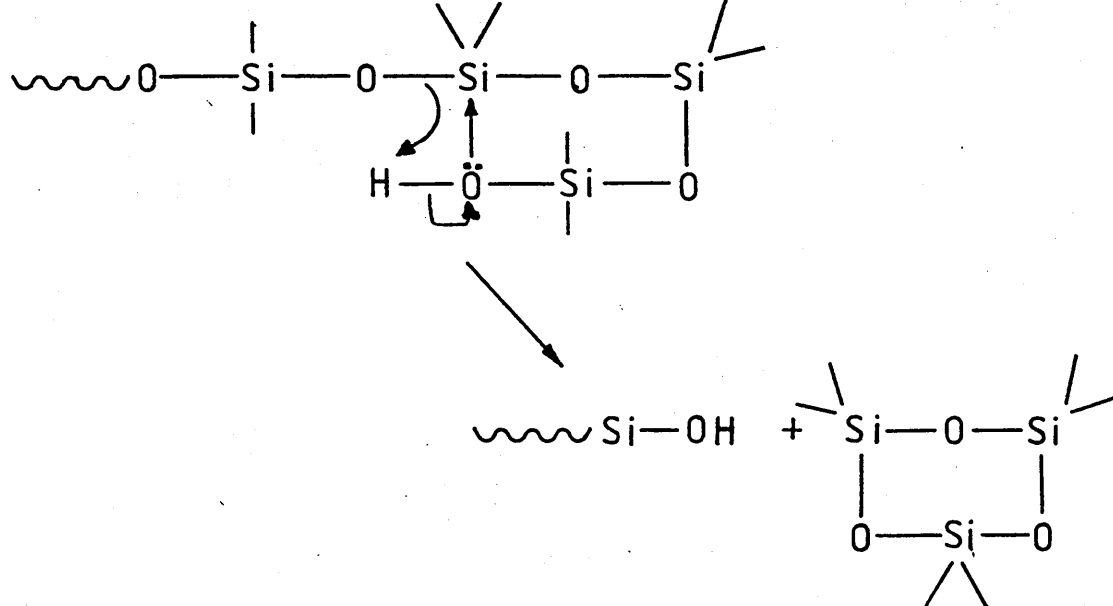


Equation 3.6c Resulting in much larger rings.



Equation 3.6d Giving a mixture of cyclics.

Grassie and Macfarlane<sup>168</sup> efficiently removed potassium hydroxide to obtain a material of optimum stability, and proposed a thermal rearrangement that only involves the terminal hydroxyl group (equation 3.7).



Equation 3.7 Thermal Rearrangement to give Hexamethyltrisiloxane.

If the hydroxyl group reacted further along the chain then higher oligomers would be produced. The presence of potassium hydroxide within the polydimethylsiloxane mixture has a powerful destabilizing effect and it is clear that a different mechanism is responsible for oligomer formation. Since the cyclic oligomers are formed in a step-wise reaction, each step must be catalysed by potassium hydroxide, or a derivative i.e. a silonate.

When volatile degradation products are continuously removed, Grassie<sup>169</sup> found that the depolymerisation reaction proceeded 30 times faster than in a closed system. The removal of the low molecular weight oligomers, prevents the polymerisation reaction taking place. This seems to be an application of the Le Chatelier Principle, and thus if hexamethylcyclotrisiloxane was selectively removed, the equilibrium would shift so as to produce more of the trimer. The results obtained from the small scale (10g) experiments are given in Table 3.1.

However the reactions that we have considered so far, do not involve gas evolution. But on opening one of the small glass tubes, ignition by a flame occurred and a small blue flame was observed for a

very short time. This is most likely to have been methane<sup>168</sup> resulting from the cleavage of a silicon-carbon bond. Another possibility could be hydrogen gas, but this would have exhibited different behaviour on burning. However such gas evolution would explain the explosions which occurred with the large scale reactions.

Although a route was available to enrich hexamethylcyclotrisiloxane within the mixture of oligomers, it was clear that this method was unsuitable for use on the desired scale. Although the desired starting material was a relatively expensive material, it was purchased for this study rather than synthesised.

### 3.3.3 Copolymerisation using Hexamethylcyclotrisiloxane

The physical appearance of the copolymer product was dependant on the molecular weight of the components and the composition of each product. A white powder was indicative of a high styrene content, whilst a gum-like material was very characteristic of a high molecular weight silicone.

The characteristic absorption bands resulting from the phenyl ring and siloxane linkage have been used to confirm the presence of both components (Fig.3.5). To give a first indication as to the composition of the copolymers, the Si-CH<sub>3</sub> absorption at 1265 cm<sup>-1</sup>, and styrene at 560 cm<sup>-1</sup> peaks were compared. Correlation data is given in Table 3.2.

Nuclear magnetic resonance spectra were recorded (Fig.3.6, Table 3.3) and the composition of the block copolymer calculated, from the integrated peak areas.

In the GPC analysis, two detectors are used; infrared (polydimethylsiloxane specific) detector and refractive index (polystyrene specific) detector. The infrared trace simply shows a single

peak indicative of polymer chains having polydimethylsiloxane components, any homopolystyrene that may be present, not being detected. However the refractive index trace gives a positive response for homopolystyrene, and negative for polystyrene chains containing polydimethylsiloxane. The sample Pss 23 appears to contain a small amount of high molecular weight homopolystyrene, amongst the polystyrene-polydimethylsiloxane block copolymer. It is possible that a few high molecular weight, living polystyryl anions terminated, prior or during to the addition of the hexamethycyclotrisiloxane, but with the majority of the styryl anions acting as an initiator for the cyclic monomer, thereby giving rise to a block copolymer. The retention time at which there is the highest number of copolymer chains, equates to a molar mass of  $42,300 \text{ g mole}^{-1}$ , based upon polystyrene calibration standards.

The thermal characteristics of the copolymers were investigated, as described in section 2.5.1. The polydimethylsiloxane glass transition temperature ( $T_g$ ) was found to be the same for both copolymers and identical to that obtained for the polydimethylsiloxane homopolymer in the blends. The polystyrene exhibited a glass transition in the region  $98^\circ\text{C} - 104^\circ\text{C}$ . It might be expected that a copolymer would exhibit a single glass transition, the position of which would be dependent on the composition of such a copolymer. However, it is found that two  $T_g$  are obtained as with polymer blends. Noshay and McGrath<sup>169</sup> have commented that, the thermal properties of block copolymers resemble those of physical blends, and have been found to display glass transition temperatures and crystalline melt temperature characteristic of each of the components. This is because block copolymers often display two-phase morphology and in the case of the polystyrene-polydimethylsiloxane block copolymers, there is evidence that the system separates into distinct microphases.

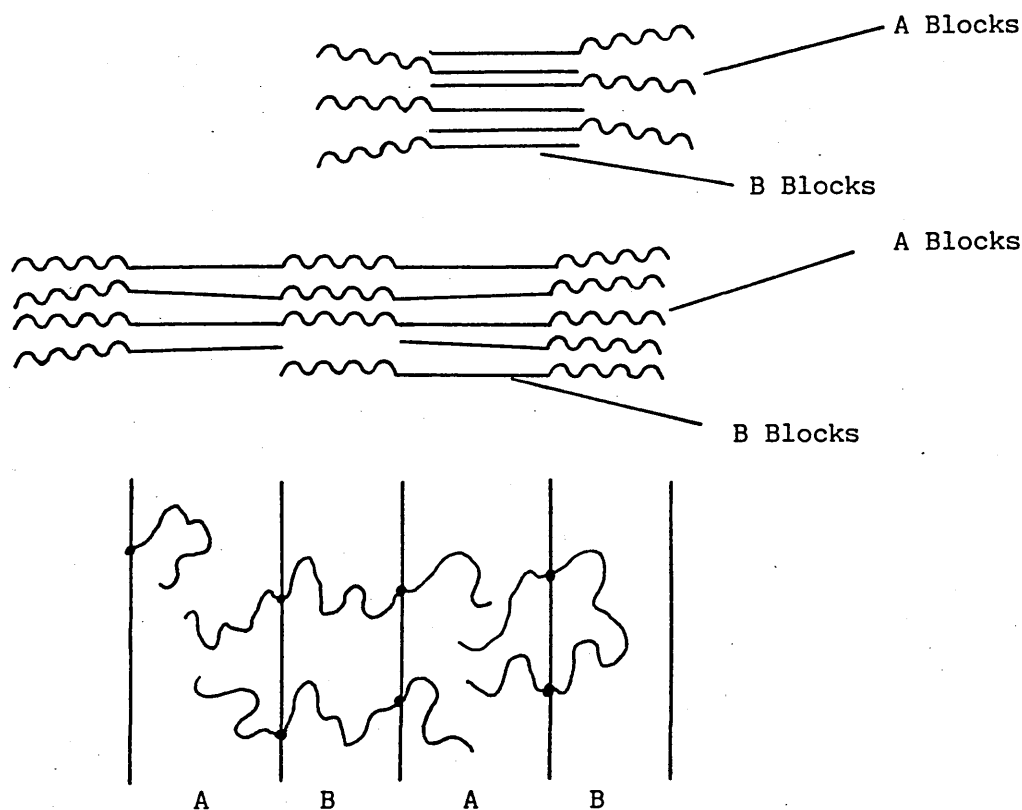


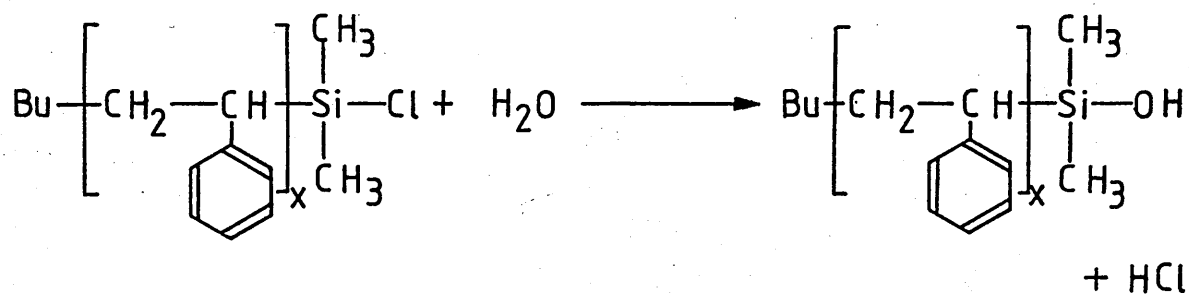
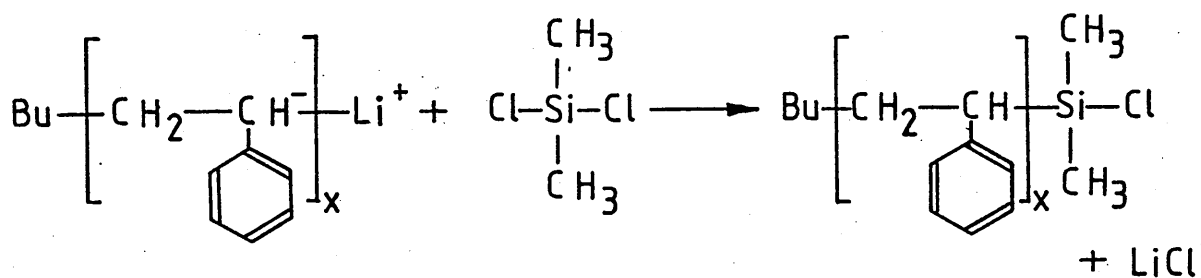
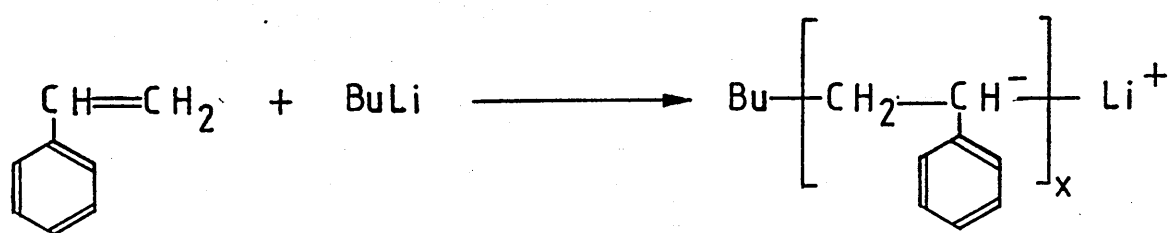
Fig. 3.16 a. Architecture  
b. Model Morphology.

This polymer system is prevented from forming separate macrophases, due to the chemical bonds linking the blocks together.<sup>170</sup> Even so, these microphases are able to exhibit their characteristic thermal properties. A number of theories<sup>171</sup> have been developed to predict the lengths of the blocks required for such phase separation. In a polystyrene - polybutadiene AB block copolymer,<sup>172</sup> phase separation would occur with the polybutadiene molecular weight 50,000 and polystyrene 5000-10,000. It is evident that a relatively short polystyrene chain is required for phase separation. Although no figures are available for our particular system, it is anticipated that the polystyrene block length would ensure that phase separation took place.

Transition broadening ( $\Delta T_g = 4.7^\circ\text{C}$ ) has been observed with polysiloxanes when blended with polystyrene. This observation has been explained as due to the influence of the polystyrene component. The polystyrene in these copolymers appears to have a much greater influence, with  $\Delta T_g = 7^\circ\text{C}$ . This is in good agreement with the work of Krause<sup>110</sup> on polystyrene-polydimethylsiloxane (AB) block copolymers where the average range over which the transition takes place was found to be  $7^\circ\text{C}$ , with little or no shift in the polysiloxane transition temperature. Thus the thermal characteristics of the siloxane component does point to some interaction existing between the two phases. Whereas the glass transition of the polystyrene component and the temperature over which the transition takes place is the same as that in homopolystyrene.

#### 3.3.4 Preparation of Hydroxyl-terminated Polystyrene

Infrared analysis of the product (Fig.3.8) from a thin film, showed absorption bands at  $1250\text{ cm}^{-1}$  (Si-CH<sub>3</sub>) and  $810\text{ cm}^{-1}$  (Si-CH<sub>3</sub>) and  $810\text{ cm}^{-1}$  (Si-C) indicative of the presence of the silane group. The absence of any peaks in the region 460-470 (Si-Cl), and the presence of the broad band at 3600-3200  $\text{cm}^{-1}$  confirm that the chlorosilane terminating group has undergone hydrolysis.



Equation 3.8 The preparation of hydroxy terminated polystyrene.

The NMR spectrum (Table 3.6. ) confirmed the structure of this prepolymer. Quantitative analysis of the spectrum yields the % silane end groups.

For example:



a) Mole %

$$\begin{aligned}
 \% \text{ Silane} &= 5 \times \text{Peak height of siloxane (B)} \\
 &\quad (6 \times \text{Peak height of styrene (A)}) + \\
 &\quad (5 \times \text{Peak height of siloxane}) \\
 &= 5 \times 2 \\
 &\quad (6 \times 99.5) + (5 \times 2) \\
 &= 1.65 \text{ mole \%}
 \end{aligned}$$

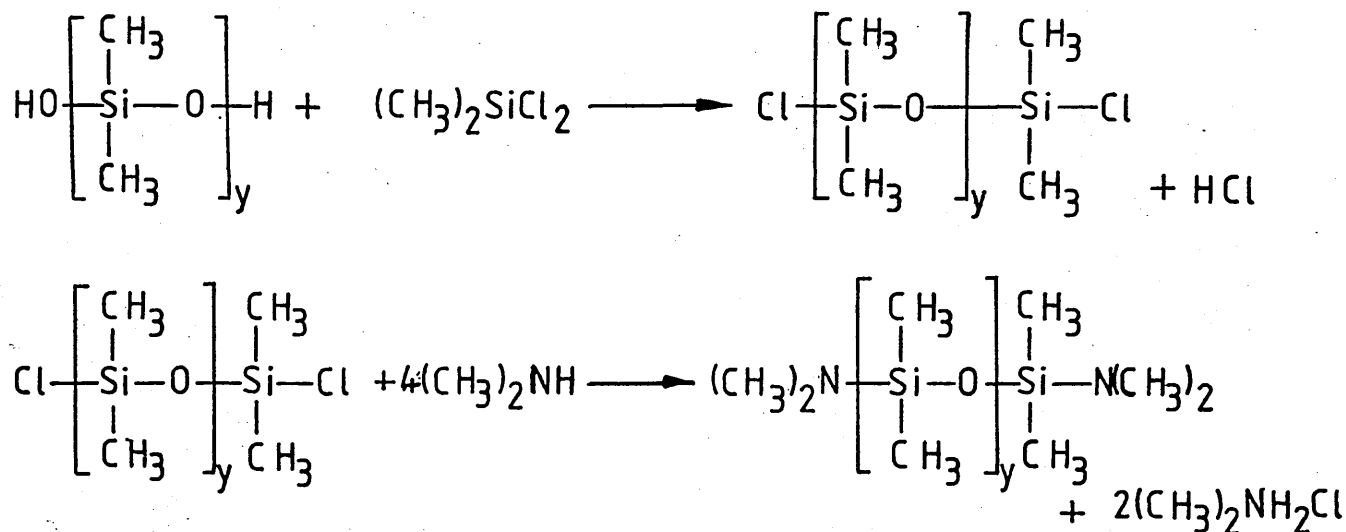
b) Weight %

$$\begin{aligned}
 \% \text{ Silane} &= 5 \times B \times 75 \\
 &\quad (6 \times A \times 104) + (5 \times B \times 75) \\
 &= 1.21 \text{ weight \%}
 \end{aligned}$$

The NMR spectra not only provides confirmation for the presence of the silane end group, but it is noted that the clear resolution of the methylene and methine polystyrene resonances indicate the isotactic nature of the polystyrene.<sup>139</sup>

The GPC determinations show that the system is severely effected by termination of growing chains and a heterogeneous polymer is formed.

### 3.3.5 Preparation of Amine-terminated polysiloxane

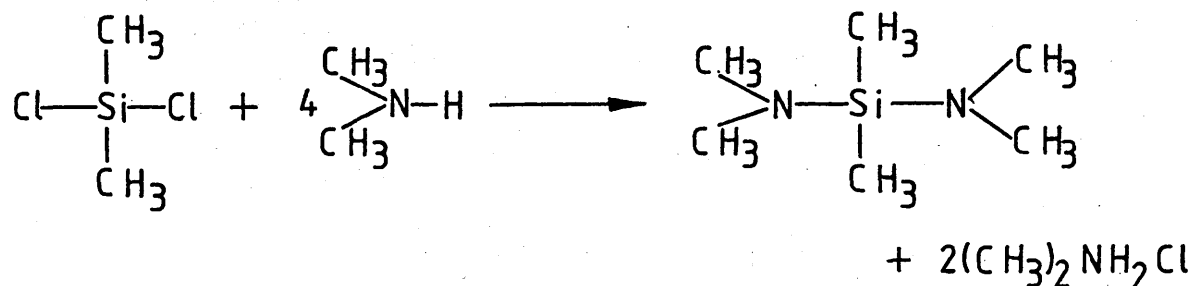


Equation 3.9 The preparation of amine-terminated polysiloxane.

Three samples of hydroxy terminated polysiloxane of molecular weights 800, 2000 and 50,000 were supplied by Dow Corning. The 2000 molecular weight sample was initially used to bring about amine termination, spectral analysis confirming such an addition. The higher molecular weight sample was then subject to the amination reaction.

The Si-Cl bands in dimethyldichlorosilane are seen at 530 and 465  $\text{cm}^{-1}$ , as strong absorbances. In the chloro-terminated polysiloxane, peaks are observed at these values but their intensity, as expected, is very low. The absence of evidence for the hydroxyl group, and the presence of these Si-Cl absorption bands, clearly indicates that chloro-termination has taken place.

It was difficult to decide whether the amino group had replaced the terminal chloro group following the second step of the reaction, because of the low intensity of the absorption bands. To be clear about the bands in such a structure, a model compound was produced (N, N-dimethylaminodimethylsilane) by reaction of dimethyldichlorosilane and dimethylamine at  $-20^{\circ}\text{C}$ .



Equation 3.10 The preparation of N, N-dimethylaminodimethylsilane

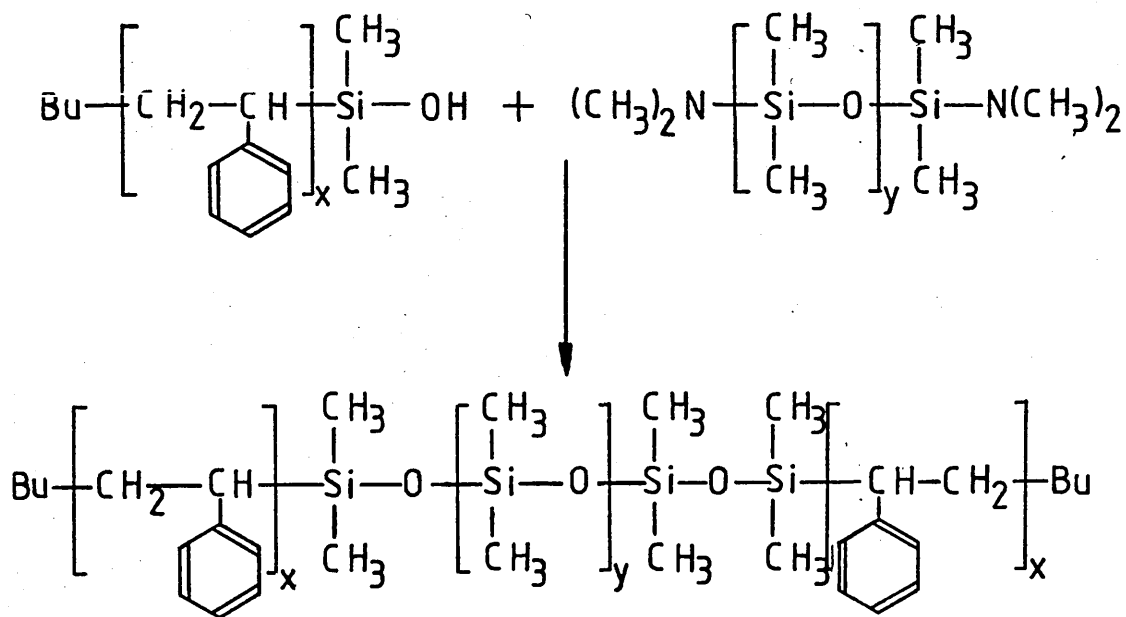
The infrared spectra revealed important information. The most intense absorbance is the Si - N peak at  $1000 \text{ cm}^{-1}$ ,<sup>173</sup> unfortunately cannot be used to identify the presence of terminal amine group in the polymer since the very intense Si-O-Si doublet masks any such absorbance.

The evidence that does indicate the presence of an amino-terminating group is the C-N peak at  $2820\text{ cm}^{-1}$  coupled with the disappearance of the Si-Cl absorption band (Fig. 3.10).

This band was observed in the products from each of the different molecular weight polysiloxanes. The viscosity was observed in each case to be identical to that of the starting material, which suggests that chain extension of the macromolecules has not occurred. The polysiloxanes of 2000 and 50,000 molecular weight were selected for copolymerisation studies.

### 3.3.6 Copolymerisation

Block copolymers of the type ABA were prepared by coupling of the terminal hydroxyl groups of the polystyrene and the dimethylaminosilyl groups of the polydimethylsiloxane.



Equation 3.11 Copolymerisation to produce ABA Block Copolymers of polydimethylsiloxane and polystyrene.

The infrared spectra indicate that each component is present in the polymer produced (Table 3.2). The appearance of peaks in the NMR spectra which can be assigned to both polysiloxane and polystyrene is further evidence for the existence of both components within the products. The chemical shifts are found to be very similar to those in the homopolymers.

It is possible that homopolymers may be present in the products, along with copolymers. Dissolution using selective solvents was used to remove homopolystyrene. Subsequent NMR analysis gave a value for polysiloxane content of 51.8% an increase of 8% in polysiloxane content caused by removal of the homopolystyrene.

The products were characterised by RAPRA, (Table 3.10). Care is required in the interpretation of the results, as any homopolymer present can complicate the analysis. However the molecular weight of the copolymers are found to be higher than the component polystyrene blocks, which does suggest that a copolymer is obtained.

The two hydroxy-terminated polystyrene display quite different thermal characteristics (Table 3.8). A slightly higher glass transition temperature is observed for the low molecular weight sample. There are two well resolved peaks for the crystalline melt temperature ( $T_m$ ) in each sample, but each sample gives rise to a different melting process. The molecular and chain motion is dependant on the environment of the chain, the molecular weight being an important factor. The greater the mobility the higher the temperature at which the glass transition ( $T_g$ ) will occur. Also the temperature at which the crystalline melt takes place will be influenced by molecular weight.

The thermograms obtained for the block copolymers show some very interesting results (Table 3.11). The glass transition of the polydimethylsiloxane segment in Pss 9.1 is unchanged from that of the

homopolysiloxane, whereas in Pss 10.1 and Pss 10.2 it is slightly decreased. There is very little change in the range over which the glass transition takes place. It was found that in the copolymers obtained by anionic polymerisation, the glass transition of the polysiloxane was also relatively unchanged, due to microphase separation. This appears also to be the case in copolymers, produced via condensation polymerisation. (Fig.3.13)

In the copolymers the cold crystallisation (exotherm) of the polysiloxane is observed at a lower temperature than in homopolymer, the shift being as much as 12% which is attributed to the presence of polystyrene component. In the crystalline melt region of the lower molecular weight polysiloxane, two distinct peaks are observed at  $-35.5^{\circ}\text{C}$  (small) and  $-43.0^{\circ}\text{C}$  (larger peak).

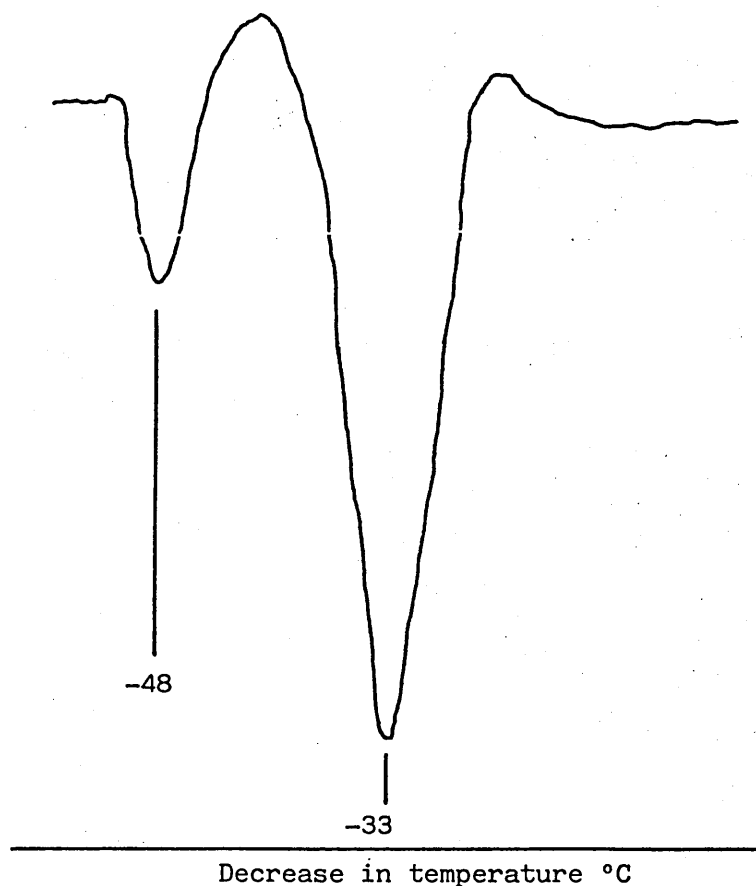


Fig. 3.17 Expanded Crystalline Melt Peak for sample Pss 10.1

However, in the respective copolymer Pss 10.2 (2000 silanol) the peak at  $-34^{\circ}\text{C}$  is the larger and the peak at  $-43^{\circ}\text{C}$  is so small that it is observed as a shoulder. It is clear that there are two crystalline forms in polysiloxanes, as shown by the two melting exotherms. The thermogram for the copolymer indicates that the polystyrene influences which crystalline form is produced, and it is different from that which is formed in homopolymer polydimethylsiloxane. It would appear that the bulk of the crystallites now require a higher temperature to undergo melting. This reversal of the relative importance of melting exotherms is not observed in the higher molecular weight polydimethylsilanol, the higher temperature exotherm is always the most important. The fact that this influence of polystyrene on the crystalline melt temperature is not observed for the higher molecular weight polysiloxane suggests that this is dependent on the molecular weight of the polysiloxane.

The thermal behaviour of polystyrene segments in the copolymer reveal interesting results. The glass transition temperature for polystyrene of sample Pss 9 showed a decrease of  $16.8^{\circ}\text{C}$  compared to homopolystyrene. (Table 3.8 and 3.11). Broadening of the transition temperature is clearly seen, for example from  $6^{\circ}\text{C}$  in homopolystyrene to  $13.5^{\circ}\text{C}$  in sample Pss 9.1. This is observed to a lower extent in the other samples. These results suggest that there is some interaction between the polystyrene phase and the polysiloxane phase in the copolymers.

RADIATION STUDIES I - POLYDIMETHYLSILOXANE

4.1 Fundamentals of Irradiation

4.1.1 Units

The quantitative unit which is used to describe the amount of radiation received by a particular substance is termed the "dose". This originates from the field of radiotherapy where patients are given a 'radiation dose', in the same way that they would receive a prescribed 'dose' of a particular medicine. Following the analogy through to its logical conclusion, the term implies that energy is transferred from the radiation to the substance within which it passes. This dissipation of energy is expressed in terms of ergs per gram of irradiated material.

A distinction must be made between 'exposure dose' and 'absorbed dose'. The amount of radiation that is incident on a substance is the 'exposure dose', measured in Roentgens (R), whereas the radiation that is actually absorbed by the substance is termed 'absorbed dose'. The 'exposure dose' is determined by measuring the ionisation produced by the same radiation beam in air. Therefore by taking into account the ratio of the mass absorption coefficients of the irradiated material and the energy that would be released in ionisation of air, the absorbed dose can then be derived in any situation.

The unit of absorbed dose, recommended by ICRU<sup>174,175</sup> (International Commission on Radiological Units), is the 'rad':

$$\begin{aligned}
 1 \text{ rad} &= 100 \text{ ergs g}^{-1} \\
 &= 6.25 \times 10^{13} \text{ eVg}^{-1} \\
 \text{since } 1 \text{ J} &= 10^7 \text{ ergs} \\
 1 \text{ rad} &= 100 \text{ ergs g}^{-1} \\
 &= 10^{-5} \text{ Jg}^{-1}
 \end{aligned}$$

Thus

$$100 \text{ rads} = 1 \text{ JKg}^{-1}$$

The new SI unit of absorbed dose is the Gray (Gy)

$$\begin{aligned}
 1 \text{ Gy} &= 1 \text{ JKg}^{-1} \\
 &= 100 \text{ rads}
 \end{aligned}$$

at higher doses of radiation:

$$\begin{aligned}
 1 \text{ KGy} &= 1 \text{ KJ Kg}^{-1} \\
 &= 10^{-1} \text{ Mrad}
 \end{aligned}$$

The SI unit of the absorbed dose rate, is the Gray per second.

$$\begin{aligned}
 1 \text{ GySec}^{-1} &= 100 \text{ rads s}^{-1} \\
 &= 0.36 \text{ Mrad hr}^{-1}
 \end{aligned}$$

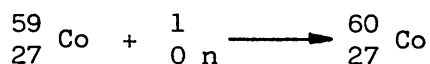
The unit that is generally used in the current literature is the Mrad, and there is seemingly a reluctance to introduce the Gray.

#### 4.1.2 Radiation Sources

Of the radioactive isotopes, Cobalt-60 is the most widely used as a gamma source. This has arisen because of its ease of preparation, fairly long half-life and penetrating power.



Cobalt-60 is produced by activation of Cobalt-59, in a high neutron flux.



(half-life 5.3 years)

After neutron capture, the pure metallic Cobalt in the form of small rods, is hermetically sealed by double encapsulation in stainless steel. The  ${}^{60}\text{Co}$  decays emitting 0.31 MeV  $\beta$ -rays and two successive  $\gamma$  photons of 1.17 and 1.33 MeV (mean energy of 1.25 MeV). The  $\beta$ -rays are absorbed in the  ${}^{60}\text{Co}$  itself, or in the encapsulating stainless steel.

A second source that is sometimes used, is  ${}^{137}\text{Cs}$ , which is obtained from the spent fuel rods of a nuclear reactor. On removal from the reactor core, the radioactivity decays in a very short period of time and the rods are processed to obtain the fission products. After extensive separation,  ${}^{137}\text{Cs}$  can be obtained from which the chloride or sulphate salt is produced, which is encapsulated in the same type of container as for  ${}^{60}\text{Co}$ .

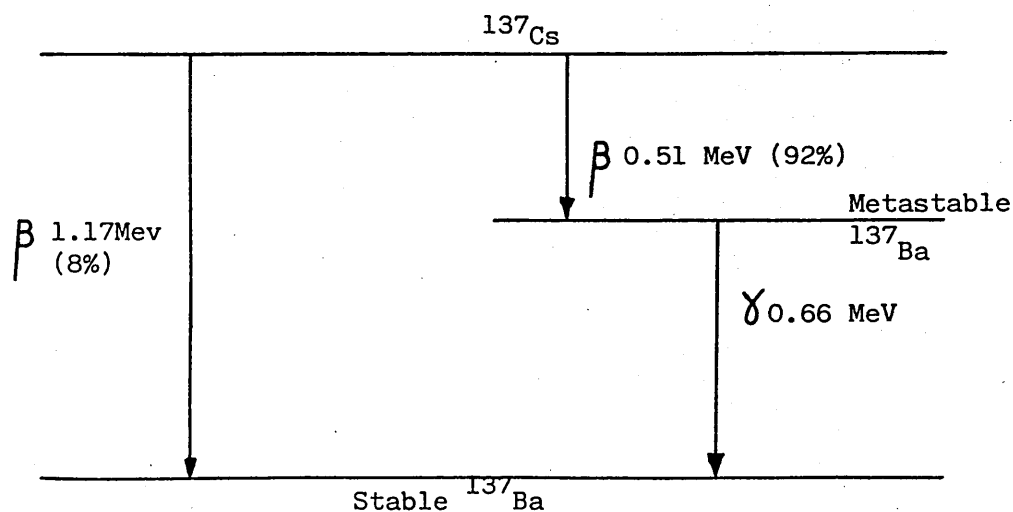


Fig.4.1 Decay of  ${}^{137}\text{Cs}$

The  $^{137}\text{Cs}$  decays (Fig.4.1) to the stable  $^{137}\text{Ba}$  by either of two routes, of which one involves emission of a  $\beta$ -ray accompanied by a  $\gamma$ -photon of energy 0.66 MeV. Table 4.1 compares the two common sources.

Table 4.1 Two Common  $\gamma$ -Sources

	Cobalt	Caesium
Atomic Weight	60	137
$\gamma$ rays MeV	1.17, 1.33	0.66
$\beta$ rays MeV	0.31	0.51 (92%) 1.17 (8%)
State	Metal	CsCl, CsSO <sub>4</sub>
Half life, years	5.3	33
Replenishment per year	12.5%	2.3%
Penetration (distances in water to reduce to 1/10th of its intensity)cm	43.2	29

At one time  $^{176}\text{Co}$  it was thought that  $^{137}\text{Cs}$  might replace  $^{60}\text{Co}$ , due to the large quantities that were available from nuclear reactor plants, but certain safety problems  $^{177}\text{Co}$  with  $^{137}\text{Cs}$  have reduced this possibility.  $^{137}\text{Cs}$  is slightly unstable to radiation, and cesium chloride is corrosive towards its encapsulating material. At the present moment  $^{60}\text{Co}$  is the  $\gamma$ -source that is preferred in industrial and research applications. The  $\gamma$ -rays, are of higher energy, hence of greater penetrating power, but it does require greater replenishment than for the  $^{137}\text{Cs}$  isotope.

#### 4.1.3 Dosimetry

There are many methods that can be employed to experimentally determine the amount of energy imparted to a material exposed to ionising radiation. They can be divided into two groups, 'absolute' and 'relative' methods, otherwise known as 'standard' and 'routine', respectively.

The radiation field of a  $\gamma$  source can be analysed using an absolute dosimeter, such as an ionisation chamber, or the Fricke dose meter.<sup>178</sup> The latter is based on the radiation induced oxidation of ferrous ion, an irreversible reaction.

Once a radiation field has been determined by an absolute method, it is possible to calibrate other radiation indicators, which can be much more practicable. These include scintillation, photographic and colourimetric dosimeters. A large number of solid substances, such as glasses, crystals, and certain plastics become discoloured when exposed to ionising radiations. All these colour changes, when measured quantitatively, can be used for dosimetric purposes.

#### 4.2 The Formation of Crosslinks

Upon  $\gamma$ -irradiation some polymers undergo crosslinking exclusively while others are degraded. However, with the majority of polymers both reactions proceed to some degree.

The materials of interest in this study are siloxanes. The predominant reaction in siloxane is crosslinking, but a small amount of chain scission does take place. It is the crosslinking reaction that leads to reduced mechanical properties and the following discussion will therefore focus on the necessary requirements for crosslink formation.

#### 4.2.1 Primary Chemical Processes

When  $\gamma$  radiation is incident on, and subsequently passes through, a polymeric material, the energy is transferred to the molecules of the absorbing medium by a number of physical mechanisms. The intensity of the  $\gamma$  radiation decreases as it passes through the polymer because of scattering and energy absorption. Three main processes are possible:<sup>4</sup>

- a) the photoelectric effect;
- b) Compton scattering; and
- c) production of electron pairs.

a) The Photoelectric Effect - This process arises when  $\gamma$ -rays of low quantum energy eject a fast moving electron which can lead to further electrons being eliminated from molecules along its path. With each electron ejected, a photon is consumed, hence the energy is dissipated within the irradiated polymer.

b) Compton Scattering - For  $\gamma$ -irradiation of higher energy, a large proportion of the energy is dissipated through 'Compton recoil electrons'. In this case the exchange of energy from the incident photon to the ejected electron is very low. In consequence a modified photon of lower energy is propelled in a direction, differing from its original track by an angle  $\theta$ . The result of this collision is that the imparted energy is shared between the ejected electron, which can have a very wide range of energies, and a photon of lower energy.

c) Production of Electron Pairs - Electromagnetic radiation having energy greater than 1.02 MeV gives rise to electron-pair production. The incident energy must be larger than the combined mass of the electron-positron pair. The energy of the incident photon is thus transferred into fast moving electrons, which interact further to ionise the polymeric molecule.

The total absorption of radiation energy by a polymeric material is the sum of absorption due to these three processes.

#### 4.2.2 Secondary Chemical Processes

Interaction of energy with the orbital electrons of molecules in the polymer results in ionisation if the imparted energy is higher than the binding energy. If the energy is less than the lowest ionisation potential, the electron is raised to a non-bonding level producing an excited molecule.

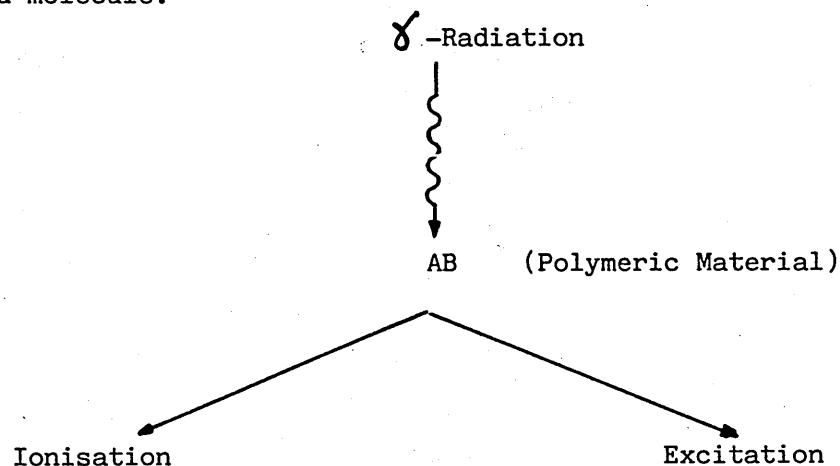


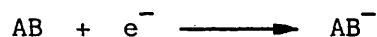
Fig. 4.2 Interaction of Radiation with Polymers

These two species which can arise from the direct interaction of radiation with polymers (Fig.4.2), can now take part in a series of secondary reactions.

a) Electron Capture by Neutral Molecules

The ionisation process is due to the elimination of an electron, which can subsequently ionise or excite other molecules. "Slow" electrons of low kinetic energy can be absorbed by the polymeric material through the following routes:

i) electron attachment



The conclusion of a number of authors<sup>179,180</sup> is that only electrons of low kinetic energy will normally add to a neutral molecule to produce an anionic species.

ii) electron capture leading to dissociation



This reaction can take place when B is a group of high electron-negativity and able to dissipate the negative charge.

b) Ionic Reactions

In the previous section, it was shown that ejected electrons can be responsible for further reactions, however this is true also for the resultant positive ion.

i) electron capture by the positive ion



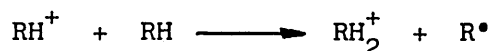
The ejected electrons can be trapped either by the neutral molecule, or the positively charged molecules. If the electrons contain a small excess of energy, they are unable to travel a large distance from the site of ionisation, therefore the above process will be favoured over

that involving neutral molecules and will lead to a highly excited molecule.

The final concentration of free radicals may vary considerably,<sup>178</sup> according to the rates of reactions (ai) and (bi) above.

#### ii) ion-molecule reactions

When ions are produced in a liquid, they have a short lifetime, since they are readily neutralised, hence no reactivity is observed. However, in a solid neutralisation is somewhat slowed down giving rise to:



In certain circumstances the ions have a lifetime long enough to bring about ionic chain polymerisation.

#### c) Reactions of Excited Molecules

##### i) dissociation into free radicals



This is one of the most prolific sources of free radicals. If the energy that is required to bring about dissociation is somewhat less than the energy of the molecule whilst in the excited state, then the subsequent fragments have sufficient kinetic energy to be removed to such a distance that recombination is not possible.

We have considered the main reactions that are probable when gamma radiation is incident on a polymeric material, and the nature of the species produced (Fig.4.2 ). The wide variety of ionic species and free radicals produced can be involved in reactions that affect the overall character of the polymer.

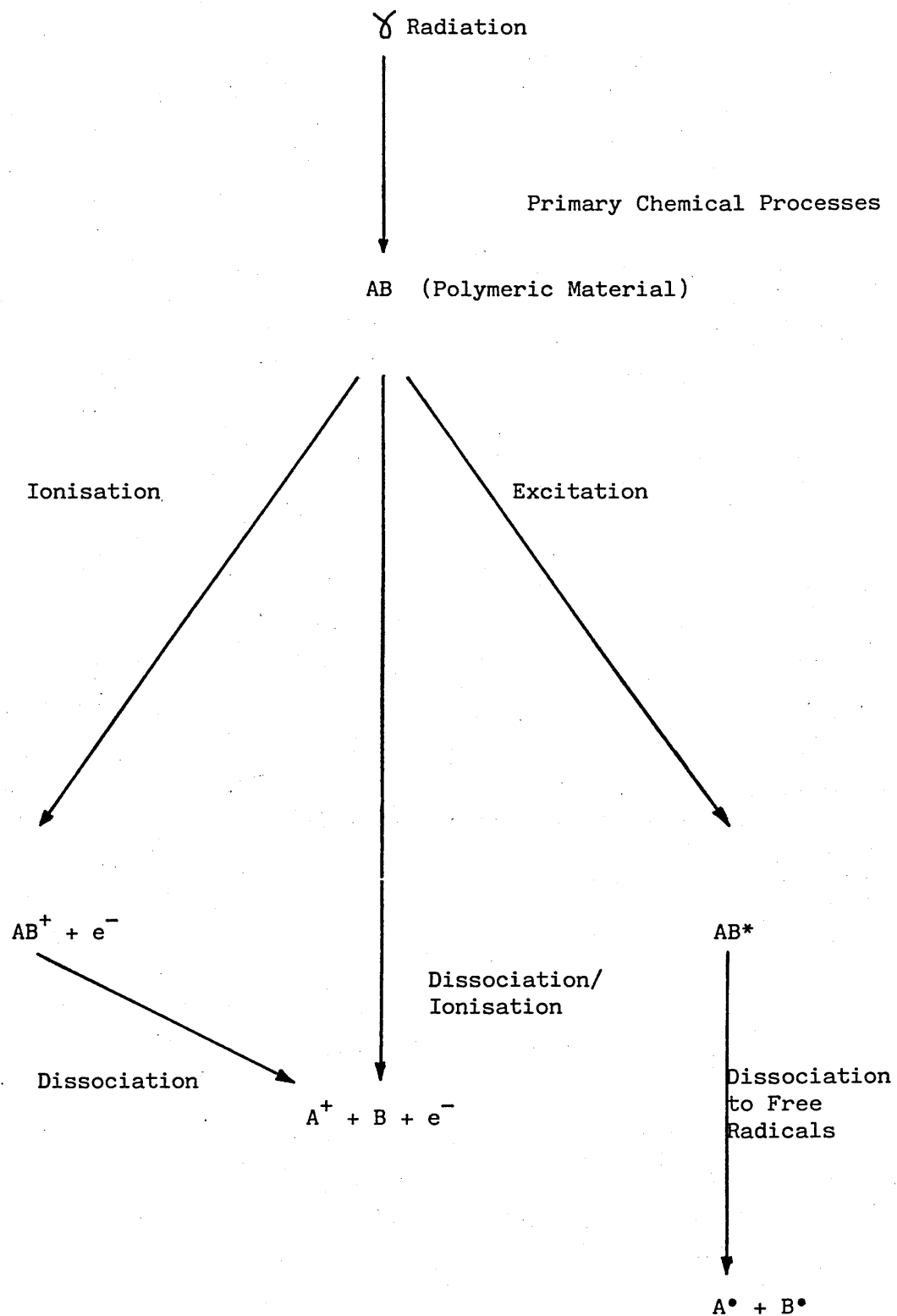


Fig.4.2b Possible Reaction Pathways



#### 4.2.3 The Crosslinking Mechanism

In a recent paper,<sup>181,182</sup> Charlesby stated that:

"The precise mechanism of crosslinking has not been generally agreed despite the many published papers."

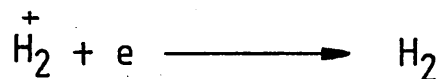
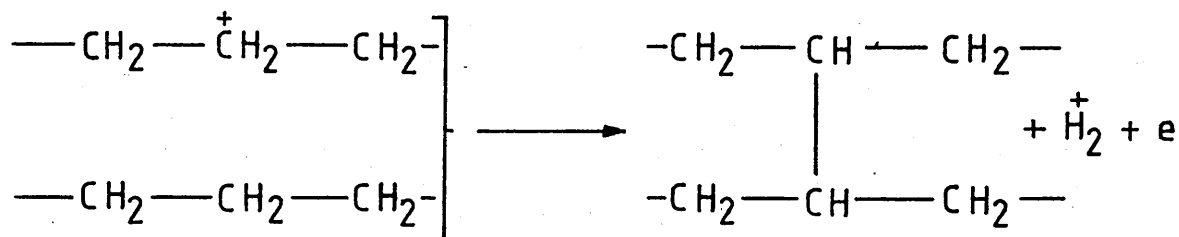
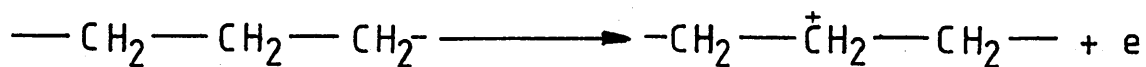
It is generally accepted that ions are responsible for some specific chemical effects, but the predominant radiation induced changes are due to free radicals. The mechanism which have been proposed fall into three main groups:

- a) those based on an ionic reaction;
- b) those in which two adjacent radicals are formed directly or indirectly as a result of a single ionisation or excitation;
- c) those assuming a combination of two mobile radicals produced independently.

##### 4.2.3.1 Ionic Mechanism

Early research in radiation chemistry concluded that ions were responsible for the observed chemical changes. Nowadays that conclusion, is not generally held, since modern techniques have been able to detect the existence of free radicals and the results of their consequent behaviour. Nevertheless there are certain features that cannot be entirely attributed to a free radical mechanism.

The ionic mechanism theory is based upon a single ionisation event and assumes that the site of ionisation is "mobile", in that the positive ion on the polymer chain can approach a neutral carbon of an adjacent chain.



It is found that as the temperature increases, the number of crosslinks formed also increases. This would appear to be due to the increased mobility of the species, be they the neutral polymer chains or the chains containing the ionised sites.

When a "radical scavenger" is introduced to the polymer in a concentration greater than the probable radical concentration, the observable physical changes are decreased. The radicals produced on irradiation are "absorbed" by the scavenger, yet the effects of crosslinking and degradation are still detectable. It is clear that the products of ionisation are involved in the crosslinking mechanism. The addition of electron donor or acceptors to polymer materials have been found useful in the study of ionic reactions, however the conclusions are ambiguous.<sup>178,180,183</sup> Makhlis<sup>178</sup> concludes that, even though a high concentration of ions may be present in the polymer system at the time of irradiation this does not mean that there is a significant contribution of ionic reactions to the end effects.

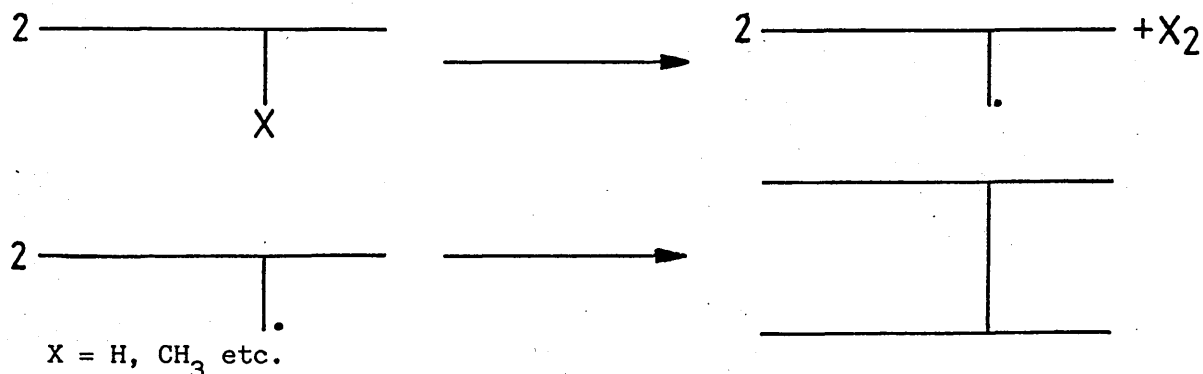
However, it is clear that ionisation results in a degree of crosslinking, in conjunction with the predominant free radical mechanism.

#### 4.2.3.2 The Role of Free Radicals in Crosslinking

One of the earliest observations was made by Oster,<sup>184</sup> who irradiated linear polyethylene with ultra-violet radiation at 254 nm to find, with surprise, that crosslinking took place. The surprising feature was to find crosslinking at such a low photon energy of 4.9 ev. A series of linear paraffins were irradiated to determine the energy that is required for ionisation. Extrapolation<sup>185</sup> of the molecular weight, to that of the irradiated polyethylene indicated that at least 10 ev could be required to bring about ionisation and crosslink formation. This evidence would seem to infer that the species responsible for crosslink formation, did not originate from an ionisation reaction. Thus crosslinking can be produced by molecules that have received sufficient energy for excitation, but less than the energy required for ionisation.

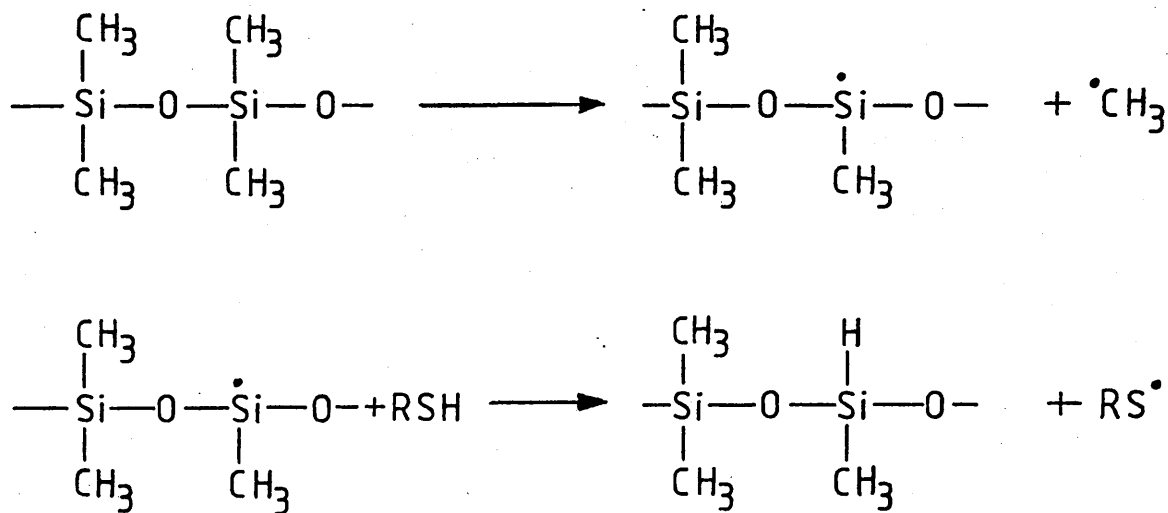
There are a number of substantial pieces of evidence which indicate that radicals are involved with crosslink formation. Using the electron spin resonance (ESR) technique, radicals have been detected in an irradiated polymer solution as well as in the solid state. The radicals have been found to be present in a concentration approximately twice that of the number of crosslinks actually formed.<sup>186</sup>

The following reactions seem to provide a basis for the crosslinking observed in polydimethylsiloxane.

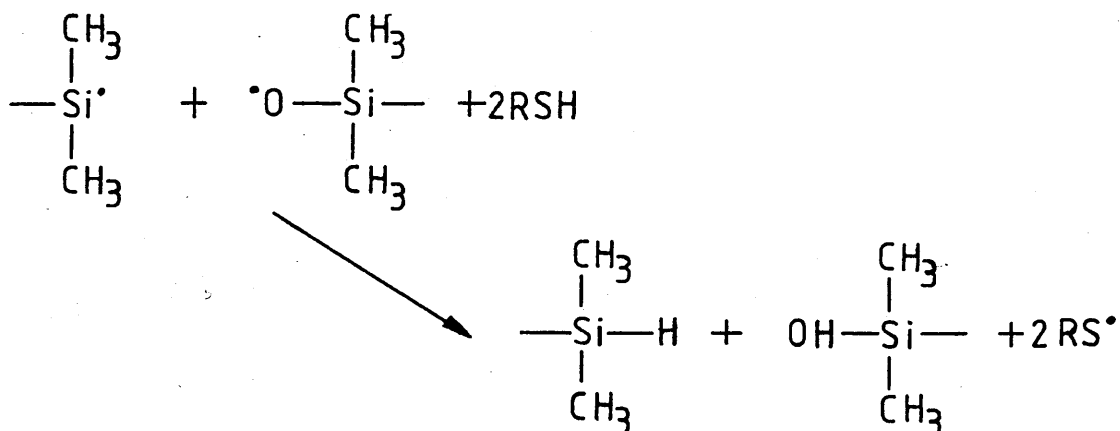


The above scheme implies that for every crosslink formed there must be two radicals. The majority of the ESR data agrees with this conclusion but Turner<sup>186</sup> suggests that further analysis be directed to some unexpected results in this area.

If a radical trap is added to a polymer, the amount of crosslinks formed at a particular dose is drastically reduced. Thus, to achieve the same degree of crosslinking, an increase in dose is required and this increase is found to be equal to the amount of radicals consumed by the additive<sup>7</sup> Polydimethylsiloxane is an ideal system to study, in that the polymer is an amorphous polymer, and it has been investigated by a number of authors. Iodine<sup>68</sup> as a scavenger was found to react directly with polymer radicals, and thereby prevent crosslink formation. However, its presence was found to increase the degree of degradation. In the same study, sulphur was found to afford substantial protection against crosslinking, also benzophenone. Turner<sup>186</sup> has reported that with a 10% by weight mixture of butylmercaptan (or diethyl sulphide) in polydimethylsiloxane, 90% of the crosslinks were prevented from being formed. The following mechanism was proposed:



The mercaptan (RSH) was also found by functional group analysis, to react with the products of main-chain scission and give the following:



Products of a Chain-Scission.

It is clear from this evidence that radicals play a very important role in the crosslinking mechanism. The degree to which ionisation is involved is somewhat uncertain.

#### 4.2.3.3. The Mobility of Radicals

It was reported by Charlesby<sup>68,187</sup> that when liquid hydrocarbons and polyethylene were irradiated with different types of radiation, the crosslink density produced was identical. Linear energy transfer (LET) is a measure of the KeV dissipated by radiation per micron of path travelled.<sup>188</sup> Radiation of low LET, such as  $\beta$ -particles ( $\approx 0.02\text{eV}/\text{\AA}$ ) was found to lead to the same number of crosslinks as higher LET radiation (neutrons  $\approx 3\text{eV}/\text{\AA}$ ). However studies of the degree of unsaturation in polyethylene showed it to be independent of the type of irradiation, only up to a level of 100 Mrads. Above that particular dose, the  $\alpha$ -particles give rise to a larger change in the unsaturation.<sup>178,189,190</sup>

Turner has reported<sup>186</sup> results of studies on polystyrene which appear to contradict the previous observations. Radiation of higher

LET gave rise to a higher number of crosslinks, compared to that obtained from low LET irradiation. This is explained as being due to a high concentration of radicals being formed in a very small volume, which enables a high degree of crosslinking to take place. It is proposed that different types of radiation would interact differently with a polymeric material, depending on:

- a) charge;
- b) size; and
- c) kinetic energy

It is clear that an  $\alpha$ -particle interacts, and hence dissipates its energy, by a totally different mechanism than a photon of  $\gamma$ -radiation. As it is generally accepted that crosslinking can be due to an ionic or a radical mechanism, it may be that each of the mechanisms is brought about by a particular type of irradiation. Hence radiation of a particular LET would favour one of the reactions (ionic or radical).

A characteristic feature of high LET radiation, is that protection by radical scavengers is drastically reduced.<sup>178</sup> This could be due to:

- a) swamping - the radical sites produced are too numerous to be trapped by the radical scavenger, hence crosslinks are produced;
- b) crosslinking formation arising through a non-radical mechanism, in which the scavenger can offer no protection.

The extent of crosslink formation with different radiation may be due to the type of polymer irradiated, the total amount of energy

imparted to the system and the precise experimental conditions.

Although all facts are not yet fully understood, it is clear that low LET radiation, such as  $\gamma$ -radiation, does give rise to detectable crosslinking.

Table 4.2 Penetration Distances of a variety of atomic particles

Radiation Type	Penetration	
	In Water (cm)	In Air (cm)
$\beta$ (electron)	0.5	400
$\gamma$ or X-ray	10	7000
Proton	0.002	2.3
$\alpha$	0.0005	0.2

Table 4.2 shows the wide range of distances that are travelled by particles of equivalent energy. With low dose  $\gamma$ -radiation (low LET), the energy is dissipated over a large volume, in other word the  $\gamma$ -radiation has to travel a long distance to dissipate its energy. Therefore the radical sites must be a finite distance apart, and it would seem that mobility is required to bring two radical sites into close proximity.

It is also interesting to note, that if a small amount of a radical scavenger is added to a polymer in such a way that each molecule is dispersed throughout the polymer matrix, then radiation protection is still observed. Immediately after irradiation, a scavenger molecule may be a long distance, in molecular terms from any radical site, yet

crosslinks are prevented from forming. Thus there must be a mechanism to explain this. It is improbable that the polymer chain, on which the radical is situated, moves to any great extent. Although the scavenger molecule will be a relatively small molecule, the majority of radical traps are based on aromatic compounds, it is unlikely that this molecule could diffuse to the radical site in time to prevent it crosslinking to a nearby radical site.

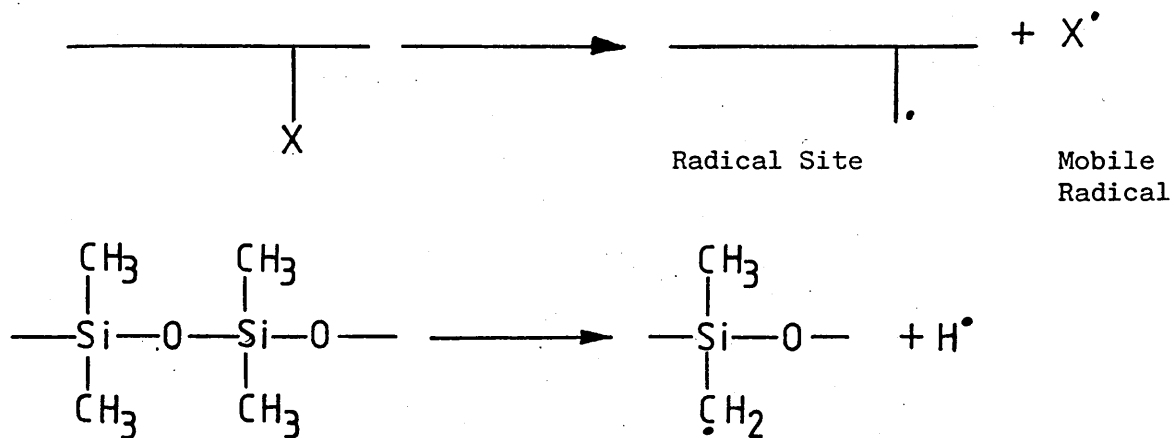
It has been reported by Wilson<sup>2</sup> that if the irradiation is performed in a hydrogen atmosphere, then the pressure of hydrogen gas affects the number of crosslinks formed. An increase in the hydrogen pressure results in a decreased number of crosslinks. This suggests that the hydrogen gas, or perhaps the products of the dissociation of molecular hydrogen, combine with the radicals produced due to the irradiation. It would appear therefore, that hydrogen radicals are the mobile species that are responsible for the formation of crosslinks.<sup>187,191</sup>

#### 4.2.4 Conditions for Crosslinking

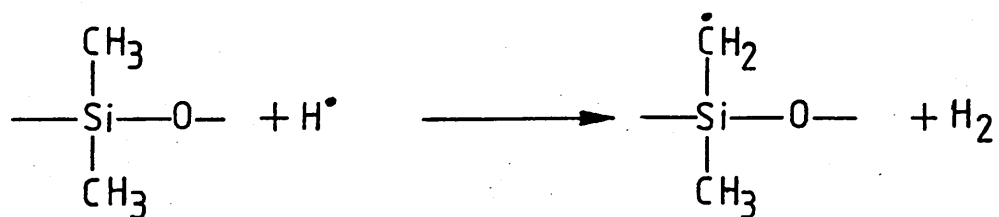
A statistical theory of crosslinking was first proposed by Flory,<sup>192</sup> who investigated the conditions that are required for the formation of an infinite three-dimensional network. This theory was further developed by Stockmayer,<sup>193</sup> to include the conditions that are required for the appearance of gel formation. more recently Charlesby applied this theory, to crosslink formation brought about by irradiation,<sup>4,7,194,195</sup> be it from an electron beam or a gamma source. Saito<sup>196</sup> has reviewed in detail the mathematical aspects of the crosslinking process although it is unnecessary to give full detail, it is essential to consider the conditions that give rise to gelation, that is an indication that crosslinking has taken place at a molecular level.



### Formation of Radicals

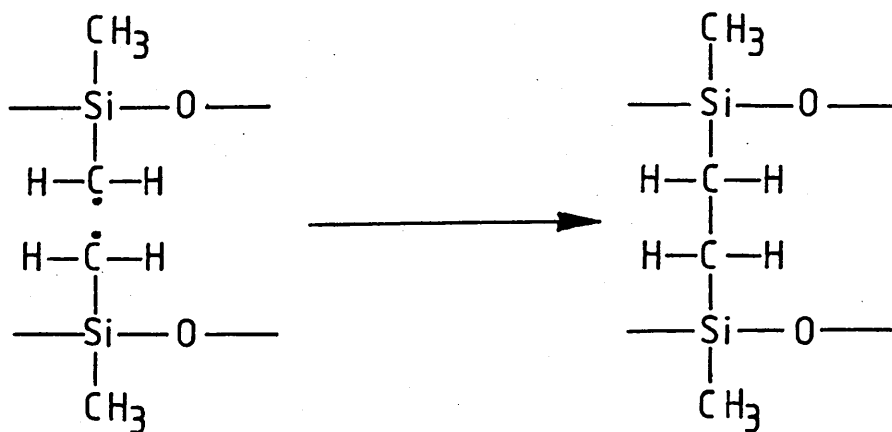


### Formation of an adjacent Radical Site

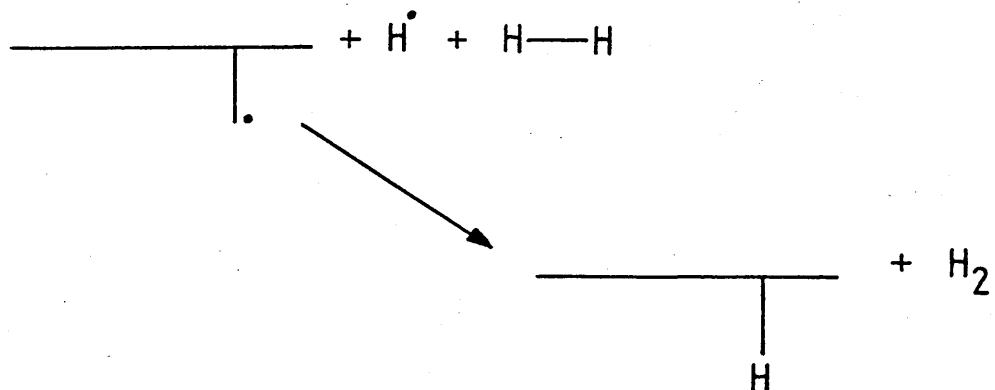


The Mobile Radical, abstracting a hydrogen atom from a nearby Methyl group.

### Crosslink Formation

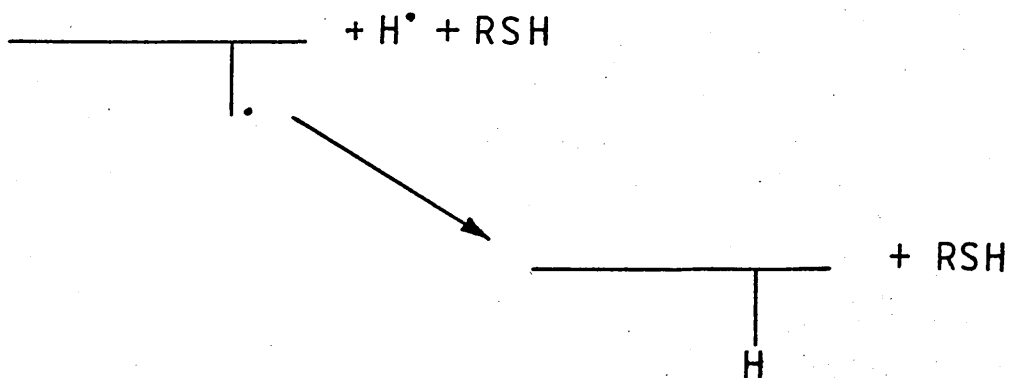
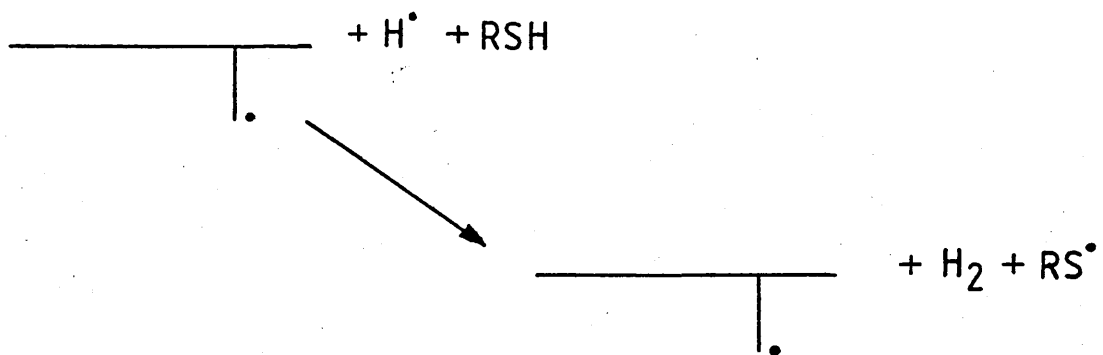


Increase in Hydrogen Gas Pressure



The high concentration of hydrogen gas prevents formation of a subsequent hydrogen molecule from the hydrogen radicals.

The typical action of a Scavenger



#### 4.2.4.1 Prior to Gelation

Theoretical considerations of crosslinking assume the polymer to be composed of linear chains of a uniform molecular weight. The early products that are formed due to crosslinking are branched polymer chains, with a progressively increasing molecular weight, resulting in corresponding decrease in the number of separate molecules.

It is assumed that:

- a) crosslinking occurs at random, i.e. each reactive group on a polymer chain has the same susceptibility to become a site for crosslinking;
- b) crosslinking only takes place between separate molecules, and hence each linkage decreases the total number of finite molecules by one.

The latter assumption does not allow more than two linkages between two chains. It is clear that this is only applicable when there is a low degree of crosslinking.

#### 4.2.4.2 Conditions required for Gel Formation

The number of crosslinked units per molecule of weight-average molecule weight ( $\bar{M}_w$ ) is called the crosslinking coefficient ( $\zeta$ ). Hence when the crosslink density is such, that there is 1 crosslink per weight average molecule, a 3-dimensional network begins to form, resulting in the polymer becoming insoluble (a gel).

∴ The critical condition for gel formation is

$$\zeta = 1$$

Assuming that crosslinking occurs in proportion to the radiation dose received, then the dose to give ( $\delta = 1$ ) is termed the "incipient gelation dose" ( $r_{gel}$ ). It follows that for any dose:

$$\delta = \frac{\text{dose}}{r_{gel}}$$

The efficiency of crosslinking is quantified by by the  $G(x)$  value, which is defined as the number of crosslinks per gram per 100 ev absorbed.

1 crosslink involves 2 crosslinked units

$\therefore$  1 crosslinked unit/molecule  $\equiv$  0.5 crosslink.

1 crosslink unit/molecule  $\equiv r_{gel}$

$\therefore r_{gel} \equiv$  0.5 crosslink.

At  $r_{gel}$  there are  $\frac{No}{2 \bar{M}_w}$  crosslinks  $g^{-1}$

where  $No =$  Avogadros Number

If  $r_{gel}$  is expressed in Mrads, 1 Mrad produces

$\frac{No}{2 \bar{M}_w} r_{gel}$  crosslinks  $g^{-1}$

$$\therefore \text{1eV produces } \frac{No}{2 \bar{M}_w \cdot 0.624 \times 10^{20} r_{gel}} \quad \text{Eqn. 4.1}$$

Thus

$$G(x) = \frac{100 \times 6.023 \times 10^{23}}{2 \bar{M}_w \times 0.624 \times 10^{20} r_{gel}} \quad \text{Eqn. 4.2}$$

$$= \frac{4.83 \times 10^5}{\bar{M}_w r_{gel}} \quad \text{Eqn. 4.3}$$

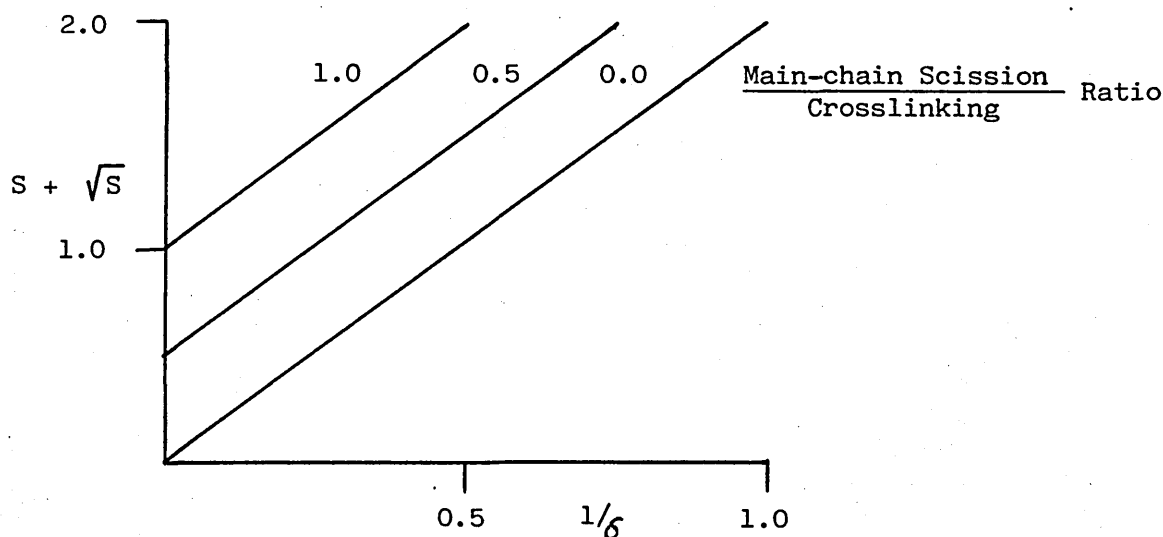
#### 4.2.4.3 Post-Gel

As the crosslinking coefficient ( $\delta$ ) increases above 1, two component develop within the polymer sample. A 3-dimensional network of unlimited (the 'gel network') size begins to form, and is found to be insoluble. The other component is soluble (the 'sol fraction') and the polymer chains are not part of the 3-dimensional network, although they may be crosslinked to a limited extent. The sol fraction can be removed by the use of selected solvents and the weight of the Gel fraction can be determined experimentally.

It is possible that whilst crosslinking is taking place, main-chain degradation can occur. Simultaneously, thus the amount of gel for a particular crosslinking level, would be reduced. If the rate of degradation is greater than the rate of crosslinking, then a 3-dimensional network never arises. Gel formation is prevented if the ratio of degradation exceeds that of crosslinking by

$$\frac{\text{Degradation}}{\text{Crosslinking}} > 2$$

When the sol fraction is plotted as a function of crosslinking coefficient, the ratio of degradation/crosslinking can be determined.



Theoretical plots of  $S + \sqrt{S}$  as a function of the crosslinking coefficient, for different ratios of main-chain scission to crosslinking probabilities.

A more useful method of plotting sol fraction, was proposed by Charlesby and Pinner.<sup>197</sup> They applied probability theory to calculate gel formation in an initially linear polymer, with a random molecular weight distribution, where scission and crosslinking is introduced at random and in proportion to radiation dose.

$$S + \sqrt{S} = \frac{2}{\delta}$$

where  $S$  = Sol Fraction (1.0 - gel fraction)

$\delta$  = crosslinking coefficient

since  $S = \frac{r}{r_{\text{gel}}}$

$$S + \sqrt{S} = \frac{2r_{\text{gel}}}{r} \quad \text{Eqn. 4.4}$$

This has the form

$$y = mx + c$$

$\swarrow$                        $\swarrow$                        $\swarrow$                        $\swarrow$   
 $S + \sqrt{S}$                        $2r_{\text{gel}}$                        $1/r$                       zero

Thus, gradient =  $2r_{\text{gel}}$

and  $r_{\text{gel}} = 0.5 \text{ Gradient}$

A plot of  $S + \sqrt{S}$  against  $1/r$  should give a straight line when the initial molecular weight distribution is random ( $M_w/M_n = 2$ ). However when the distribution of the polymer is found to be broader than the random arrangement, the above theory does not apply and the plot deviates from linearity.<sup>198</sup> The linear plot would be expected to pass through the origin when  $1/r = 0$ , however a positive intercept on the  $S + \sqrt{S}$  axis is possible. Simultaneous main chain scission, in

addition to the crosslinking mechanism, results in such a deviation. The value of which, is related to the relative rates of the two processes.<sup>199</sup> With an increase in susceptibility for chain scission, the intercept value is found to increase.

#### 4.3 Experimental

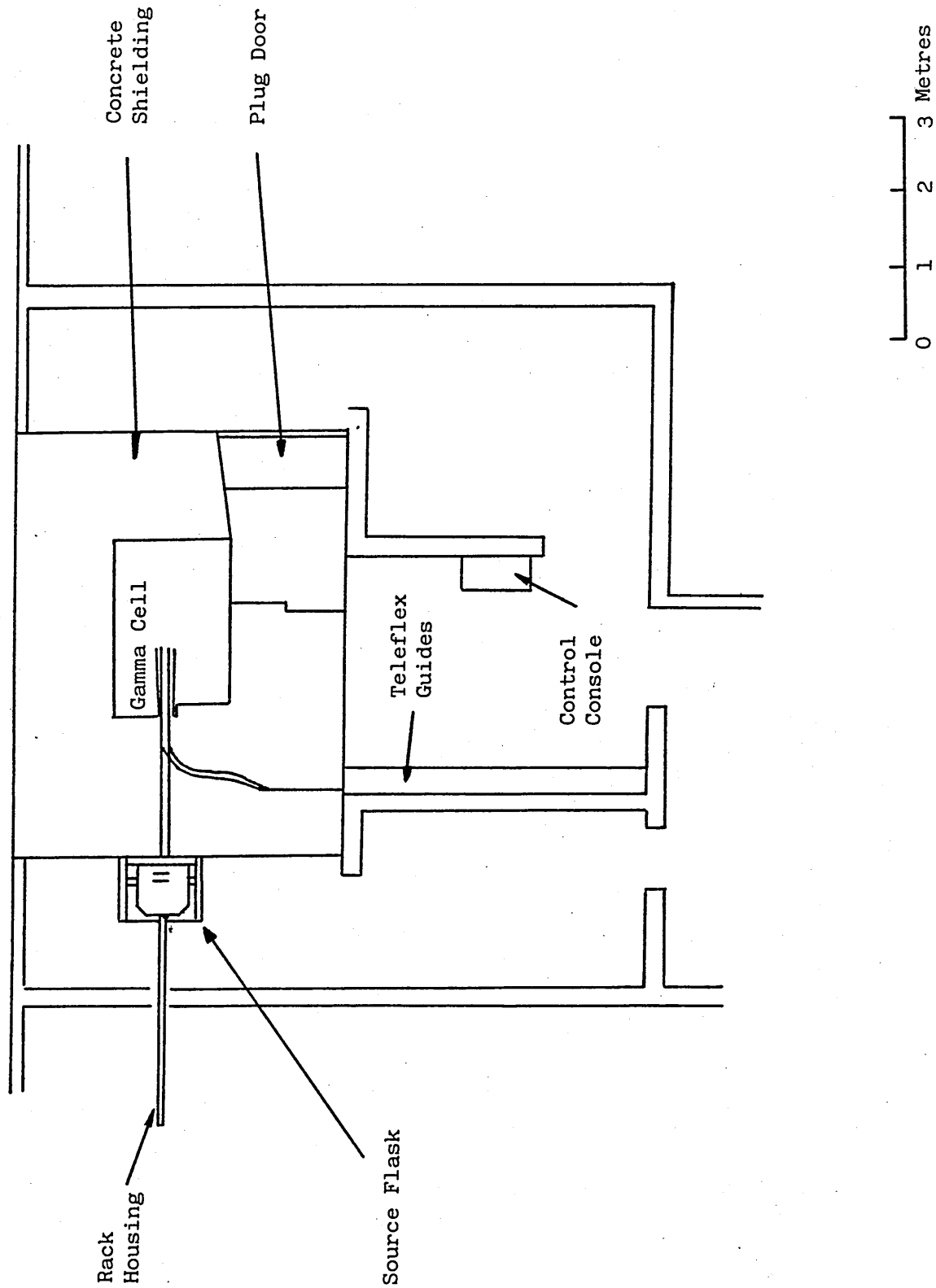
##### 4.3.1 Irradiation Facilities

The facilities that were available for this investigation were at the Central Electricity Generating Board, Souther Region Laboratories at Berkeley, and Irradiated Products Limited, Swindon.

Berkeley - "Pencils" of  $^{60}\text{Co}$  are arranged in a cylindrical array, attached to a retractable mechanism (Fig.4.3 ). The walls are of thick concrete, with a lead lining to provide additional protection. The source can be withdrawn to the lead flask by remote control and the concrete door can be hydraulically opened to enable the operator to deposit samples at various positions around the source. The required dose, determines the location of the sample, and the length of time they spend in the irradiation cell. The door is closed and the source introduced to the irradiation cell. The exposure time depends on the dose-rate activity of the cell (around  $0.2 \text{ Mrad h}^{-1}$ ) and the total absorbed dose requested.

Annually certain of the cobalt pencils are renewed and the dose rate is therefore maintained at a practical level of intensity. With each batch of samples irradiated within the cell, a small piece of poly(methyl methacrylate) (2mm x 8mm x 25mm) was placed alongside the samples to, monitor the dose received. The degree of colour change in the plastic is proportional to the amount of reaction taking place,

Fig.4.3 Plan of the Gamma Cell  
located at Berkley CEGB





which is dependent on the radiation received. The colour change is determined at 292 nm, which enables an exact dose to be recorded.

Irradiated Products Ltd. - This facility is a pool arrangement. The  $^{60}\text{Co}$  tubes are mounted in a circular array at the bottom of a 20 foot pool of water where the intensity at the surface is acceptable in terms of safety. Samples are placed in watertight cylinders then lowered into the centre of the array. The dose rate is known ( $1.5 \text{ Mrad h}^{-1}$  or  $0.5 \text{ Mrad h}^{-1}$ ) and exposure in the pool is timed, so an accurate total absorbed dose can be obtained.

#### 4.3.2. Polymer Samples

Studies were carried out using a high molecular weight homopolydimethylsiloxane ( $\bar{M}_n$  253,300) and a Silanol terminated polydimethylsiloxane liquid ( $\bar{M}_n$  = 50,000).

Polymer samples were sealed in thick walled glass tubing under a low argon pressure. After irradiation, the glass tube was opened and the sample analysed in a number of ways.

#### 4.3.3. Soxhlet Extraction

Published reports<sup>52,200,201</sup> of studies on siloxanes have used benzene at room temperature over a 5 day period to extract the sol fraction. Delides<sup>58</sup> and Langley,<sup>202</sup> in separate studies, found toluene to be suitable and preferred in terms of its low toxicity. In their work the irradiated polymer sample (0.2 - 1.0g) was placed in the solvent and left soaking for two days, then the solvent removed and replaced with a fresh volume. The gel was dried, then extracted further to constant weight. However Rijke<sup>203</sup> working on polyethylene used a Soxhlet apparatus and found his results to be in agreement with earlier methods.

In this study a soxhlet apparatus, with toluene as solvent, was used to extract the soluble fraction from the individual polymer samples. Double surface condensers were used in the apparatus to prevent solvent loss. Samples were stored in a refrigerator prior to extraction and after opening the thick walled glass sample tube, a sample of polymeric material (0.2 - 0.35g) was removed using a scalpel. The polymer sample was cut up into small pieces (approx. 3mm x 3mm x 2mm) and the pieces placed in cellulose single thickness thimbles (Whatman) and continuously extracted with toluene over a two day period. The thimbles were vacuum dried at room temperature and weighed, then extracted further to constant weight. Each sample was extracted at least in duplicate and in the majority of cases, in triplicate, with good agreement.

Prior to extraction of irradiated samples uncrosslinked polydimethylsiloxane was extracted using a soxhlet apparatus for 20 hour. It was found that no residual gel was present in the thimble, indicating that the polydimethylsiloxane sol is easily removed with such an arrangement.

#### 4.3.4 Swelling

The crosslink density, and the distance in terms of monomer units between crosslinked units was calculated from the swelling of the siloxane in a solvent. A sample similar to the size used in soxhlet extraction, generally in the range (0.037g - 0.097g), was cut from the silicone polymer and accurately weighed. The sample was immersed in a large excess of solvent ( $10 \text{ cm}^3$ ). Studies of soxhlet extraction found toluene to be more efficient than hexane. The reported<sup>204</sup> solubility product of hexane  $\delta = 7.3 (\text{cal/cm}^3)^{1/2}$  is closer to that of polydimethylsiloxane  $\delta = 7.5 - 7.6$ <sup>205,206</sup> than is toluene  $\delta = 8.9$ .<sup>204</sup> Delides and Shepherd<sup>207</sup> also found toluene to be satisfactory in similar studies on

irradiated polydimethylsiloxane.

The swollen polydimethylsiloxane sample was removed after a specific interval of time and the surface solvent blotted with filter paper, then the sample quickly weighed. Care was taken to minimise solvent evaporation. The sample was then vacuum dried (5 mm Hg) at room temperature to a constant weight. This swelling procedure was repeated over 2 x 20 hour periods, to obtain a swollen equilibrium state.

The weight increase of each sample is expressed as grams of solvent absorbed per gram of rubber:

$$S_1 = \frac{m_1 - m}{m} \times \frac{100}{1} \quad \text{Eqn. 4.5}$$

where  $m$  = weight of vacuum dried sample before swelling

$m_1$  = \_\_\_\_\_ do. \_\_\_\_\_ after swelling

$S_1$  = weight of solvent absorbed/g siloxane

When the swollen gel is in equilibrium with pure solvent, Florys<sup>208</sup> equation is applicable for calculating the crosslink density.

$$\ln(1 - V_2) + V_2 + \mu V_2^2 = NV_1 \left( V_2^{\frac{1}{3}} - \frac{V_2}{2} \right) \quad \text{Eqn. 4.6}$$

where  $N$  = moles of crosslinks/cm<sup>3</sup> polymer  
(crosslink density)

$\mu$  = polymer solvent interaction parameter  
( $\mu = 0.465$  in toluene)

$V_1$  = molar volume of toluene (106.235 cm<sup>3</sup> mol<sup>-1</sup>)

$V_2$  = volume fraction in the swollen state at  
equilibrium.

The volume fraction  $V_2$ , was calculated from using the following equation.

$$V_2 = \frac{1}{\frac{1}{\rho_r} + \frac{s_1}{\rho_s}} \quad \text{Eqn. 4.7}$$

$\rho_r$  = density of silicone ( $0.9615 \text{ g cm}^{-3}$ )

$\rho_s$  = density of solvent ( $0.8690 \text{ g cm}^{-3}$ )

$s_1$  = grams of solvent absorbed/gram of siloxane rubber.

The density of each individual polymer sample was determined using a gravity bottle, and found to be  $0.9615 \text{ g cm}^{-3}$ .

From the derived crosslink density, the following calculations can be performed.

a) distance between crosslinks

$$d = (N_o \times n)^{1/3} \quad \text{Eqn. 4.8}$$

$n$  = moles of crosslinks/ $\text{cm}^3$  polymer

$N_o$  = Avogadroes number

b) number average molecular weight between the crosslinks ( $\bar{M}_c$ )

$$\bar{M}_c = \frac{\rho}{n} \quad \text{Eqn. 4.9}$$

$\rho$  = density of siloxane ( $0.9615 \text{ g cm}^{-3}$ )

$n$  = moles of crosslinks/ $\text{cm}^3$  polymer

#### 4.3.5 Thermal Analysis

It is clear that radiation induces structural changes within the siloxane matrix, the most noticeable being the formation of an insoluble gel after sufficient radiation has been absorbed. Prior to gel formation there is an increasing number of polymer chains becoming linked together and the thermal behaviour of the polymer is expected to be widely different from a non-irradiated siloxane sample.

A polydimethylsiloxane gum, was irradiated over a wide range of doses (0.01 - 75 Mrads), spanning the pre-gel and post-gel regions. A portion of each sample was set aside for gel-sol studies, crosslink density investigations, and some for thermal analysis, using the Mettler oven. The procedure that was followed, has been described previously in section (2.5.1). The important point to note, is that there must be maximum contact between the polymer and the internal base of the sample container, which is placed in the thermal chamber. The siloxane offered no problem prior to gelation, in that it was able to flow. However the gel had to be cut into a thin strip, such that the maximum surface area of contact was achieved. The polymer sample (10-15 mg) was cooled to  $-175^{\circ}\text{C}$ , then heated at a rate of  $10^{\circ}\text{C min}^{-1}$  to  $30^{\circ}\text{C}$ .

#### 4.3. Sol Analysis

The gel is insoluble and therefore the possible analytical techniques are restricted to those previously outlined. The low molecular weight fractions present within the polydimethylsiloxane samples were separated and analysed by gas-liquid chromatography.

a) unirradiated polydimethylsiloxane.

The polydimethylsiloxane gum (50g) was dissolved in tetrahydrofuran

to form a viscous silicone fluid which was then precipitated into vigorously stirred methanol. The silicone gum was separated by precipitation and the solvent removed from the filtrate by rotary evaporation to leave a clear liquid, suitable for analysis by gas-liquid chromatography.

b) irradiated polydimethylsiloxane

The sol fraction present within each irradiated siloxane sample was extracted in a soxhlet extractor using hexane as solvent, over a sufficient period of time to ensure that all the sol was completely removed. Hexane was removed by rotary evaporation to yield a small amount of clear liquid for analysis by gas-liquid chromatography.

c) siloxane oligomers

Octamethyltetracyclosiloxane ( $D_4$ ) was repeatedly distilled from a liquid mixture of cyclic oligomers (Section 3.2.1), analysed by Gas Liquid Chromatography, and found to be 99% pure. Samples of the tetramer were degassed, through a three-stage freeze-thaw cycle, and sealed under nitrogen in thick walled glass tubing. These samples were irradiated at a number of different doses and, after irradiation, the liquids were analysed by gas-liquid chromatography.

In each case liquid sample was analysed by infrared spectroscopy to ensure that no solvent is present (methanol, tetrahydrofuran or hexane), the analysed by gas-liquid chromatography. A 5  $\mu$ l sample was injected onto a 9 foot column (2% Ov 17) at an injection temperature of 340°C, within a temperature programmed oven, initially at 120°C and rising to 300°C at 8° min<sup>-1</sup>. Increased resolution of the more volatile components (low molecular weight) was gained when the oven temperature

was held constant at 85°C for 5 minutes, before the temperature-programming was started and the temperature allowed to rise to 300°C at 12° min<sup>-1</sup>.

#### 4.3.7 Gel Permeation Chromatography

Previous workers have shown quite conclusively that as the absorbed dose increases the molecular weight increases, to a maximum, immediately prior to the onset of gelation. Further molecular weight studies on the gel are not possible due to its insolubility. In this study samples were analysed by RAPRA using 4 columns (1x10<sup>6</sup> Å, 1x10<sup>5</sup> Å, 1x10<sup>4</sup> Å and 1x10<sup>3</sup> Å) with tetrahydrofuran as solvent with a calibration against polystyrene standards.

### 4.4 Results and Discussion

#### 4.4.1 Soxhlet Extraction

##### 4.4.1.1 Polymer Samples

Other studies of the irradiation behaviour of polydimethylsiloxanes have been concerned with materials of lower molecular weight than the samples under investigation. Equation 4.3 shows that

$$G(x) = \frac{4.83 \times 10^5}{\bar{M}_w \text{ r}_{\text{gel}}}$$

$$\text{r}_{\text{gel}} = \frac{4.83 \times 10^5}{\bar{M}_w G(x)}$$

the dose required for incipient gelation (r<sub>gel</sub>) is inversely proportional to the molecular weight of the sample. This relationship is to be expected since a long chain siloxane polymer could require a smaller number of crosslinks than would a shorter chain to fulfil the requirements for gelation, i.e. for the crosslinking coefficient (δ) to have the value of 1.

From a number of studies, Charlesby<sup>7</sup> has reported the radiation doses required to give gel formation for siloxanes of different molecular weights and the results are shown in Table 4.3.

Table 4.3 Radiation Dose to give Gel Formation in

Polydimethylsiloxanes (Adapted from Charlesby)<sup>7</sup>

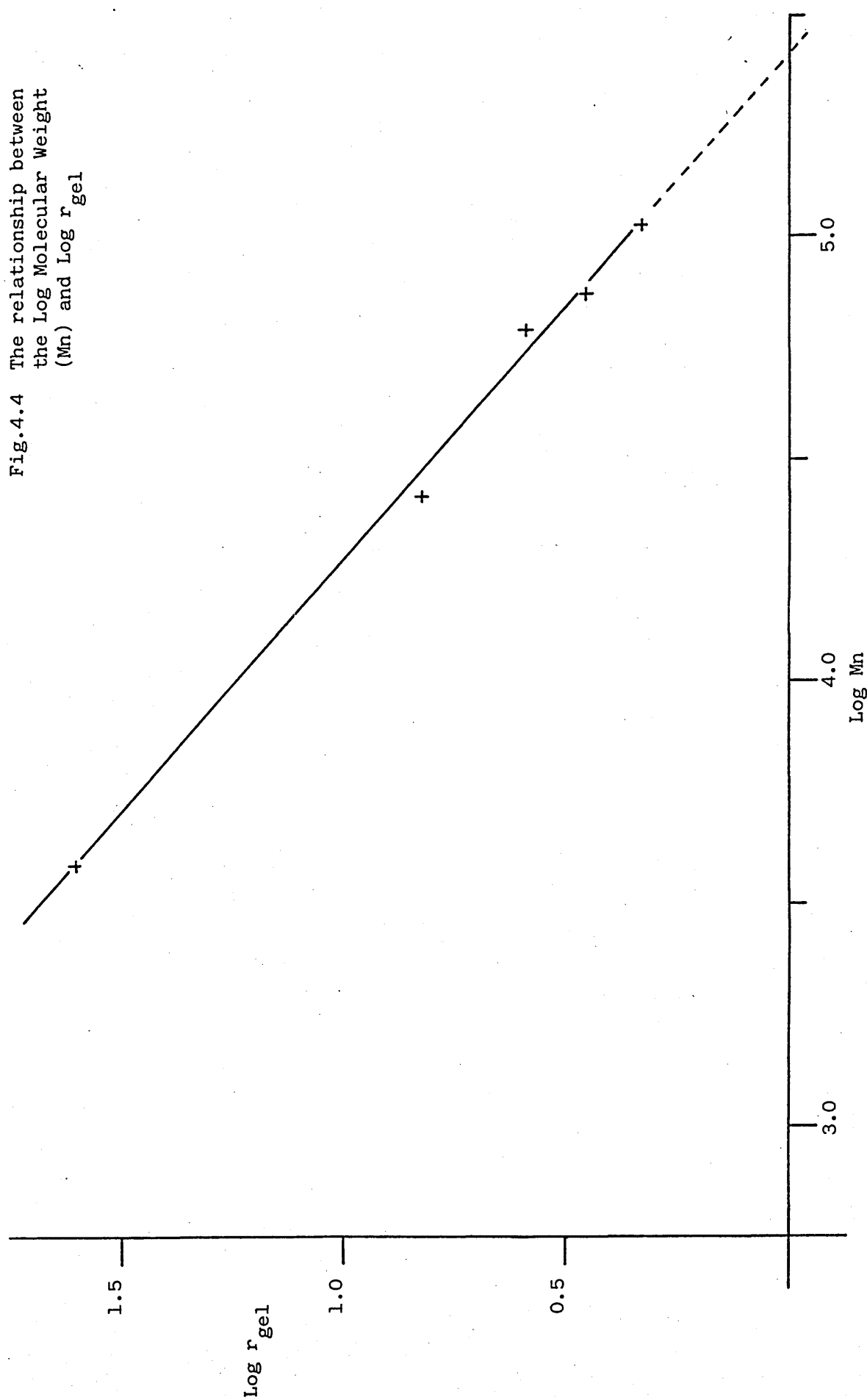
Molecular Weight (Mn)	Log Mn	Number of Monomers per Weight Average Molecule	rgel (Mrads)	Log rgel
106,000	5.025	1530	2.07	0.316
80,000	4.90	1080	2.85	0.455
62,000	4.79	840	3.92	0.593
26,400	4.42	360	6.7	0.826
3,900	3.59	53	40.3	1.605
1,200	3.08	16	179	2.25

Molecular weight determination of the siloxane gum under investigation was carried out by RAPRA and values of  $\bar{M}_w = 674,800$   $\bar{M}_n = 253,300$  were obtained. If  $\log \bar{M}_n$  is plotted against  $\log r_{gel}$  an approximately linear relationship is obtained (Fig.4.4) which indicates the dose range for incipient gelation for the siloxane sample of interest which is estimated to be in the range 0.8 - 1 Mrad.

On irradiation of the siloxane gum the changes observed were rather dramatic; in that the polymer initially became a very viscous elastic material (0.01 - 0.1 Mrad) and at the onset of gelation, converted to a non-flowing rubber (0.2 - 1.5 Mrad). At higher doses, this rubber-like material became much harder and rigid and eventually at very high doses (30 - 75 Mrads) a brittle, glassy solid was formed, which readily crumbled under gentle pressure. Throughout the range of doses investigated the polydimethylsiloxane remained transparent.



Fig.4.4 The relationship between  
the Log Molecular Weight  
(Mn) and Log  $r_{gel}$



A second sample, a Silanol terminated chain having  $\bar{M}_n = 55,430$  and  $\bar{M}_w = 100,640$  was also investigated. From Fig.4.4 it was estimated that gelation would take place at approximately 4 Mrads. In this case the observed changes on irradiation were less dramatic. The sample remained in almost the same physical state throughout, except that at the onset of gelation there was an increase in viscosity. Even at high doses, the silanol retained its elasticity, with no apparent increase in hardness and rigidity.

#### 4.4.1.2 Results

Results obtained from soxhlet extraction of the irradiated siloxane gum are given in Table 4.4 and illustrated in Fig.4.5(i) and 4.5(ii). Samples were extracted to constant weight, with lower dose samples requiring a longer extraction time to reach constant weight, and the mean of two or three replicate extractions and their variations are shown.

It can be seen from Fig.4.5(i) and (ii) that there is an increase of gel formation, with absorbed dose up to a maximum of approximately 2.5 Mrads. From this dose, no further increase in gel is observed and even at very high doses 100% gel is never achieved. Although the limited range over which gelation occurred (2 Mrad) makes it rather difficult, in practice to investigate a large number of samples. Fig.4.5(ii) shows that the three values obtained in this range are satisfactory for determination of the incipient gelation dose. Extrapolation of the curve in Fig.4.5(ii) to zero gives an  $r_{gel}$  value of 0.3 Mrad and substitution of this value in Equation 4.3 yield a  $G(x)$  value of 2.4.

An alternative method for determining  $G(x)$  is use of the empirical relationship derived by Charlesby and Pinner, the basis of which has

Table 4.4 Extraction Data of Irradiated Polydimethylsiloxane

Dose (Mrad)	% Gel
0.01	0
0.049	0
0.082	0
0.11	0
0.21	0
0.55	$23.3 \pm 0.6$
0.99	$63.6 \pm 2.1$
1.67	$74.6 \pm 0.8$
3.41	$81.1 \pm 1.5$
5.03	$81.9 \pm 1.5$
10.1	$83.5 \pm 1.5$
20.2	$84.0 \pm 1.0$
28.2	$83.2 \pm 2.0$
49.1	$88.5 \pm 1.0$
68.7	$83.0 \pm 1.0$

Table 4.5 Solubility Data for Irradiated Polydimethylsiloxane

applied to the Charlesby - Pinner Relationship

Dose (Mrads)	1/Dose (Mrads <sup>-1</sup> )	Gel Fraction	Sol Fraction	$\sqrt{\text{Sol}}$	S + $\sqrt{\text{Sol}}$
0.01	100	0	1.0	1.0	2
0.049	20.4	0	1.0	1.0	2
0.082	12.2	0	1.0	1.0	2
0.11	9.1	0	1.0	1.0	2
0.21	4.8	0	1.0	1.0	2
0.55	1.818	0.233	0.767	0.876	1.643
0.99	1.01	0.636	0.364	0.603	0.967
1.67	0.60	0.746	0.254	0.504	0.758
3.41	0.293	0.811	0.189	0.435	0.624
5.03	0.199	0.819	0.181	0.425	0.606
10.1	0.1	0.835	0.165	0.406	0.571
20.2	0.049	0.840	0.160	0.400	0.560
28.2	0.035	0.832	0.168	0.410	0.578
49.1	0.020	0.885	0.115	0.339	0.454
68.7	0.015	0.830	0.170	0.412	0.582

Fig.4.5i Percentage Gel as a function  
of Absorbed Dose (Mrads).

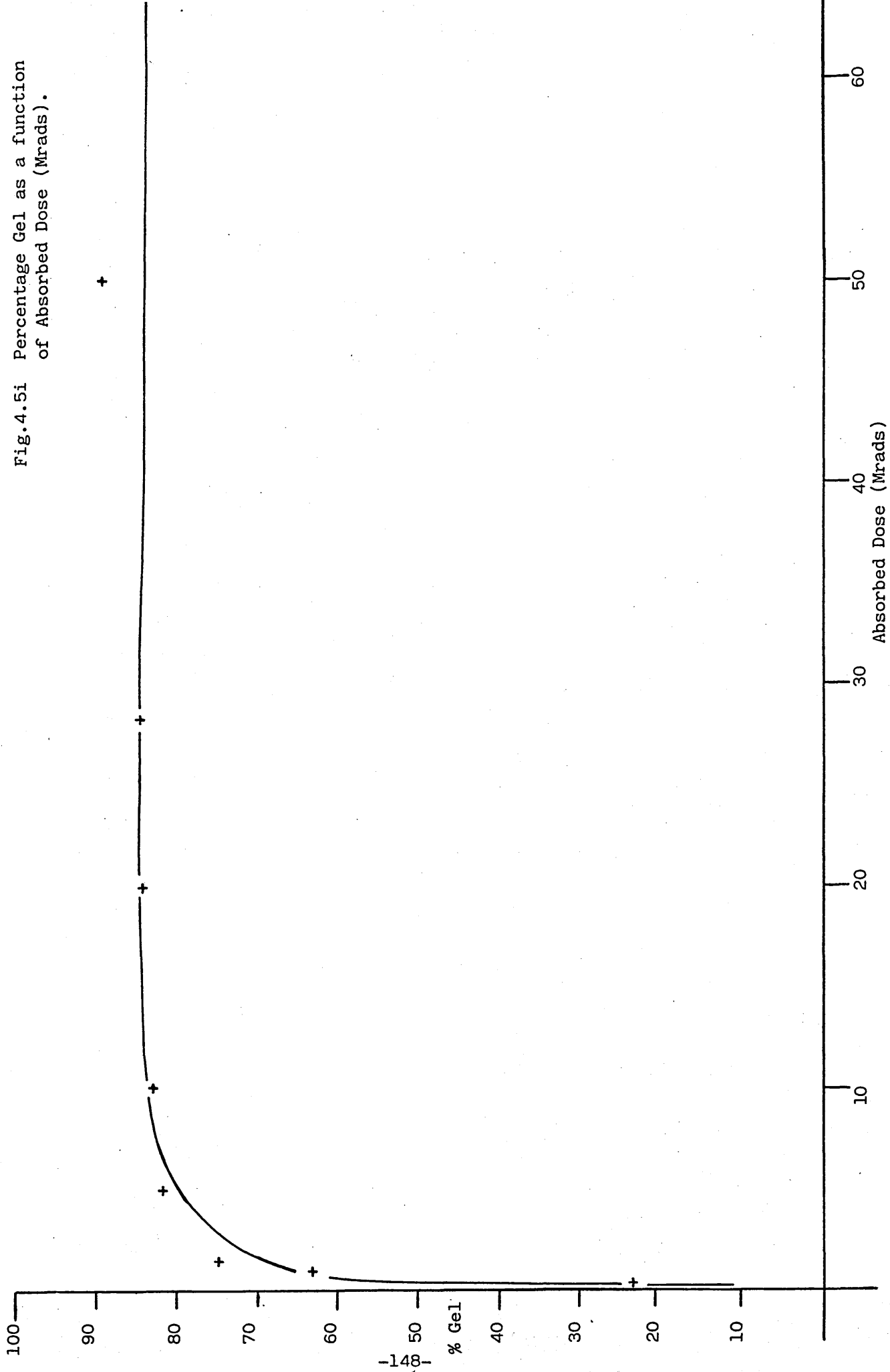
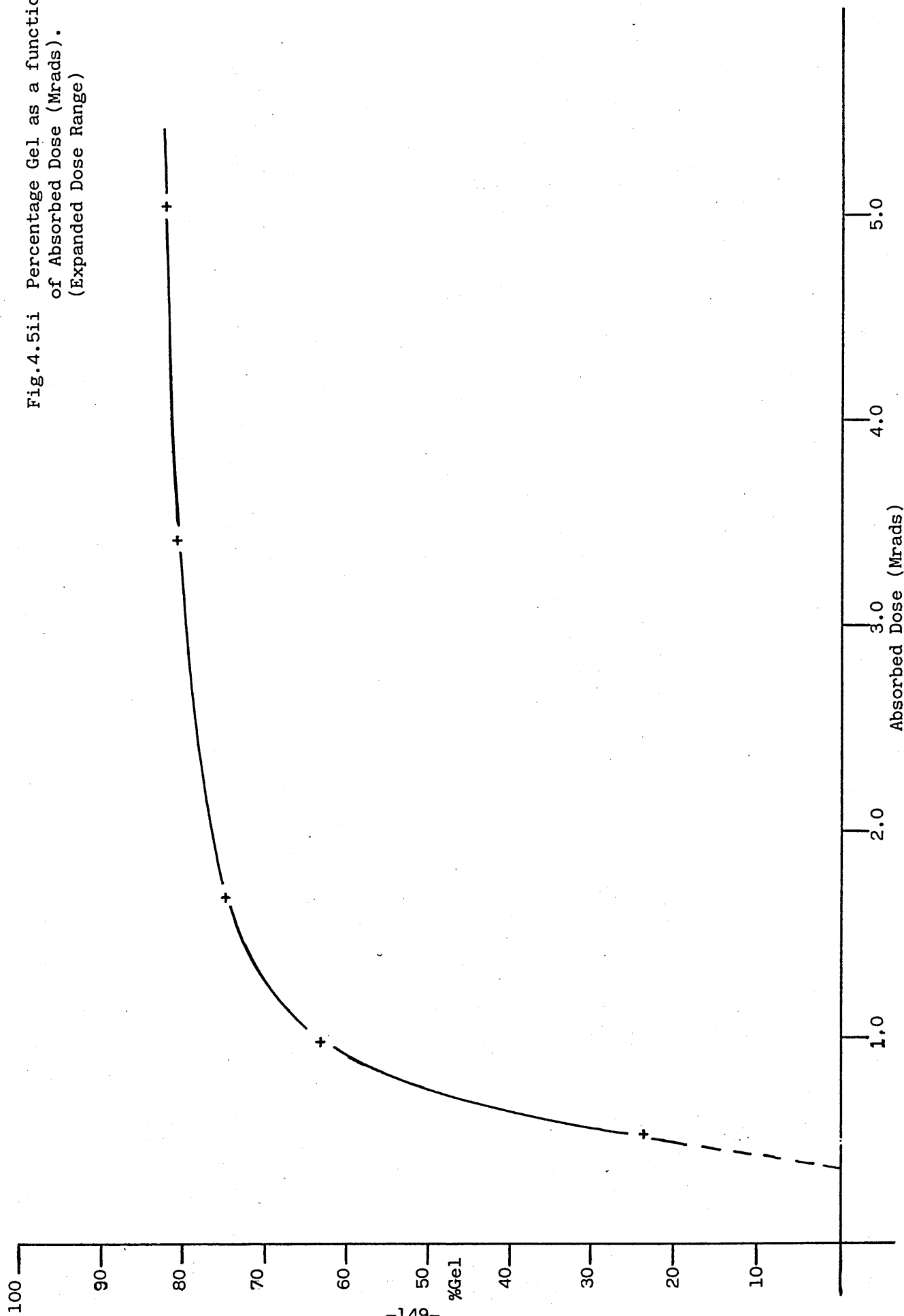
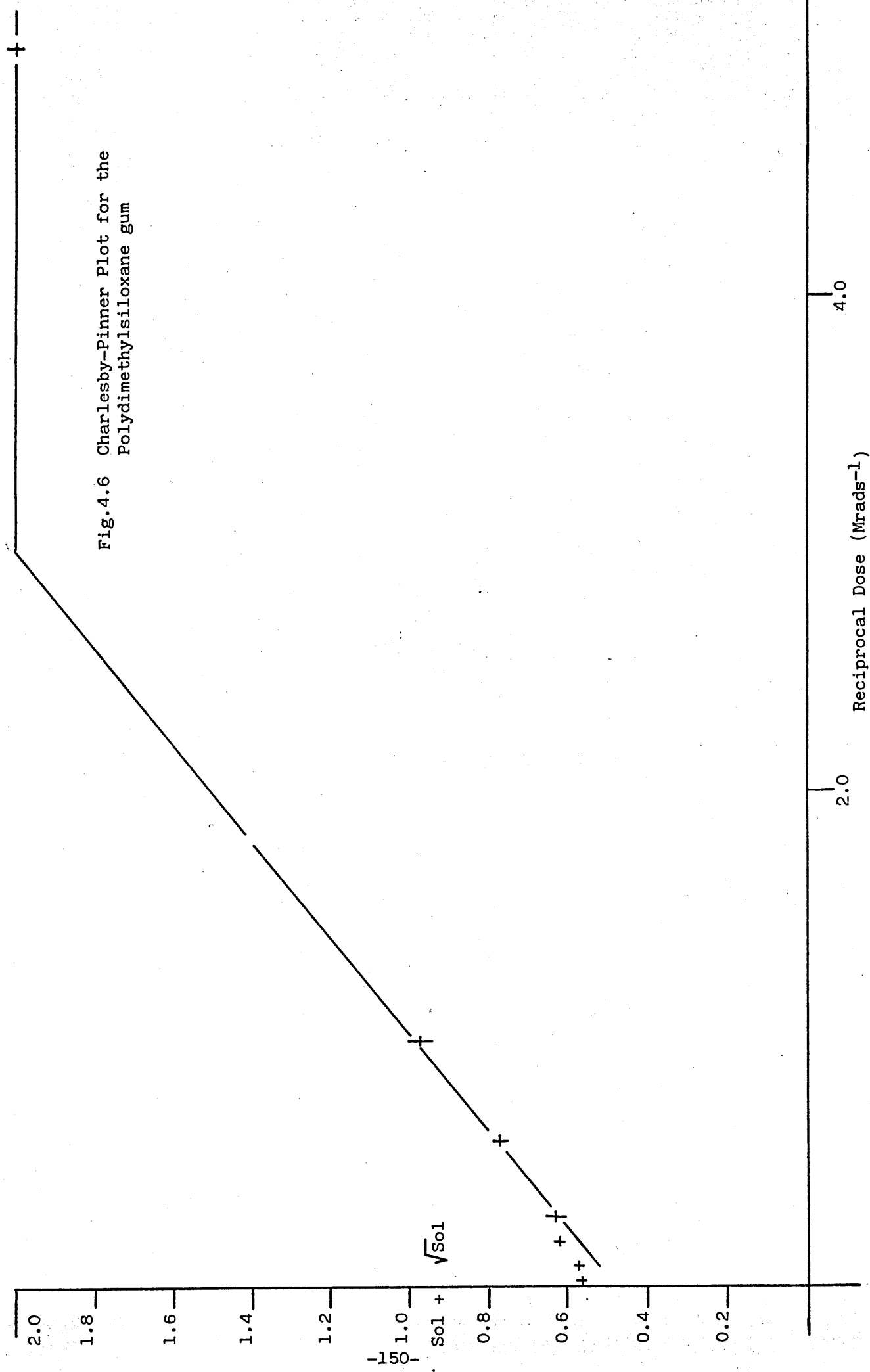


Fig.4.5ii Percentage Gel as a function  
of Absorbed Dose (Mrads).  
(Expanded Dose Range)





previously been outlined (4.2.4 ). The data is presented in Table 4.5 and Fig.4.6. The gradient of the line enables  $G(x)$  for the polydimethylsiloxane to be determined.

$$\text{gradient} = 0.514$$

$$\therefore r_{\text{gel}} = 0.26$$

$$\text{and } G(x) = 2.8$$

The second siloxane homopolymer (silanol terminated) was used as a preformed block for the synthesis of block copolymers via condensation polymerisation. It was therefore of interest to investigate its behaviour on irradiation.

The ampoule sealing procedure was slightly modified due to the physical state of this sample. The silanol could not be poured into the glass ampoule since its presence on the internal surface at the point of sealing would be unsatisfactory. Thus an ampoule of thick walled glass was prepared with a narrow constriction, for the seal, and the silanol was transferred to the ampoule via a long capillary tube. Prior to sealing, a freeze-thaw cycle was used to degas the liquid polymer, which was then sealed under argon at reduced pressure.

From Fig.4.4 it can be seen that for a siloxane of this particular molecular weight, gelation should occur in this range 3-4 Mrad. The gel data is given in Table 4.6 and Fig.4.7 and Fig.4.8.



Fig. 4.7 Percentage Gel as a function of Absorbed Dose (Mrads) for the Silanol Sample.

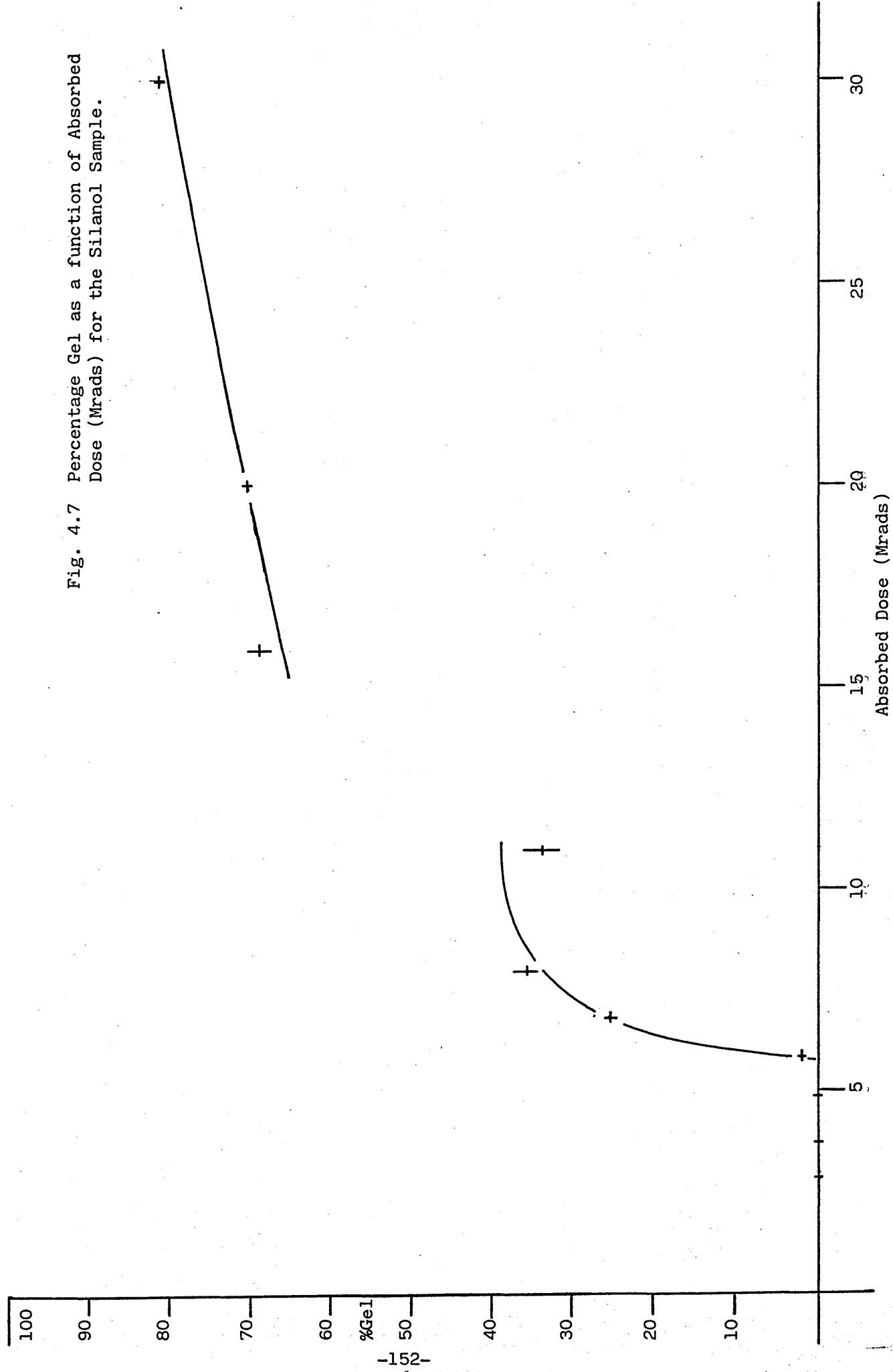


Table 4.6 Solubility Data for the Irradiated

Silanol-Terminated Polymer

Dose (Mrad)	% Gel	Dose Rate (Rad h <sup>-1</sup> )
2.8	0	0.41 x 10 <sup>5</sup>
3.75	0	
4.92	0	
5.90	1.4 ± 0.1	
6.90	25.6 ± 0.5	
8.04	36.3 ± 2.0	3.92 x 10 <sup>5</sup>
10.8	33.4 ± 4.0	
15.8	67.4 ± 3.0	
19.9	71.4 ± 1.5	
30.1	82.5 ± 1.5	

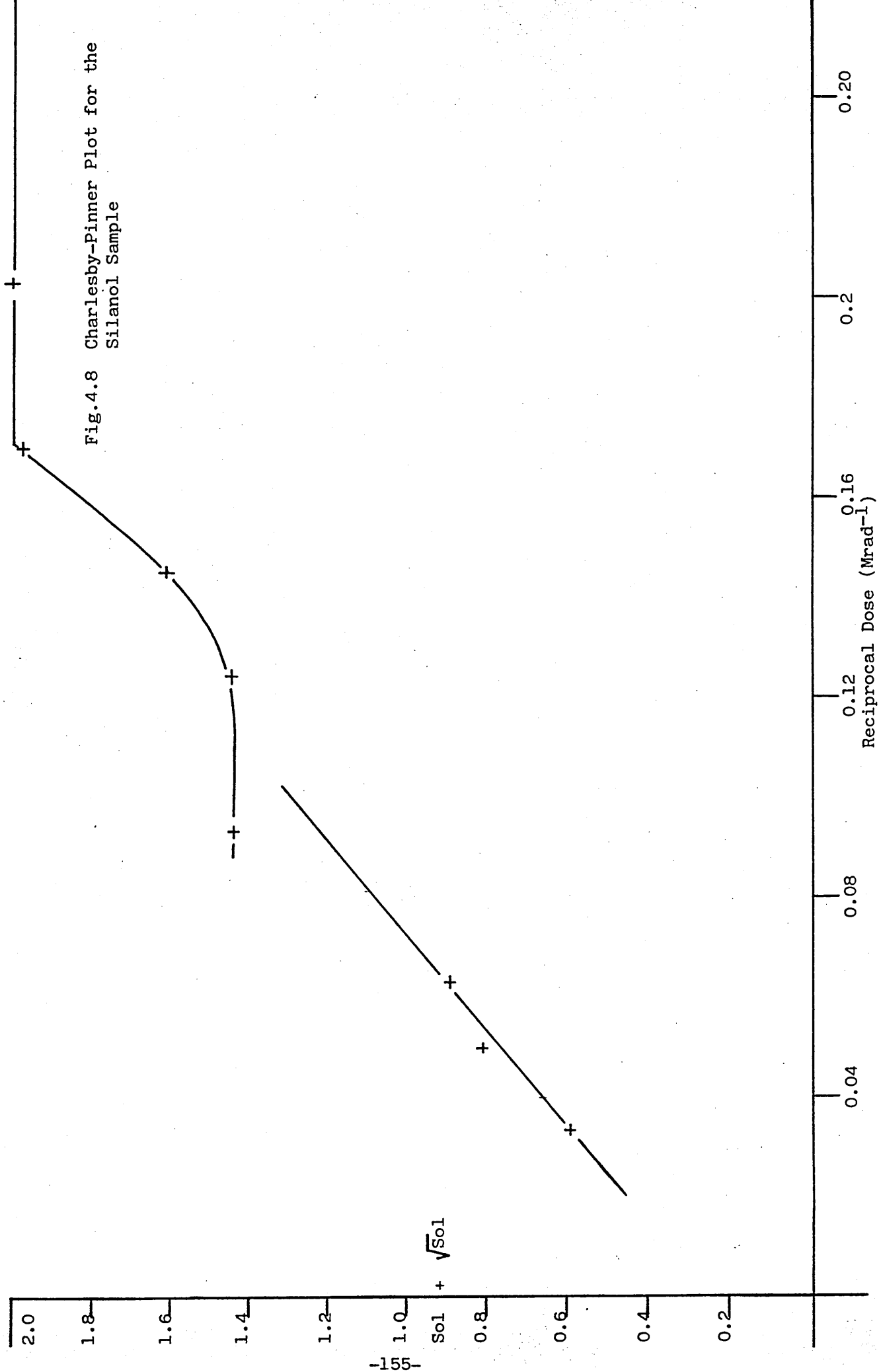
It is clear from this data that there is some inconsistency which is discussed a little later. However the dose for incipient gelation can be determined from the Fig.4.7 and is found to give  $r_{gel} = 5.8 \pm 0.1$  Mrads, and thus  $G(x) = 0.83$ . Using the Charlesby-Pinner plot  $r_{gel}$  is estimated as 5.1 Mrad which gives a value of 0.94.

Table 4.7 Solubility data of the Irradiated Silanol-Terminated  
Polymer applied to the Charlesby-Pinner Relationship

Dose (Mrad)	1/Dose (Mrad <sup>-1</sup> )	Gel Fraction	Sol Fraction	$\sqrt{\text{Sol}}$	S + $\sqrt{\text{Sol}}$
2.8	0.357	0	1.0	1.0	2.0
3.75	0.267	0	1.0	1.0	2.0
4.92	0.203	0	1.0	1.0	2.0
5.90	0.170	0.014	0.986	0.993	1.979
6.90	0.145	0.256	0.744	0.863	1.607
8.04	0.124	0.363	0.637	0.798	1.435
10.8	0.093	0.334	0.666	0.816	1.482
15.8	0.063	0.674	0.326	0.571	0.897
19.9	0.050	0.714	0.286	0.535	0.821
30.1	0.033	0.825	0.175	0.418	0.593

#### 4.4.1.3 Discussion

Very little information is available concerning post-irradiation effects in polymeric materials, due to the short lifetime of the species which are responsible for such reactions. To investigate any such effects, the samples would have to be analysed in an appropriate manner both during irradiation and immediately following exposure to the  $\gamma$ -source. It was totally impracticable to venture into this area, so it was assumed that the post-irradiation effects, if they exist, are due to short lived species and that any such effects will have been completed well before the samples are removed from the irradiation chamber.



Since soxhlet extraction was the experimental approach used for determining  $\eta_{sp}/c$  and  $G(x)$ , a number of aspects concerning the technique require comment.

A regular check was made of the weight loss due to the thimbles used in these experiments. Vacuum dried thimbles not containing any sample were subject to the same extraction routine as those containing samples and were found to return an average weight loss of 0.45%. This weight loss was found to be a consistent value for the different batches of thimbles used, and this could be allowed for when thimbles containing samples were extracted.

On rotary evaporation of the toluene solvent after extractions were completed, a yellow liquid residue was found in addition to soluble polymer. This liquid was found whether or not sample had been extracted, so it was clear that this residue originated from the toluene. The liquid had a strong aroma resembling that of benzaldehyde. Infrared analysis showed a strong carbonyl and carboxylic acid bands and thin-layer chromatography revealed several components in the liquid.

Gas-liquid chromatography (GLC) using a 10% Ap1 column at 130°C showed the yellow residue to comprise benzaldehyde and benzoic acid, with a trace of residual toluene. Soxhlet extraction using benzaldehyde-free toluene for 100 hours, produced appreciable quantities of benzaldehyde and benzoic acid in the toluene. Thus during extraction, toluene is being oxidised to benzaldehyde, then further to benzoic acid. It was confirmed using GLC that the oxidised components do not distill into the thimble containing the polymer sample, and thus this was not regarded as an obstacle to the use of this technique.

Comments by Kang, Saito and Dolo<sup>210</sup> suggested that a "limited extraction period" using a soxhlet apparatus gave a higher percentage

gel than an alternative method they used. In their method irradiated polyethylene gum, held in 100-mesh stainless steel basket, was immersed in boiling xylene for a 24 hour period. They found that the xylene condensate in contact with the gum in a Soxhlet apparatus was only at 90°C, whilst in their method the temperature of the xylene was 139°C. Rijke and Mandelkern<sup>203</sup> confirmed such an observation, but in their study they used a hot-liquid-jacketed Soxhlet extractor and thereby maintained the xylene temperature near to that of its boiling point.

In this study, it was essential to obtain an extraction system which was efficient and which could cope with a large through-put of samples. The data in Table 4.8 clearly shows that a 24 hour extraction is insufficient to effect complete extraction of sol in the dose range studied. From Fig.4.9 it is seen that the time taken for complete sol removal is dependent on the absorbed dose. A long extraction time is needed to achieve a constant gel value. For high doses, above 1.67 Mrads, it would appear that 60-80 hours is sufficient, however lower doses need an extraction time of the order of 140 hours.

Our irradiation of the polydimethylsiloxane from the onset of gelation was observed to take place between 0.2 and 0.55 Mrads (Fig.4.5). It would have been ideal if one or two experimental points could have been located within this range, but by extrapolation of the data an incipient gelation of 0.3 Mrads was obtained which gives  $G(x) = 2.4$ .

It is important to note that after 2.5 Mrad of radiation the maximum amount of gel (approximately 83%) had been reached and increasing the irradiation dose did not lead to any further crosslinking or chain scission. However, it is possible the extracted soluble polymer may contain chains that are linked together, but which have not become part of the 3-dimensional gel network.

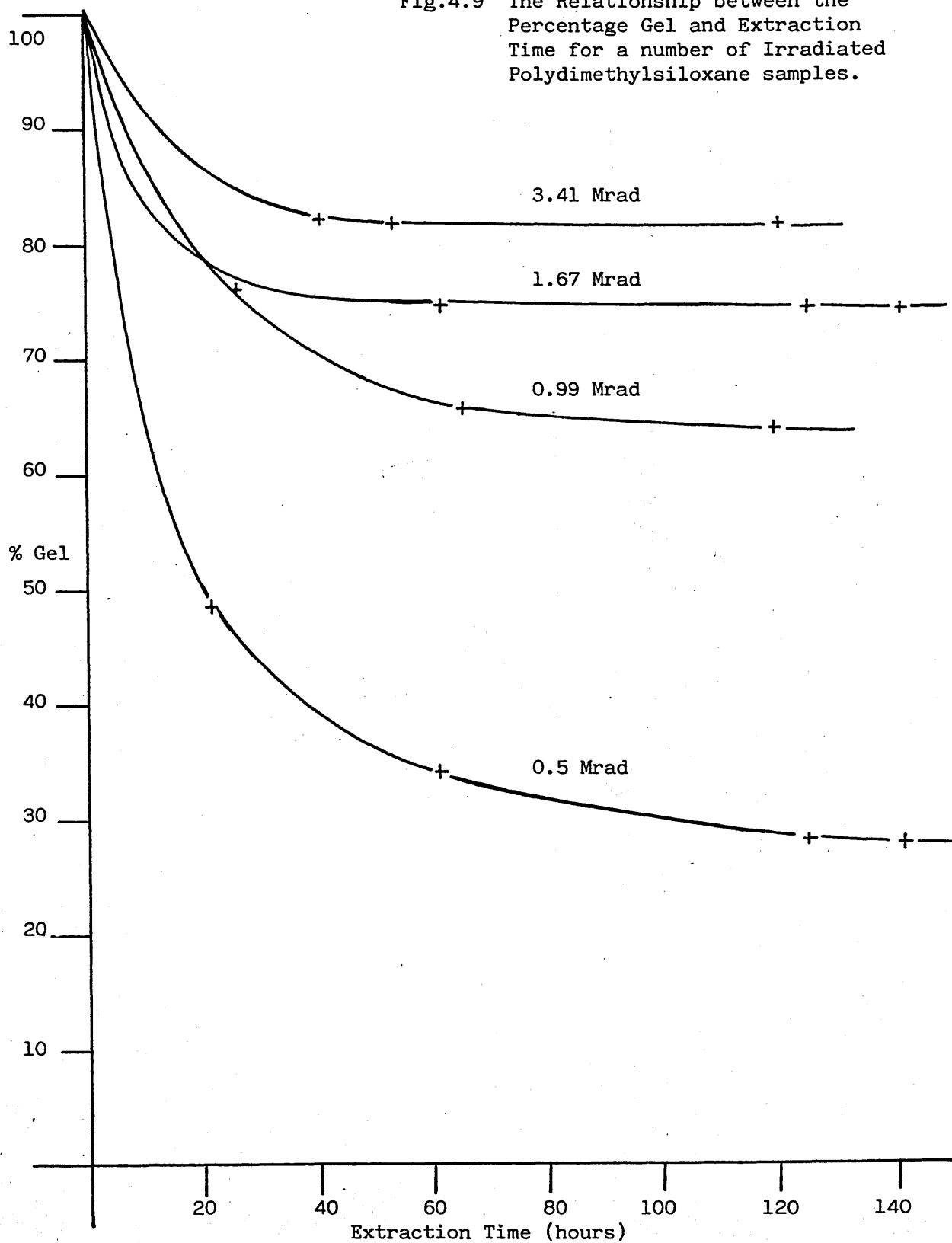
Table 4.8 Percentage Gel present in a number of Irradiated

Samples after Different Extraction Times.

Dose (Mrads)	0.55	0.99	1.67	3.41
Extraction Time (Hours)	% Gel by Extraction			
22	48.3			
26			75.6	
42				
54				82.0
62	33.9		74.7	81.1
66		65.5		
120		63.9		
126	28.1		74	81.1
142	27.1		73.8	

When using the Charlesby-Pinner relationship, greater emphasis has been given to data in the low dose region for calculating the gradient of the curve (Fig.4.6), which leads to  $r_{gel} = 0.26$  Mrad and  $G(x) = 2.8$ . It must be emphasised that the Charlesby-Pinner relationship is regarded as empirical, applicable to polymers that have a random distribution of molar masses, and where the crosslink density is proportional to dose. The data would suggest a slight deviation from the theoretical relationship, which can be ascribed to the non-random distribution of the polydimethylsiloxane gum. The molecular weight distribution of which was found by GPC to be 2.66 Saito<sup>196</sup> and Kang Saito and Dolo<sup>210</sup> have suggested a modified form of the Charlesby-Pinner relationship, to take

Fig.4.9 The Relationship between the Percentage Gel and Extraction Time for a number of Irradiated Polydimethylsiloxane samples.





account of such a non-random distribution. They presented a 'normalised' Charlesby-Pinner plot for a molecular weight distribution of 11.5 which is given as a positive curve, as opposed to a straight line. In this study the polydimethylsiloxane gum is much nearer that of a random distribution, than the example given by their workers, so in this case a linear relationship has been assumed.

Extrapolation of the line that has been used to determine  $r_{gel}$ , to  $1/r = 0$  gives an intercept at  $0.45 \text{ sol} + \sqrt{\text{sol}}$ . This reflects the fact that at an infinite dose, 100% gel is not achieved. Two possible explanations exist, the first is that low molecular weight oligomers are present within the gum, which have not undergone crosslinking and therefore remain soluble. However from the relationship between incipient gelation dose and the molecular weight (Fig.4.4), it would be expected that chains greater than  $2000 \bar{M}_n$ , would have become cross-linked and therefore part of the gel. A sample of this siloxane gum was irradiated at 600 Mrads, and even at this dose a maximum gel of 85% was obtained, yet from Fig.4.4 molecules of molecular weight 100-150  $\bar{M}_n$  should have become part of the crosslinked matrix with such irradiation. This explanation has also been contradicted by Delides and Cook,<sup>199</sup> who thoroughly extracted any low molecular weight oligomers that may have been present in a polydimethylsiloxane sample, and they still obtained a maximum gel of less than 100%. The second explanation which seems to be much more acceptable, is that the soluble fraction is due to chain scission reactions which occur simultaneously with the cross-linking reactions.

The deviation between the extrapolated line and the experimental data points in the high dose region, can be explained by the 'saturation theory'.<sup>199</sup> As the degree of crosslinking increases within the gel, the

monomer units available, to form a crosslinking site decrease. There is also a decreased motion of the polymer chains, hence the ability to form crosslinks is therefore reduced, which is reflected in a decrease in the rate of crosslink formation. The Charlesby-Pinner relationship begins to break down at this point, where the number of crosslinks formed are no longer directly proportional to the absorbed dose. Delides and Cook<sup>199</sup> have investigated this area, and have derived equations which take account of this factor, thereby obtaining a straight line plot.

The two methods that have been used to determine  $G(x)$  give values of 2.4 and 2.7. These values in the literature<sup>201-203</sup> Charlesby and Ormerod<sup>211</sup> quote a value of  $G(x) = 2.6 \pm 0.3$  for polydimethylsiloxane which was obtained by averaging the values obtained by earlier workers from a variety of techniques, radiation sources and molecular weight samples.

As can be seen from Table 4.6 two sets of data were acquired for the silanol terminated sample which were obtained at two different irradiation sessions. The data up to 10 Mrad were obtained at a dose rate of  $0.41 \times 10^5 \text{ rad h}^{-1}$ , whilst those at higher doses were obtained at a higher dose rate of  $3.92 \times 10^5 \text{ rad h}^{-1}$ . An increase in the dose rate by a factor of 10. The first set of data (low dose rate) would suggest that a maximum gel of 35% results. Whereas for the samples irradiated at the higher dose rate, the gel reaches 82%. Repeated extractions confirmed the values for gel obtained, and there are no reasons to suspect that the absorbed doses are other than those stated. It would appear therefore that the amount of gel produced is dose rate dependent.

In an excellent review on the role of free radicals in radiation induced reactions, Turner<sup>186</sup> stated that:

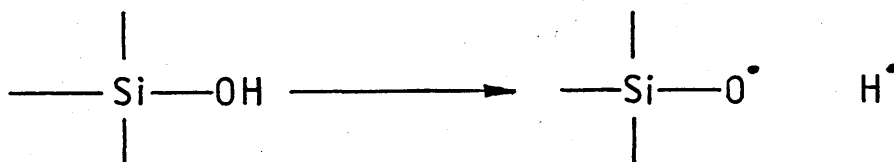
"In general the radiation chemistry of polymers is not noticeably influenced by variation in dose rates";

he continued:

".... In connection with this statement it should be noted that the dose rates studied are usually confined to the range of  $10^{-2}$  -  $10$  Mrads  $\text{min}^{-1}$ ."

These values are equivalent to  $6 \times 10^5 \text{ rad h}^{-1}$  \_\_\_\_\_  
 $6 \times 10^8 \text{ rads h}^{-1}$ . It would appear that the above statement by Turner relates to studies at a relatively high dose rate, whereas in this work, the range of interest is much lower. In contrast the radiation induced reactions of poly(ethylene tetraphthalate) were found to be dependent on the dose rate of gamma-radiation. In recent years, a number of investigations have been made in this area, because of the effect on the ageing of materials of low levels of radiation, in nuclear installations. In nuclear installations, a variety of polymeric materials receive radiation exposure at a relatively low dose rate ( $\approx 10^3 \text{ rad h}^{-1}$ ) for long periods of time, perhaps up to 40 years. Studies by Gillen and Clough<sup>23,212</sup> investigated problems associated with ethylene based elastomers, to find that crosslinking dominates over scission at high dose rates, but that scission becomes more important relative to crosslinking as the dose rate in air is lowered. This is attributed to oxidative degradation,<sup>da</sup><sup>10</sup> the diffusion of oxygen into the polymer bringing about chain scission which resulted in a reduced gel fraction. This theory is supported by Yoda,<sup>213</sup> who suggests that oxygen can penetrate into the whole material during the irradiation period, giving rise to overwhelming oxidation reactions.

This particular idea can be applied to the problem associated with the silanol data. Prior to irradiation as much air as possible was removed by the freeze-thaw procedure, before sealing these samples under an argon atmosphere. However, it is likely that the nature of the end group in this sample could initiate a chain scission reaction thereby preventing a substantial gel being formed.



The oxygen radical could induce chain scission within its own chain, or on adjacent chains. Hydrogen radicals could combine to form hydrogen gas, or by reaction with a methyl radical, which may result from crosslinking, could produce methane.

Extrapolation of Fig.4.7, gives a  $r_{gel}$  value of 5.8 Mrads. When use is made of the data from irradiation at low dose rates in the Charlesby-Pinner plot (Fig.4.8), the gradient, which is based on 3 data points, again gives a  $r_{gel}$  value of 5.8 Mrads. The emphasis is given to the low dose data, since we have no data below that of 67% gel for the higher dose rate region, and extrapolation would be very inaccurate. However, if the higher dose rate data is considered as a separate plot, the gradient gives a  $r_{gel}$  value of 5.29 Mrads, which is somewhat surprisingly close to the previous result. Using the characterisation performed by RAPRA ( $\bar{M}_w = 100,640$   $\bar{M}_n = 55,430$ )  $G(x)$  is found to be 0.83. This  $G(x)$  value is very much lower than the one obtained from the polydimethylsiloxane gum, which clearly indicates the importance of the chain scission reaction.

#### 4.4.2 Swelling Measurements

##### 4.4.2.1 Results

It was clear from the soxhlet extraction that the more highly crosslinked samples reached the minimum percentage gel far quicker than those having received a lower dose of radiation. This is an effect that is similarly observed with swelling behaviour studies of irradiated polymers in organic solvents. Table 4.9 (Fig.4.10) shows the time required to reach an equilibrium value of the mass of solvent (toluene) absorbed per mass of sample (PDMS). The relationship between the amount of solvent absorbed and radiation dose is illustrated in Fig.4.11.

Table 4.9 Swelling Data for Irradiated Polydimethylsiloxane

Gum immersed in Toluene

Swelling Time (Hours)	Mass of Solvent absorbed/ gram of Polymer		
	1.03 Mrads	2.62 Mrads	5.16 Mrads
14	17.675	5.965	3.553
32	19.709	5.902	3.602
120	21.840	5.935	3.679

Calculations using equation 4.7 gives the volume fraction in the swollen state at equilibrium ( $V_2$ ) and substitution into the Flory-Renner equation yields the moles of crosslinks/cm<sup>3</sup> polymer, i.e. the crosslink density (Table 4.10, Fig.4.12).

Fig.4.10 The Relationship between the time taken to achieve equilibrium swelling for a number of irradiated samples

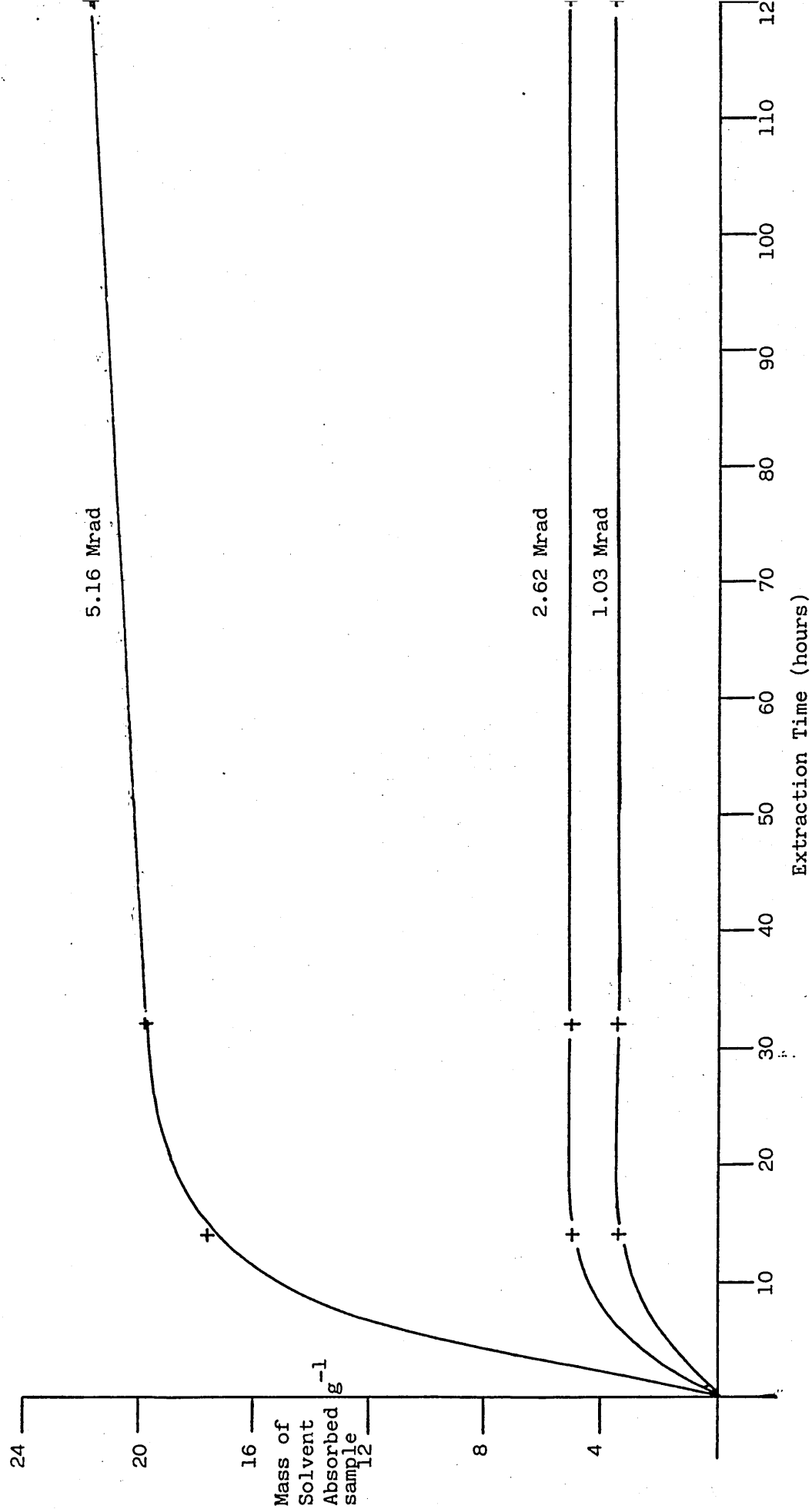


Fig.4.11 The Relationship between the Mass of solvent absorbed/gram Polymer Sample and the absorbed dose (Mrads)

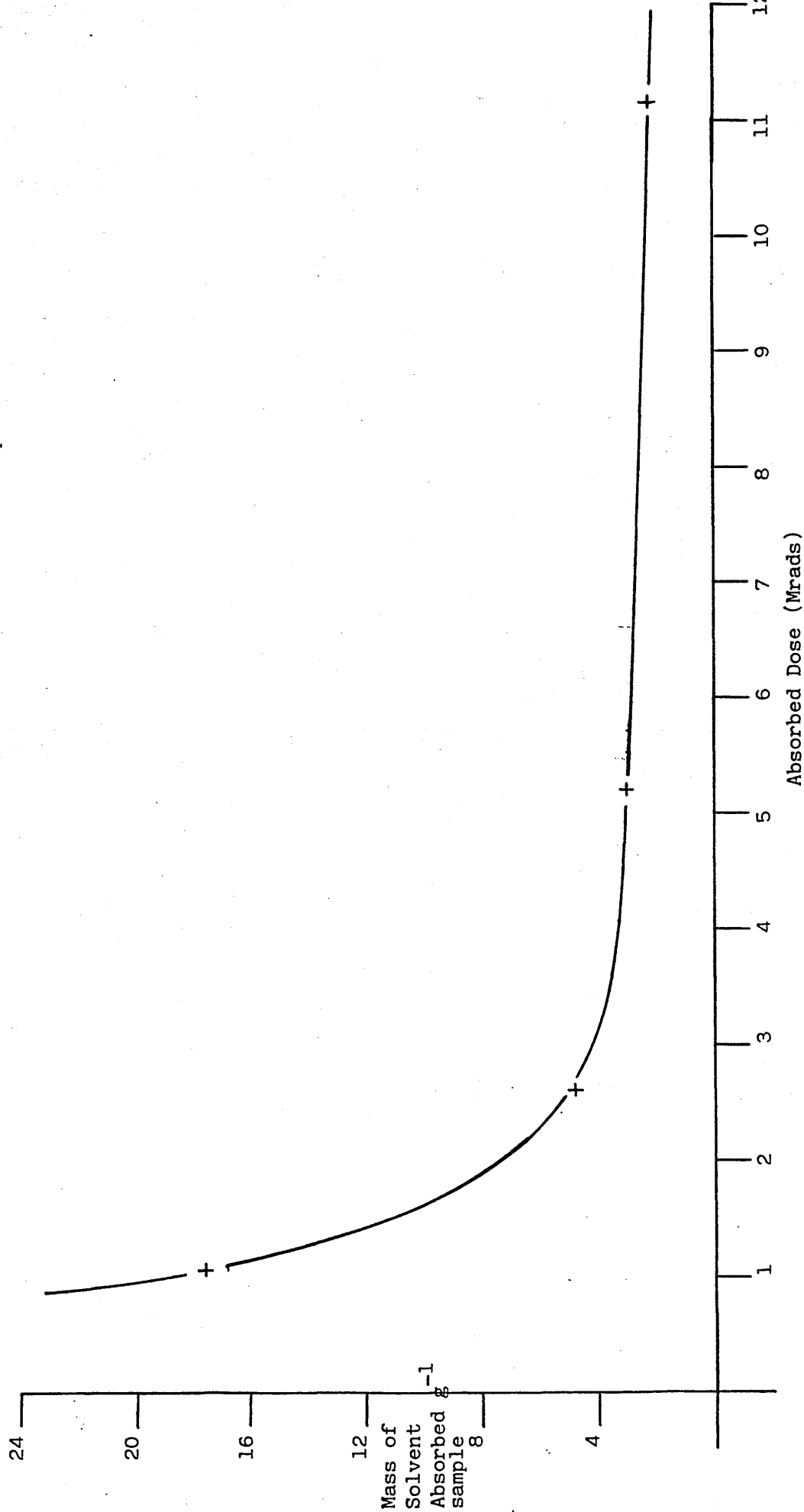


Table 4.10 Derived Swelling Data for Irradiated Polydimethylsiloxane

Dose (Mrads)	Mass of Solvent/gram of sample	Volume fraction in the swollen state ( $V_2$ )	Crosslink density(N)
1.03	21.840	0.04086	$-1.548 \times 10^{-6}$
2.62	5.935	0.13552	$-2.536 \times 10^{-5}$
5.16	3.679	0.20185	$-7.303 \times 10^{-5}$
11.14	2.710	0.25558	$-1.344 \times 10^{-4}$
30	2.325	0.28537	$-1.539 \times 10^{-4}$
50	2.310	0.28713	$-1.191 \times 10^{-4}$
75	2.244	0.29310	$-8.053 \times 10^{-5}$

The irradiated siloxane gum, after extraction using a soxhlet apparatus to remove the sol component, was then swollen in toluene, and the results compared (Table 4.11) with those from samples which still have the sol component present. From this data the crosslinked density at which gelation takes place can be calculated (Table 4.12, Fig.4.13).

Table 4.11 Swelling Data for Extracted Toluene and Unextracted Polydimethylsiloxane Gum

	Radiation Dose (Mrads)			
	1.03	2.62	5.16	11.14
Extracted (Mass of solvent/gram of crosslinked sample)	27.823	6.092	3.647	2.699
Unextracted (Mass of solvent/gram of crosslinked sample)	21.840	5.935	3.679	2.710



Fig. 4.12 The Relationship  
between crosslink  
density and  
absorbed dose

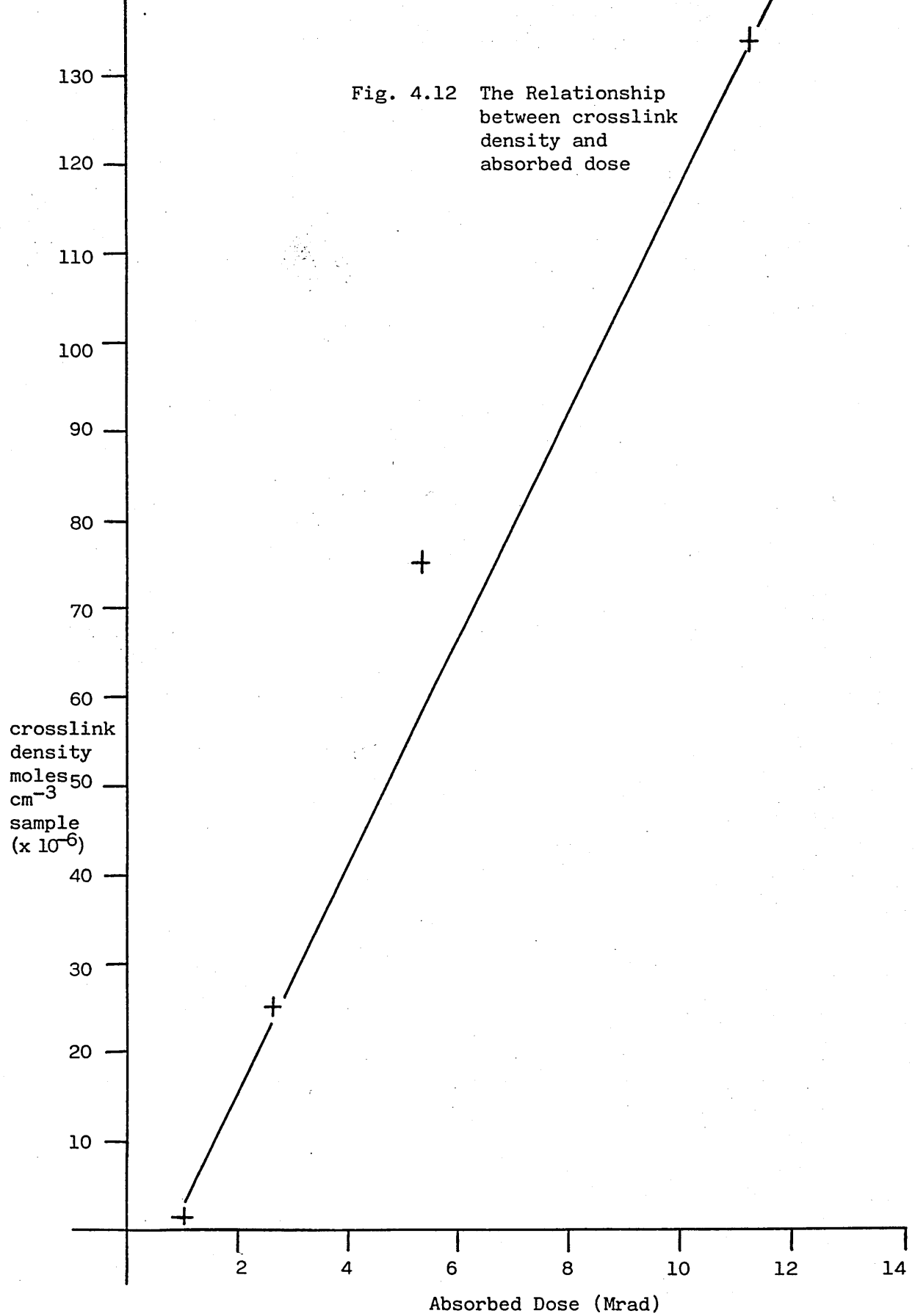


Fig.4.13 The Relationship between the percentage gel and the respective crosslink density in irradiated polydimethylsiloxane

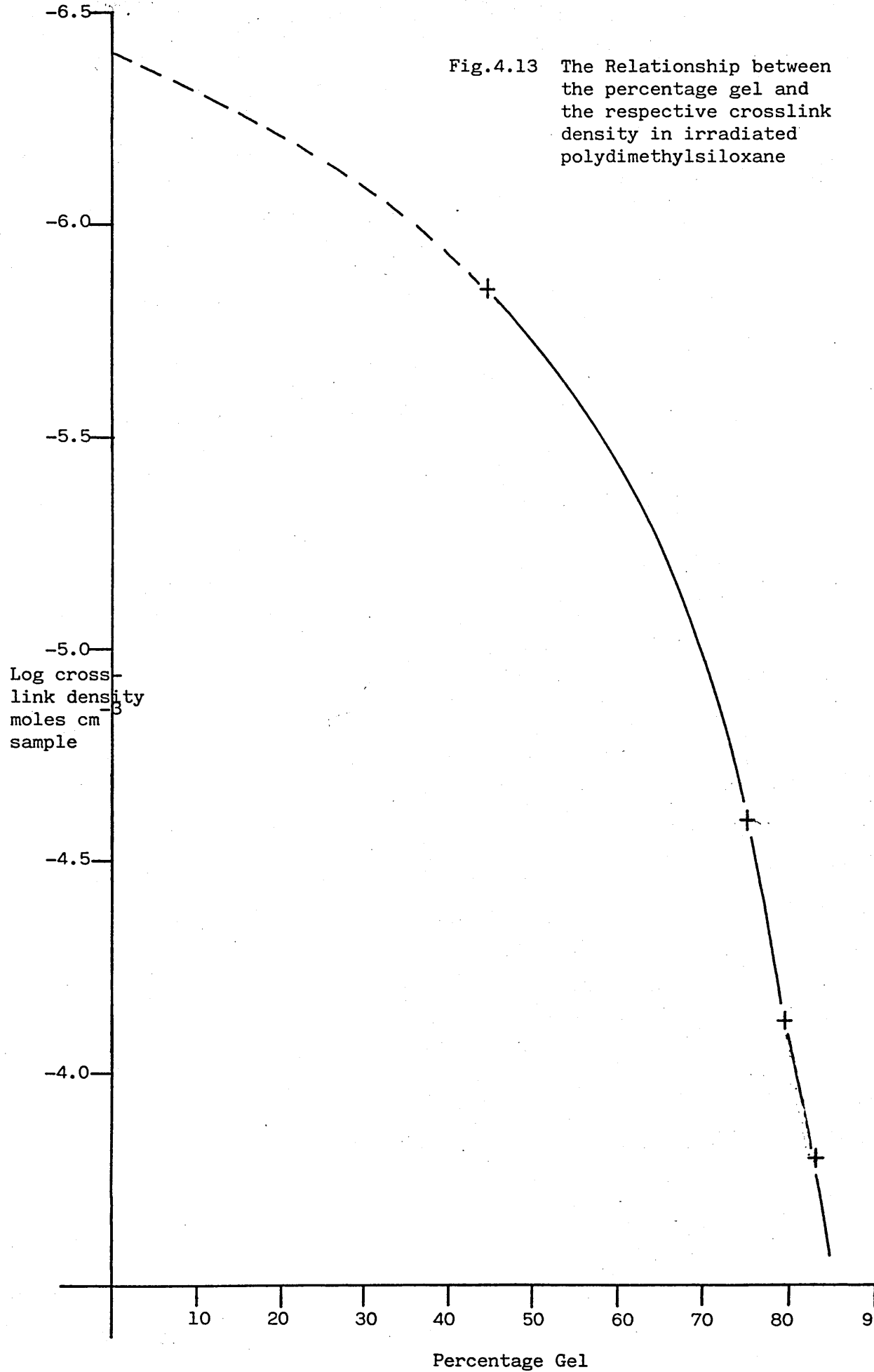


Table 4.12 Gel content and Crosslink Density for

Irradiated Polydimethylsiloxane

Dose (Mrads)	Crosslink Density (N)	% Gel
1.03	$1.548 \times 10^{-6}$	44.1
2.62	$2.5355 \times 10^{-5}$	75.6
5.16	$7.303 \times 10^{-5}$	79.0
11.14	$1.344 \times 10^{-4}$	83.0

4.4.2.2 Discussion

In this technique the crosslinked gum was removed from the container of pure solvent whilst in a swollen state. It is important that the surface solvent is removed as quickly as possible, and that the weighing procedure is not unnecessarily prolonged. In this work removal of solvent and the weighing of the swollen sample took place over a period of only 20 seconds, thereby minimising the possibility of errors through volatilisation of solvent. Samples of similar size are used in the different experiments.

Once the mass of the swollen sample has been recorded, the solvent is removed, using a vacuum drying system, to determine the dry weight of the sample. It is possible that whilst the sample is immersed in the solvent part of the sol component leaches from the matrix into the solvent. This seepage can be minimised by frequent removal from the solvent and drying of the sample.

The time taken to reach an equilibrium swollen state has been shown in Fig.4.10, which confirms what might be predicted. A lower dose sample has a small number of crosslinks which is observed as a

low % gel. The distance between the crosslinks sites is therefore very large, giving a very open 3-dimensional matrix. Within this open matrix, a large number of uncrosslinked polymer chains can be accommodated, which could be removed by soxhlet extraction. This type of sample requires a relatively long period of time to come to an equilibrium swollen value, since a large amount of solvent absorption is possible.

As the dose increases, the amount of solvent absorbed decreases since, with an increased dose, the number of crosslinks increases and the polymer chain becomes more rigid.

The theory of radiation induced reactions, devised by Charlesby,<sup>7,201</sup> assumes that crosslinks are introduced proportional to the absorbed dose. The fall-off in the rate of increase in the crosslink density, at the higher doses has been explained as being due to two factors:

- a) restriction of Chain mobility; and
- b) decreasing number of free sites available to produce radicals.

It is apparent that the maximum number of crosslinks per  $\text{cm}^3$  of sample is reached around 16 Mrads, with a marginal increase resulting from higher doses. This is exemplified by the swelling data for 30, 50 and 75 Mrads sample. There is a very small decrease in the mass of solvent absorbed, in the 30-75 Mrad range.

It is assumed that when the polymer network is first formed, the structure can be taken as 'Ideal'. Subsequent interaction of the solvent with the polymer is assumed to be independent of the crosslinking density. For the low dose region, the polymer-solvent interaction parameter ( $\mu$ ) is taken as 0.485, which was used in similar work conducted by Delides and Shepherd.<sup>207</sup> They found  $\mu$  to be linearly

dependant on the absorbed dose from 0.485 at 3.5 Mrads to 1.105 at 500 Mrad. These findings have been incorporated into the calculations of crosslink density at the different absorbed doses.

A comparison of the swelling data of extracted and the unextracted samples reveal some interesting results. There is a large difference in the amount of solvent absorbed for the low dose sample; the extracted sample absorbing some 27% more solvent. With increased absorption of gamma radiation, this difference decreases until the difference is negligible. In the low dose extracted sample, the sol component has been removed from the crosslinked gel, leaving an open network, which will allow more solvent to be accommodated within the crosslinked matrix. However at higher doses, the fact that the sol has been removed, does not appear to affect such an absorption of solvent. This leads us to conclude that the absorption of solvent is dependent on the chain network rather than the amount of sol present.

The relationship between the crosslink density and % gel, appears to be exponential. Extrapolation of the data gives a value of  $5.5 \times 10^{-7}$  moles/cm<sup>3</sup> of sample, for the crosslink density, at the point of gel formation. Crosslink formation commences from the initial point of absorption of radiation; the crosslink density initially having a very low value, which increases with absorption of gamma radiation. When there is one crosslink per chain, and the crosslinking coefficient  $\delta = 1$ , the gel becomes observable.

#### 4.4.3 Thermal Analysis

##### 4.4.3.1 Results

Over two decades ago, there was interest in the suggestion that radiation induced damage in organic materials could be detected using

thermal analysis, which could form the basis of a dosimetric technique. Murphy and Hill,<sup>215</sup> having made this suggestion, investigated the radiated-induced changes in biphenyl, polyvinyl chloride, polytetrafluoroethene and polydimethylsiloxane in the 100-800°C temperature range. They investigated a siloxane rearrangement, characterised by an exothermic peak at approximately 360°C, and noted that the irradiated siloxane gave a much 'flattened' peak. It is clear that such a rearrangement is being restricted, because of the greater rigidity brought about by the radiation-induced crosslinks. No other temperature region was studied, hence there is no comment on behaviour below 0°C. Since that time, thermal analysis of radiation induced changes has received a somewhat limited degree of attention. A number of studies have been concerned with radiation induced polymerisation reactions.<sup>216</sup> Thompson<sup>217</sup> investigated changes in the glass transition temperature (T<sub>g</sub>) for a number of polymethylmethacrylate samples, finding that a relationship exists between T<sub>g</sub> and the dose received. The catalyst induced crosslinking of polydimethylsiloxane was studied by Barrall and Flandera.<sup>218</sup>

Thermal analysis data for the irradiated polydimethylsiloxane gum, with the sol component still present, is given in Table 4.13 and Fig.4.14.

The cold crystallisation data (exotherm) and that of the melting peak (endotherm) are given in Table 4.14. What is rather surprising is the change in the shape of the endotherm peak, which occurs right from the onset of absorption of radiation. There is also a smaller change in the appearance of the exotherm peak; with interesting trends observed in the relationship with dose (Fig.4.15 and 4.16).

Results from the soxhlet extraction of the silanol terminated polydimethylsiloxane clearly indicated that the terminating group

Table 4.13 Glass Transition Data for Irradiated Polydimethylsiloxane

Dose Mrad	Mass mg	T <sub>g</sub> °C	T <sub>g1</sub> °C <sup>1</sup>	T <sub>g2</sub> °C <sup>2</sup>	Δ T <sub>g</sub> °C
0	7.68	-123.5	-125.2	-121.5	3.75
0.01	11.05	-122.94	-125.0	-119.6	5.4
0.049	13.42	-122.78	-125.5	-119.2	6.3
0.082	12.09	-122.44	-125	-119.0	6.0
0.11	10.00	-122.18	-124.5	-120.0	4.5
0.21	16.15	-121.4	-124	-117.4	6.6
0.303	11.68	-103.9	-107	-100.0	7.0
0.50	15.37	-102	-104.5	-99.0	5.5
1.03	15.79	-102.3	-104	-98.5	5.5

Table 4.14 Exotherm and Endotherm Data for Irradiated Polydimethylsiloxane

Dose Mrads	Mass mg	Exotherm			Endotherm *		
		Temp. °C	mJ	J/g	Temp. °C	mJ	J/g
0	7.68	-78			-39.5		
0.01	11.05	-84.6	256.8	23.24	-37		
0.049	13.42	-87.0	308.7	23.00	-38	372.8	27.8
0.082	12.09	-90.3	244	20.18	-36		
0.11	10.00	-93.5	176.3	17.6			
0.21	16.15	-95.2	40.38	3.9	-39.3	294	28.3
0.303	11.68	-	-	-	-39	383	28.3
0.50	15.37	-	-	-			
1.03	15.79	-	-	-			

\* In each sample the endotherm peak is observed, but full results were not determined in all cases.

seriously affects the formation of a 3-dimensional network. Tables 4.15 and 4.16 show thermal analysis data from this material.

#### 4.4.3.2 Discussion

Polydimethylsiloxane has been thermally characterised by many authors, and the results from this work, discussed in Chapter 2, were found to be in excellent agreement with values quoted in the literature. However, to date no study has been carried out on an analysis of the radiation behaviour of polydimethylsiloxane by DSC.

When polydimethylsiloxane is cooled to  $-170^{\circ}\text{C}$ , the amorphous polymer is in the glassy state. When energy is applied to the polymer, through controlled heating, pronounced molecular changes occur at certain temperatures. The glass-rubber transition temperature being a very important parameter which represents the minimum service temperature for amorphous elastomers. It is clear that when the polymer chains are part of a crosslinked 3-dimensional matrix, this transition from a rigid, glassy state to a rubbery state is significantly different from that of the non-irradiated polymer.

With a very low degree of crosslinking, below the onset of gelation, many of the chains lack a crosslink site. However the commencement of chain motion, brought about by controlled heating, takes place at a slightly higher temperature. With additional absorption of radiation, further crosslinks are introduced into the polymer sample, which will restrict the motion of the chains, further increasing the glass transition temperature. There is an increase of  $2.1^{\circ}\text{C}$ , from  $-123.5^{\circ}\text{C}$  to  $-121.4^{\circ}\text{C}$ , on absorption of up to 0.2 Mrads  $\gamma$ -radiation. This increase is rather small, but very significant. This increase is comparable to the attachment of bulky pendant groups to polymer chains which of themselves are very flexible. The incorporation of the bulky side-groups,



Fig.4.14 The variation of the Glass transition temperature of irradiated polydimethylsil

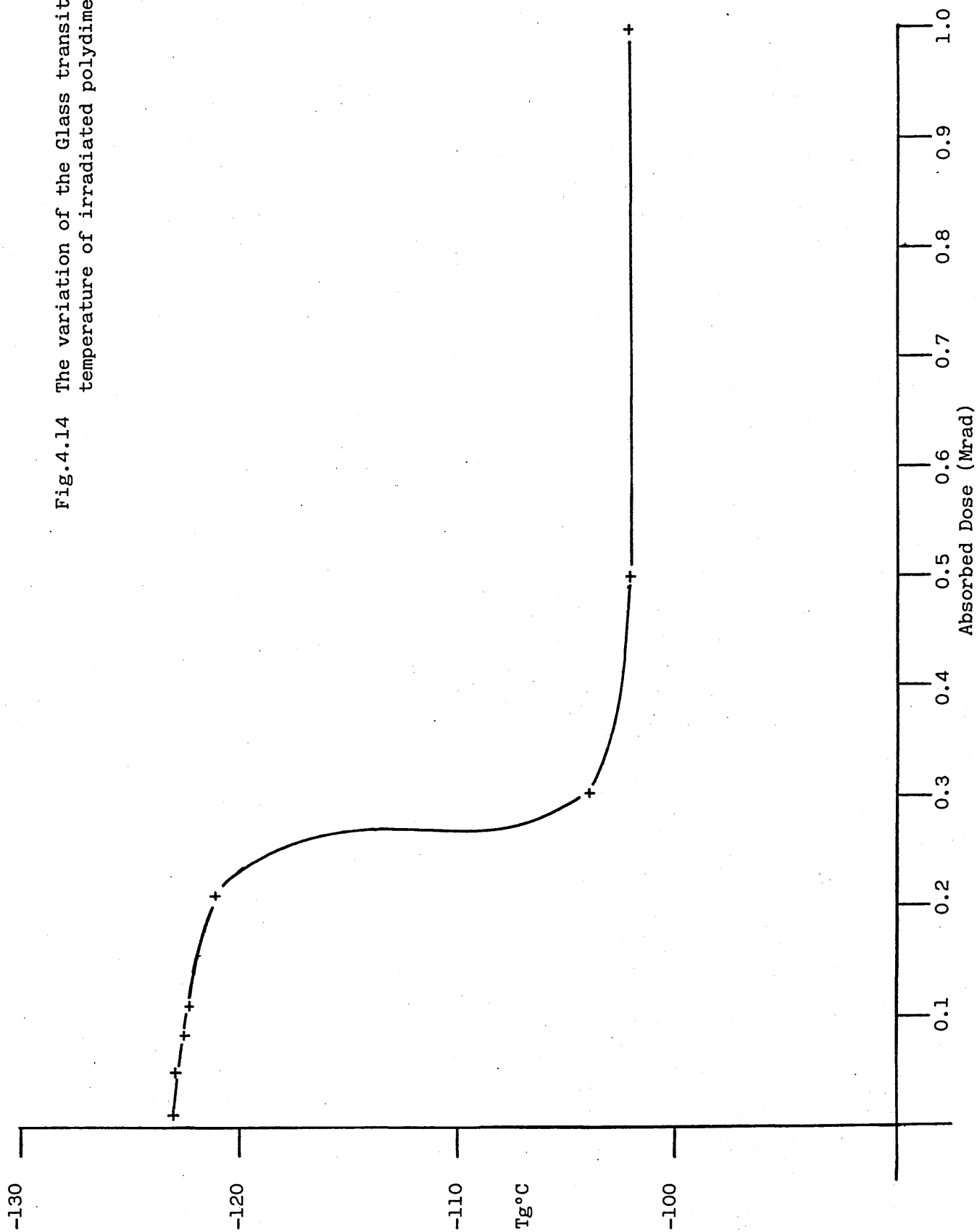


Fig.4.15 The Relationship between  
the Temperature of the  
Exotherm and Irradiated  
Polydimethylsiloxane

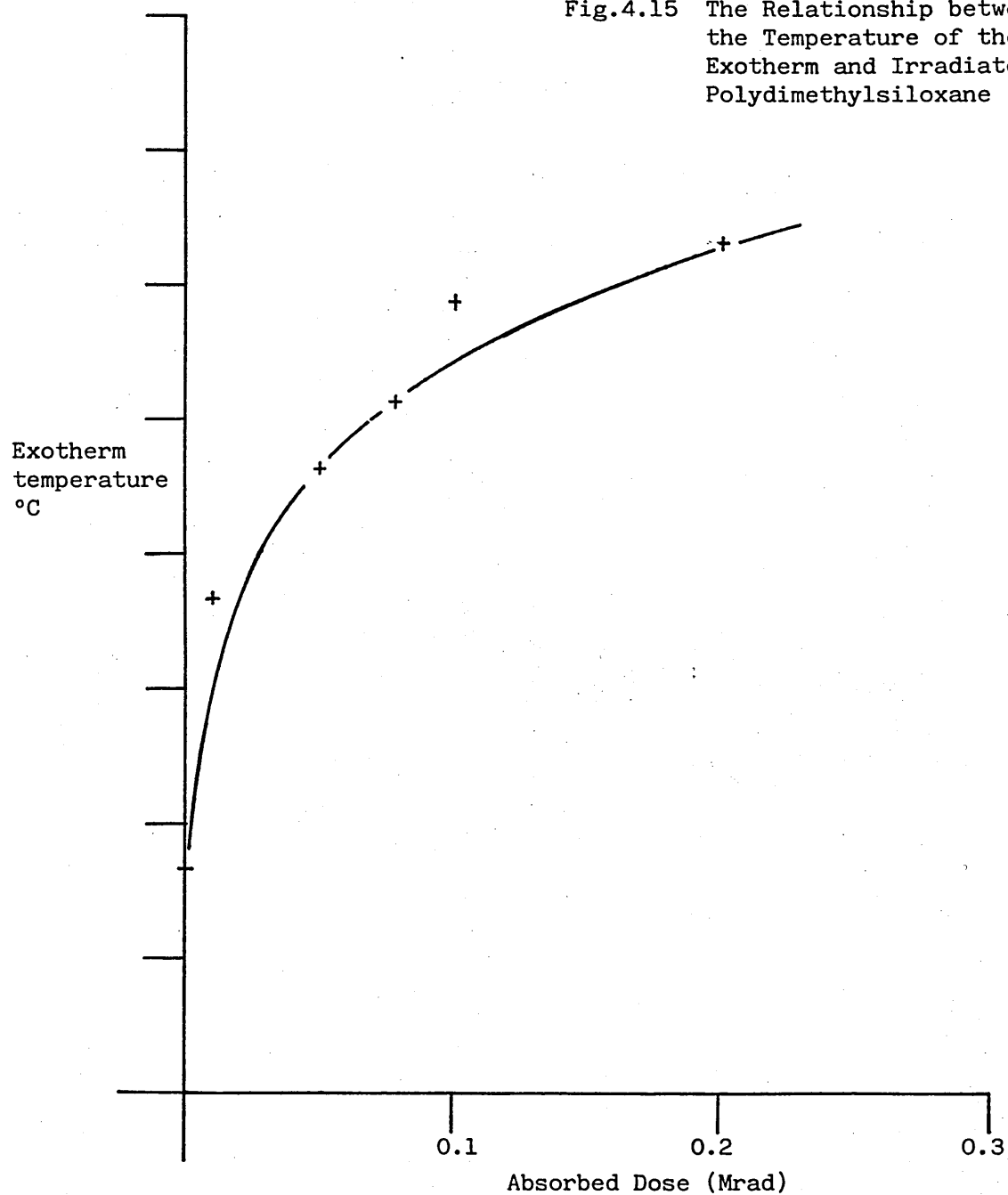


Fig.4.16 The Relationship between  
the Enthalpy of the  
Polydimethylsiloxane  
and the absorbed dose

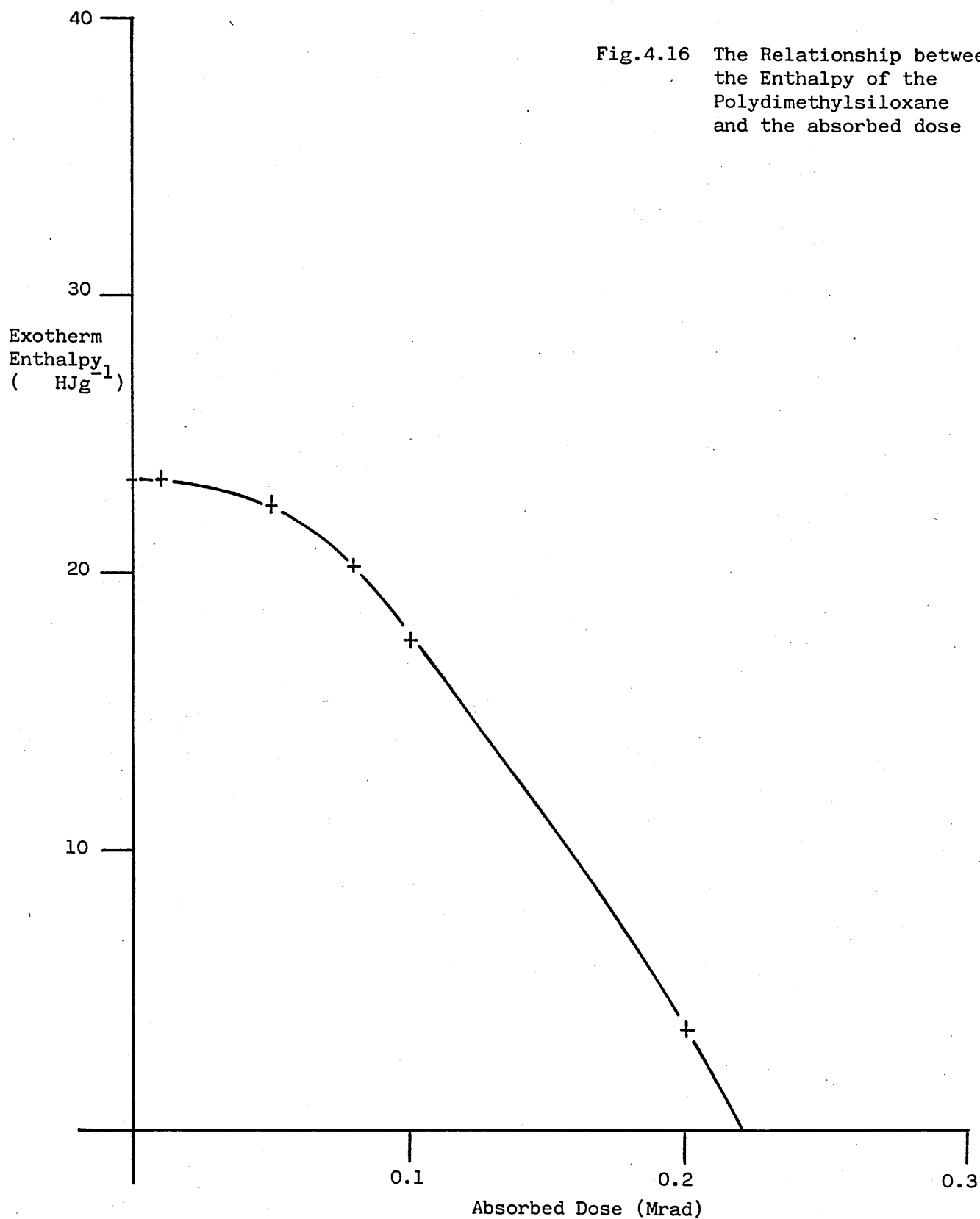


Table 4.15 Glass Transition Data for the Irradiated Silanol

Terminated Polymer

Dose Mrad	Mass mg	T <sub>g</sub> °C	T <sub>g1</sub> °C	T <sub>g2</sub> °C	ΔT <sub>g</sub> °C
0	19.005	-122.66	-124.2	-120	4.2
2.8	16.390	-122.5	-124	-119.5	4.5
3.75	16.215	-121.65	-123.5	-120	3.5
4.92	18.140	-121.0	-122.5	-119	3.5
5.90	16.965	-121.0	-123	-119	4.0
6.90	18.160	-120.5	-122.5	-118.5	4.0
8.04	19.470	(a)			
10.8	19.520	(a)			

(a) not detectable

Table 4.16 Exotherm and Endotherm Data for Irradiated Silanol

Terminated Polymer

Dose Mrads	Mass mg	Exotherm			Endotherm		
		Temp. °C	mJ	J/g	Temp. °C	mJ	J/g
0	19.005	-83.9	468.5	24.65	-41.8S -34.2	572	30.11
2.8	16.390	-87.1	254.5	15.53	-41.5S -36.5	511	31.19
3.75	16.215	-87	200.6	12.37	-41.8S -36.5	494	30.5
4.92	18.140	-86.7	410.5	22.6	-41.8 -36.5	563	31.0
5.90	16.965	-86.5	377	22.26	-41.8 -36.5	515	30.74
6.90	18.160	-85.1	382	21.06	-41.8 -36.5		
8.04	19.470	-88.4	341	17.56	Single -37	589	30.29
10.8	19.520	-91.3	105	5.4	Single -37	610	31.2

restricts the rotational motion of the chain, thereby resulting in a higher glass transition temperature.

Further irradiation above 0.2 Mrads results in gelation, and this process is signified by a sudden increase in the glass transition temperature, of the order of 17.5°C. This is indicative of a substantial change in the internal structure of the polymer sample. Concomitant with this change in the glass transition temperature there is a decrease in the heat capacity of the transition. The ability of the chain to commence rotational motion being restricted, results in less of a transformation actually taking place. Eventually with continuing absorption of radiation, the glass transition becomes ill-defined. After gelation, the absorbed energy gives rise to additional crosslinks between the previously crosslinked chains, resulting in a distinctly immobile matrix. The highly crosslink chains are no longer able to give rise to any rotational motion, neither are the polymer chains that are separate from the 3-dimensional matrix.

The endotherm peak occurs in the region -36 to -39.5°C for the irradiated polymer which indicates that the polydimethylsiloxane is an amorphous polymer at room temperature. As the polymer sample is cooled the chains orientate into an ordered crystalline arrangement, with a subsequent decrease in the entropy of the polymer chains. The transition from crystallinity to being an amorphous polymer, requires energy, so in the heating cycle, an endothermic peak is observed. The melting endotherm commenced at -64°C, peaked at about -39.5°C and was complete by -24°C.

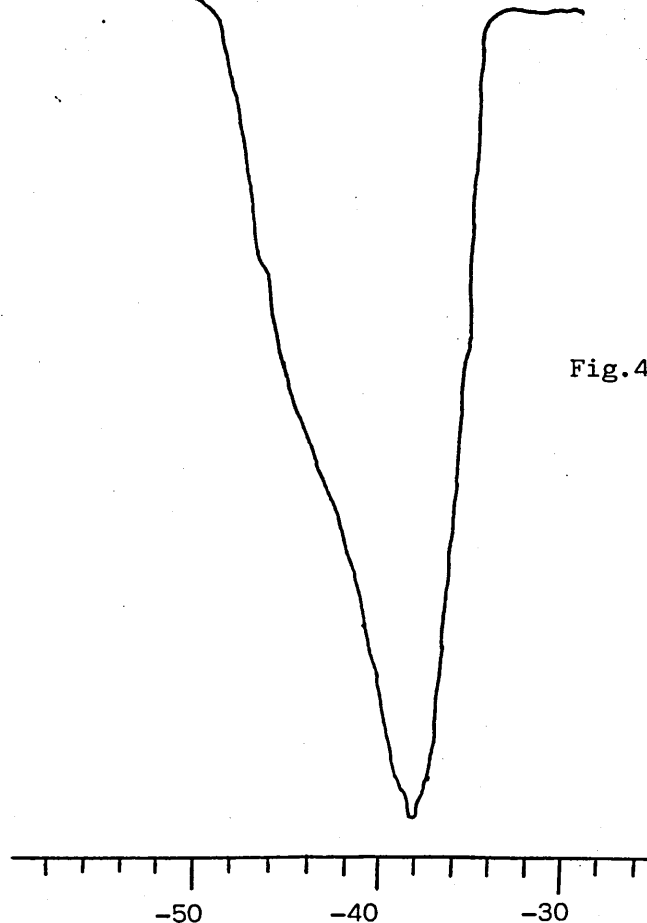


Fig.4.17 A typical melting endotherm indicating two different crystal structures.

With the irradiated materials, the low dose samples gave similar results.

The presence of both a main peak and a smaller shoulder at  $-41^{\circ}\text{C}$  indicates the presence of two different crystal structures. (Fig.4.17). In the thermal characterisation of polydimethylsiloxane, carried out by Lee, it was shown that the position was dependant on the cooling and heating rate of the thermal cycle. A slow heating rate would allow sufficient time for the low melting point crystals to reorganise and then to form a second type of crystal which melts at a higher temperature. The cooling and heating rate of the thermal cycle in this study is constant throughout, the variation in this case being the amount of radiation absorbed by the sample. The presence of crosslink units within the polymer clearly effects the crystalline order and hence the rate of formation of such an ordered structure. After gelation has taken place, the 0.3 Mrad sample gives a reduced shoulder

peak, whilst at 0.5 Mrad and above only one sharp peak is observed, at  $-39^{\circ}\text{C}$ . It appears whilst there is a substantial sol component present two crystalline forms result.

It is interesting to note however, that the enthalpy of melting is almost the same for both the un-irradiated and irradiated samples ( $28 \text{ Jg}^{-1}$ ). Despite the major changes which have taken place within the polymer structure, the degree of crystallinity remains constant.

The most significant effect that radiation has on the thermal character of polydimethylsiloxane is exhibited through the enthalpy of the cold crystallisation peak (exotherm), and the temperature at which it occurs. The presence of the cold crystallisation peak indicates that whilst in the cooling cycle, part of the polymer remains uncrystallised below the melt temperature. When in the heating cycle, these remaining amorphous regions dissipate heat upon the transition to crystallinity. The slower the rate of cooling the more time there is for the polymer chains to crystallise, hence no exotherm peak is observed.

When the cold crystallisation peak disappears, it is an indication that all the amorphous material has crystallised during the cooling cycle. It is observed that there is a link between the enthalpy of the exotherm and the radiation dose received (Fig.4.16), which gradually decreases until the onset of gelation, when no peak is observed. The enthalpy of the exotherm appears to be inversely dependent on the crosslink coefficient, below the value of 1.

In a sample which has received a very low dose of radiation the crosslinks will be scattered around the polymer matrix. On cooling, a portion of the unattached chains can remain in the amorphous state

below the melt temperature. With increased absorption of radiation there will be more crosslinking and consequently fewer unattached chains. Thus, there will be a smaller portion available to remain in the amorphous state below the melt temperature, hence the enthalpy of the cold crystallisation transition is reduced. On gelation the theory predicts that all the chains have an average of one crosslink. There are now no unattached chains, to give a cold crystallisation peak, and the polymer undergoes crystallisation at the normal transition temperature ( $T_m$ ).

It would therefore appear that the formation of gel encourages crystallisation at the melt temperature ( $T_m$ ). It is perhaps easier to form crystalline regions from the lightly crosslinked gel, than from the unattached chains. This would then explain, why all the crystallisation occurs in one step at the melt temperature, rather than in two steps as in the un-irradiated sample. The temperature of the exotherm decreases from  $-76^{\circ}\text{C}$  to  $-94.7^{\circ}\text{C}$  with increasing dose. Since there would be less amorphous material as the dose increases, orientation of the chains can occur much more readily, and the transition is observed at a lower temperature.

The thermal analytical results from the silanol terminated polymer are rather different in detail, but show similar features. The glass transition temperature appears to follow the same trend as with the gum; there is an increase of  $2.1^{\circ}\text{C}$  on the formation of the gel.

The exotherm data also show similar trends. The simultaneous decrease in the cold crystallisation temperature and enthalpy with increasing irradiation dose points to a decreasing amount of amorphous material available for rearrangement whilst in the heating cycle. However, in this case, a peak is still observed after gelation is found to have taken place. It seems that whilst there is still a large amount



of sol present, within the lightly crosslinked matrix, not all of the amorphous material can undergo crystallisation at the melt temperature, hence the continuance of the exotherm peak.

#### 4.4.4 Sol Analysis

##### 4.4.4.1 Results

Gas-liquid chromatography (GLC) has been used on many occasions, for the analysis of siloxane oligomers, of both the cyclic and linear variety. Table 4.17 gives data from the GLC analysis of a number of siloxane samples from this study, analysed under identical conditions. Relatively large molecular weight components were predicted to be present in the samples, hence the isothermal temperature programme rate was set at  $8^{\circ}\text{C min}^{-1}$ . This was selected for two reasons; first to facilitate sample analysis within a reasonable period of time, but, more importantly, to obtain sharp symmetrical peaks for accurate analysis.

Sample KD F14 (obtained courtesy of Dr. K. Dodson) was a low molecular weight siloxane sample, obtained by preparative gel permeation chromatographic separation of siloxanes. It was used as a cyclic calibrant since it consisted of a series of ascending cyclic oligomers. This was subsequently used for the identification of cyclic peaks in the soluble extracts from un-irradiated and irradiated samples.

It is clear that from the data that a number of peaks are observed with very similar retention times in the low molecular weight region of the 1.03 Mrad sample. The temperature programme was therefore adjusted such that for the temperature was initially fixed at  $80^{\circ}\text{C}$  for 5 mins, then allowed to rise at  $8^{\circ}\text{C min}^{-1}$  to  $300^{\circ}\text{C}$ . This expanded the chromatogram thereby increasing the accuracy of identification.

Table 4.17 Gas Liquid Chromatography Data for a number  
of Polydimethylsiloxane Samples

Cyclic Siloxane Number	KD F14	Unirradiated	1.03 Mrads	75 Mrads
	9	7.5	8	9
	10			
D <sub>4</sub>	14	15	13 15.5 18 22 27	16.5
D <sub>5</sub>	30	30 38	31.5 38 41 44.5	30 44.2
D <sub>6</sub>	51.5	52.5	51.5	51.5
D <sub>7</sub>	75	76.5	74 82	59 74.5
D <sub>8</sub>	97.5	89 98	89 97.2 104	97.5 106.5
D <sub>9</sub>	119	118	118 132	119 124 132
D <sub>10</sub>	137.5	136.5	136.5 144.5	136 144.7
D <sub>11</sub>	153	153	152.5	152.5 156.5
D <sub>12</sub>	169	168.5	168	168.5
D <sub>13</sub>	183	182.5	182	182
D <sub>14</sub>	196	196	195.5	195.5
D <sub>15</sub>	210	209	208.5	208.5 216
D <sub>16</sub>	222	221	220.5	221
D <sub>17</sub>	233	232.5	232.5 238.5	232.2 239
D <sub>18</sub>	244	243.5	242.5	243.5
D <sub>19</sub>	255	254.5	253.5	254.5
D <sub>20</sub>	265	264.5	263.5	264

#### 4.4.4.2 Discussion

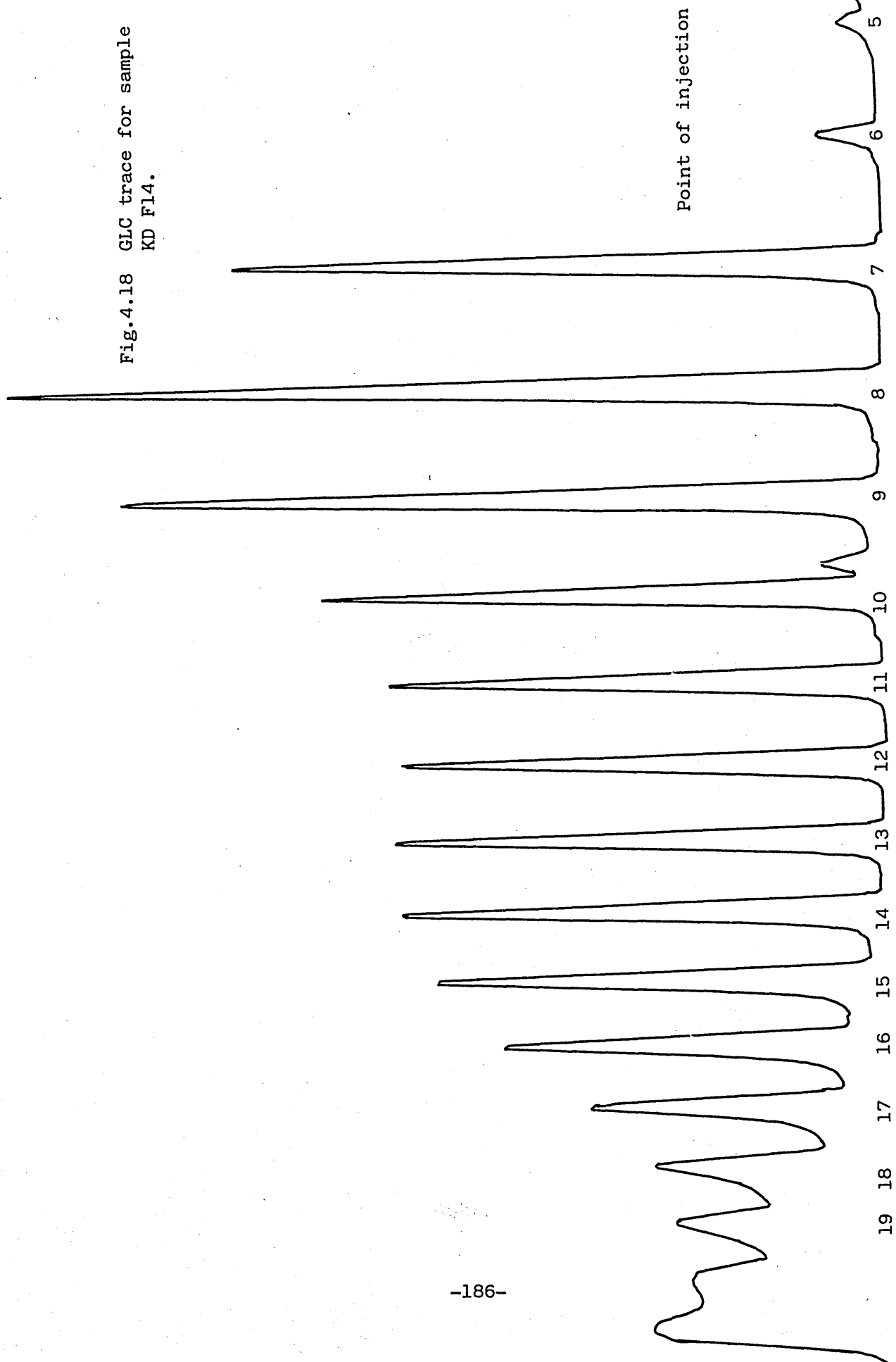
The identification of the cyclic oligomers was based on various "markers". It has been reported by Carmichael<sup>219</sup> that in the distribution of cyclic oligomers of siloxanes, there is a minimum concentration observed at the  $D_{11}$  cyclic oligomer. Analysis of KD F14 (Fig.4.18) showed a minimum in the region of  $D_{11} - D_{12}$ . In addition, using a selection of low molecular weight standards, the retention distance of the trimer ( $D_3$ ), tetramer ( $D_4$ ) and pentamer ( $D_5$ ) were determined which then allowed confirmation of the oligomer peaks. The 'Cyclic Number' is plotted against the retention distance in Fig.4.19, to give an almost sigmoidal plot, which is believed to be a function of the isothermal temperature programme.

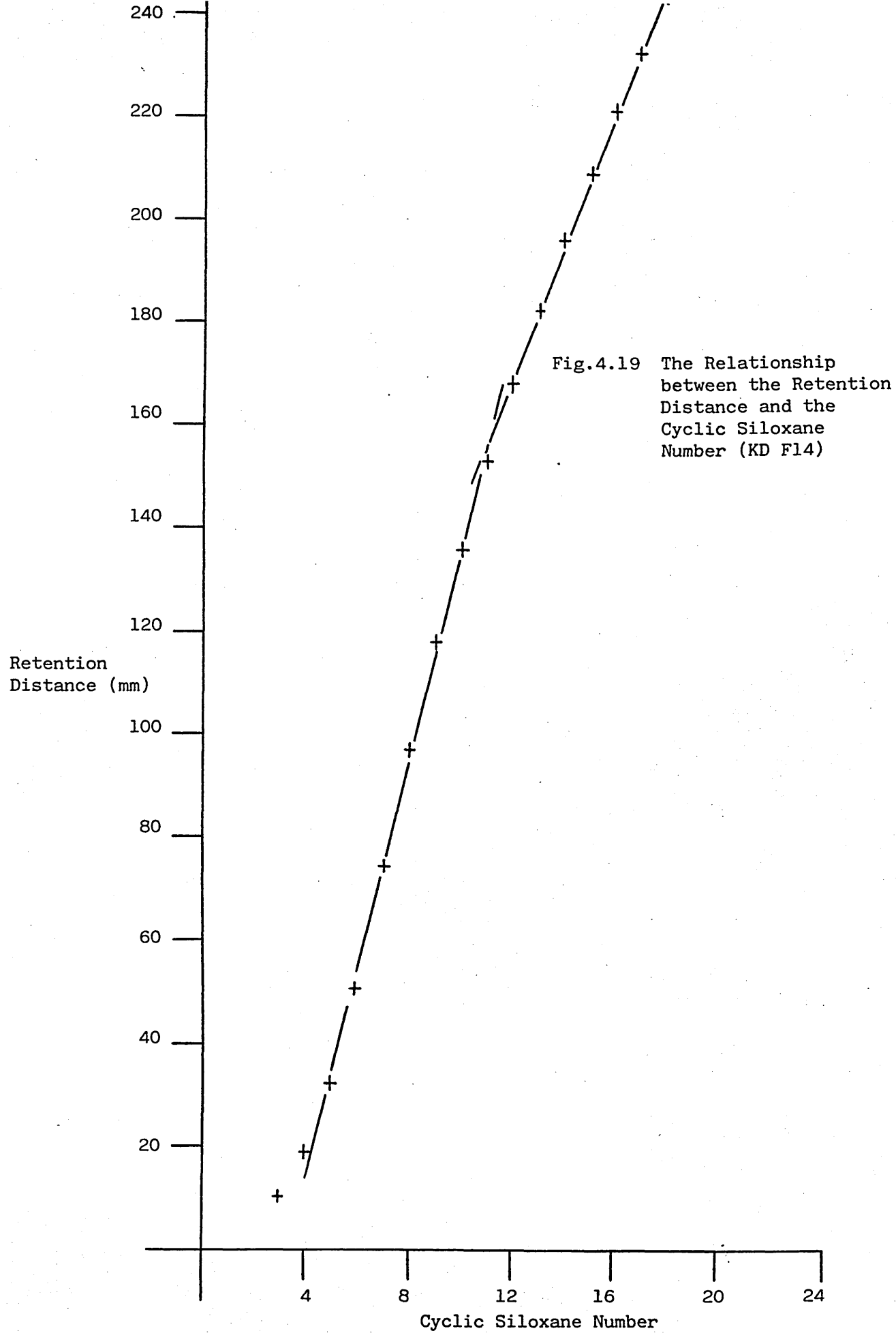
The polydimethylsiloxane gum used in this study was prepared by Dow Corning via the hydroxide polymerisation of a  $D_3/D_4$  mixture. It is clear from the GLC evidence that substances other than cyclic oligomers are present (Fig.4.20) which may be processing aids, or linear oligomers from the polymerisation process.

The extracted sol of the sample irradiated at 1.03 Mrad appears to be substantially different to that extracted from un-irradiated polydimethylsiloxane. There are additional peaks and differences in the amounts of certain cyclic peaks that are present (Fig.4.21). The appearance of new peaks below that of the Hexamer ( $D_6$ ) points to the formation of linear oligomers arising from chain scission reactions. This is better illustrated in Fig.4.22, where the new peaks are clearly observed.

Using the three linear siloxane oligomers, hexamethyldisiloxane, octamethyl trisiloxane and decamethyltetrasiloxane, it was difficult to extrapolate the data in Fig.4.23, with any degree of certainty to identify the unknown peaks. Equilibrium studies, carried out by

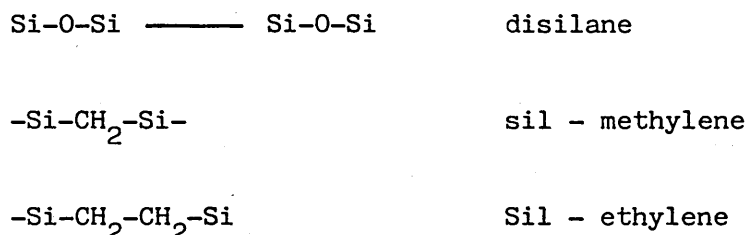
Fig.4.18 GLC trace for sample  
KD F14.





Carmichael,<sup>219</sup> found that the retention distance of the linear species was midway between that of cyclic oligomers. In our study, more than one unknown occurs between the cyclic peaks, which suggests that species other than the linear oligomers are produced.

Radiation studies of hexamethyldisiloxane<sup>5,220</sup> and octamethyltrisiloxane<sup>221</sup> gave peaks which cannot be identified as simple linear or cyclic oligomers. Even though the starting materials in each of these studies differed, they both suggest the presence of a range of dimeric species which could be produced via oligomeric intermediates. Typical linkages could be:



In the low molecular weight range, the un-irradiated sample contains octamethyltricyclicsiloxane (D<sub>4</sub>) and possibly the trimer (D<sub>3</sub>), hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM), the linear oligomers arising from the method of preparation. The sample irradiated at 1.03 Mrad showed two regions of interest:

- i) a low molecular weight range, up to the cyclic hexamer (D<sub>6</sub>);
- ii) the range between the heptamer (D<sub>7</sub>) and the dodecamer (D<sub>11</sub>).

In the low molecular weight range, a number of new peaks occur which are not present in the unirradiated sample, the majority appearing after the tetramer (D<sub>4</sub>). There are three possibilities for the formation of such species.

Fig.4.20 GLC trace for a low molecular weight sample extracted from unirradiated polydimethylsiloxane gum.

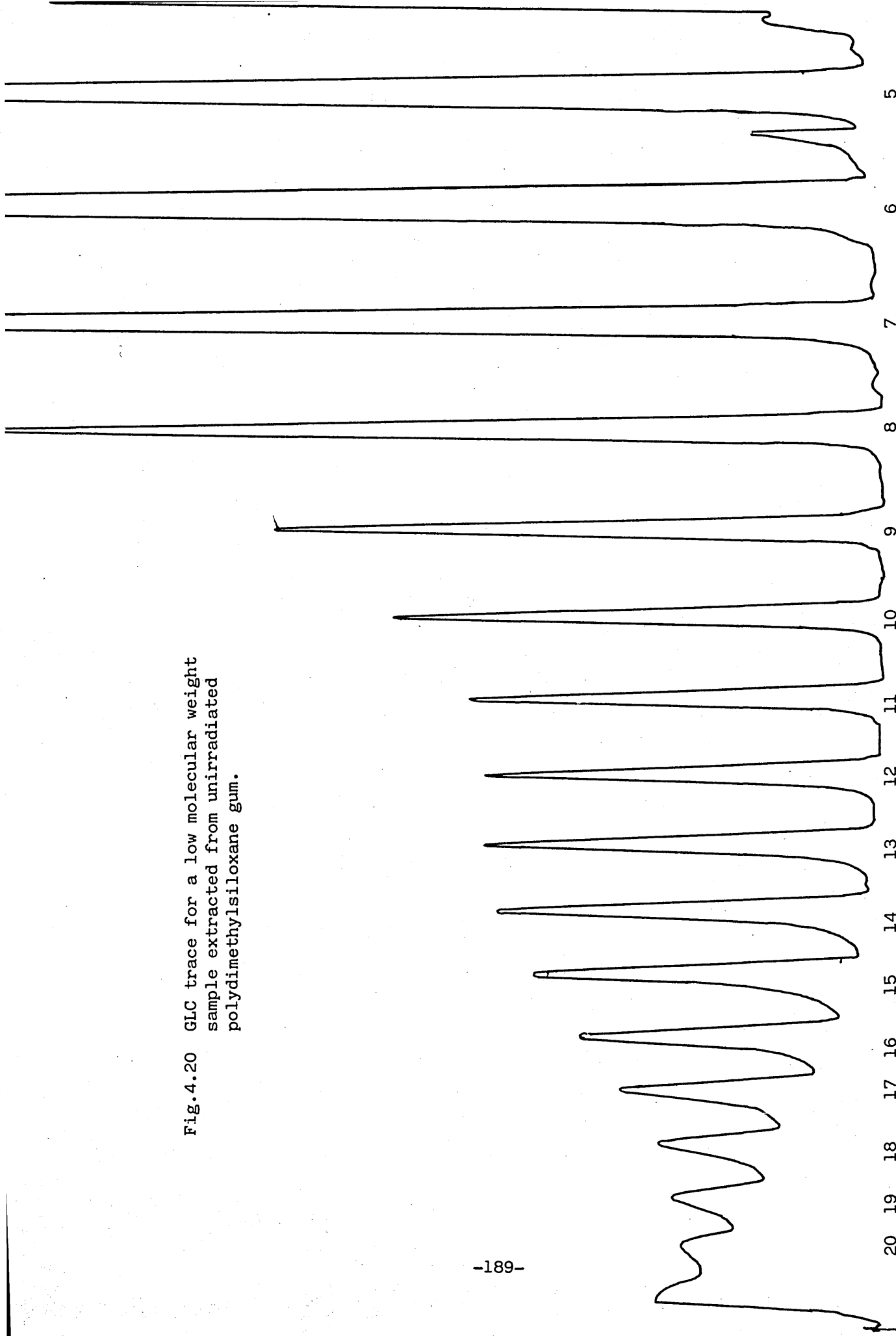


Fig.4.21 GLC trace of a sample extracted  
from irradiated polydimethylsiloxane  
(1.03 Mrads).

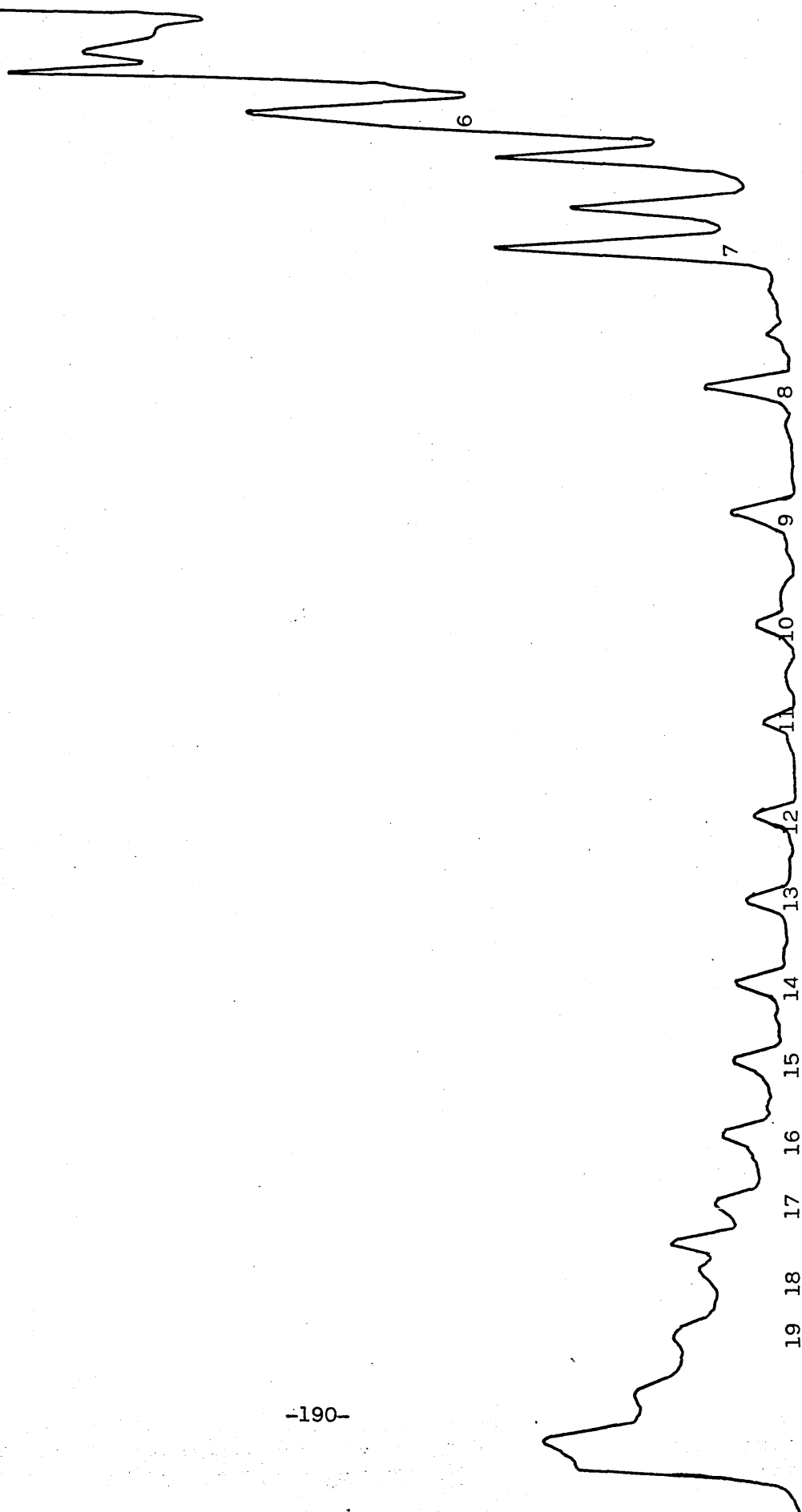




Fig.4.21 continued

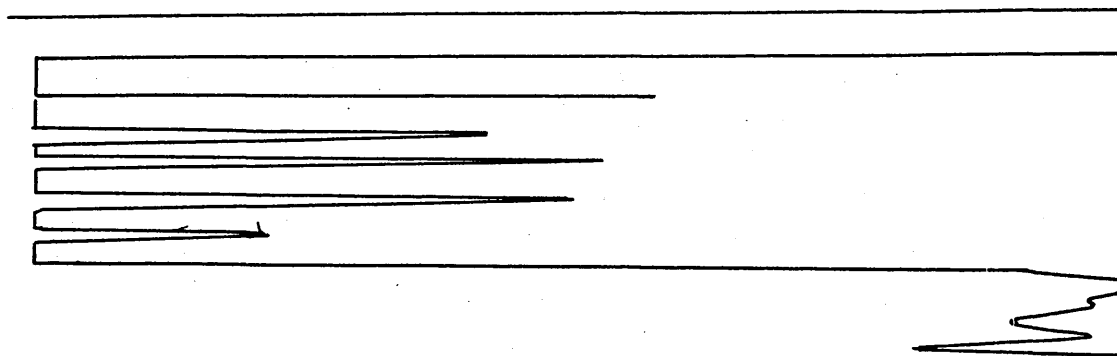
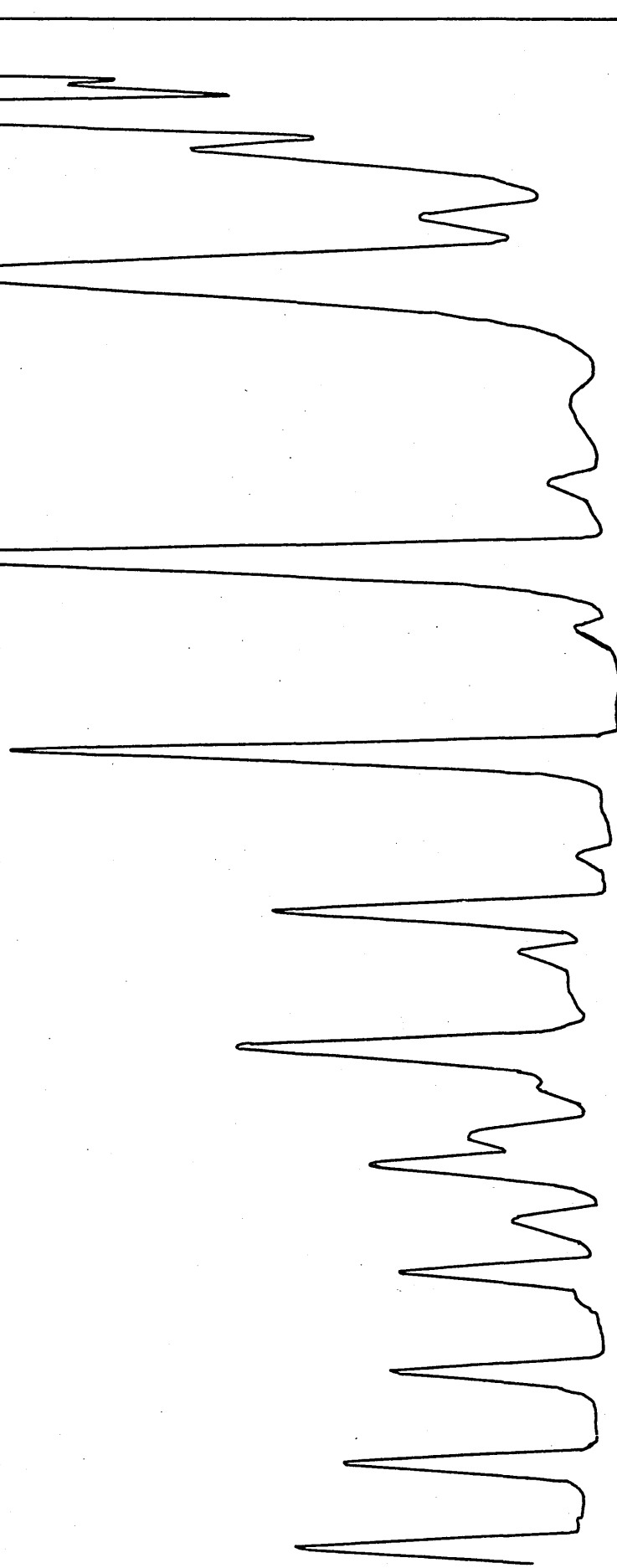
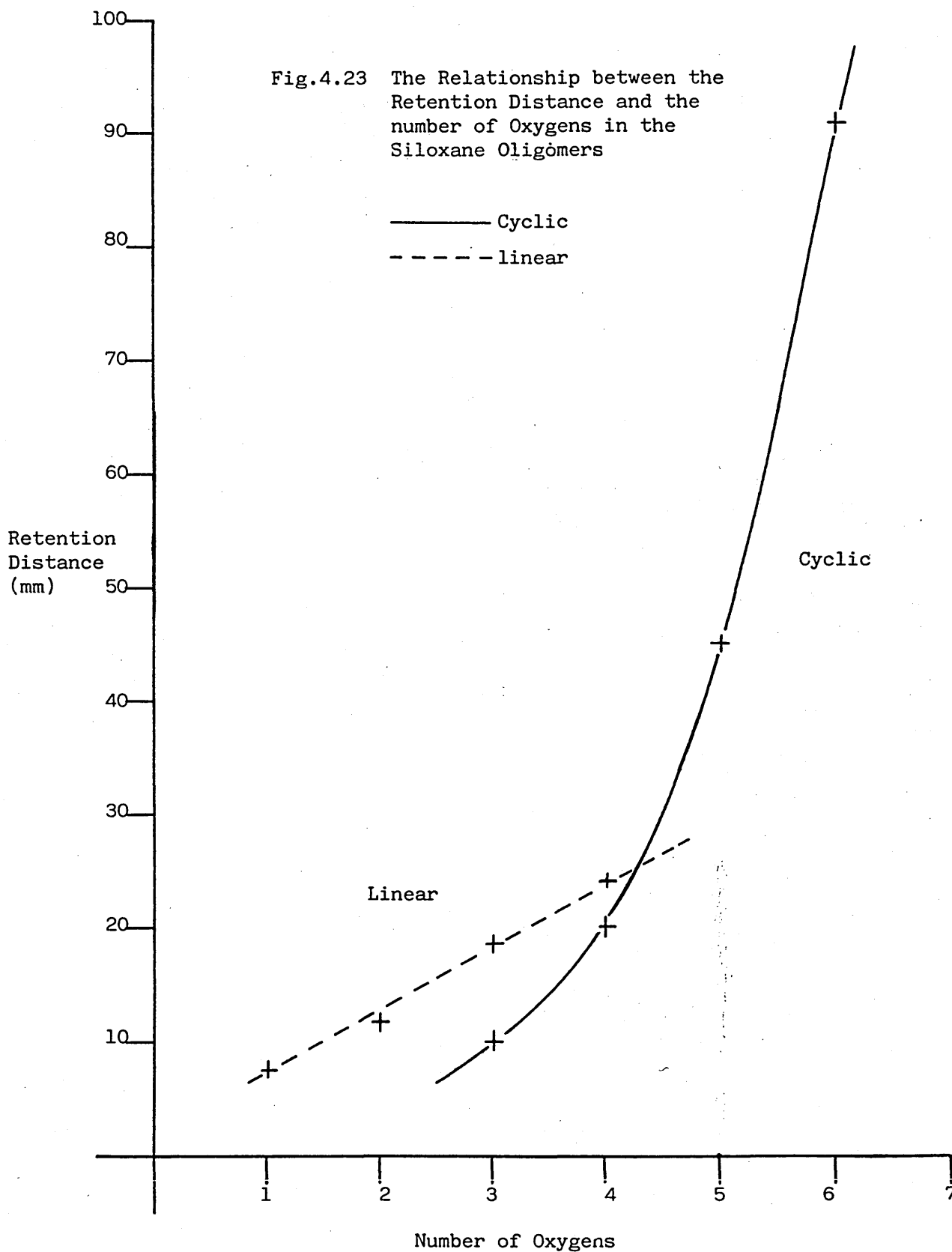


Fig.4.22 GLC trace of a sample extracted  
from irradiated polydimethyl-  
siloxane (1.03 Mrads).  
Expanded low molecular weight  
region.





a) It is possible that ring cleavage of the tetramer may be responsible for such a range of oligomeric intermediates and dimeric species, similar to results found using hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM) as starting materials. However, when pure tetramer was irradiated at 1 and 2.5 Mrads no such peaks were detected using GLC techniques. Thus the tetramer, at this radiation level, is not responsible for these unknown peaks.

b) Within the un-irradiated sample, relatively small amounts, of MM and MDM have been detected. It is confirmed<sup>5,220,221</sup> that these starting materials do give rise to non-cyclic oligomers. However the peak heights of the unknown species in the irradiated sample (1.03 Mrad) suggests that their presence is not entirely due to linear oligomers.

c) The polymer chains are readily crosslinked into a 3-dimensional gel network on absorption of  $\gamma$ -radiation. Simultaneous chain scission also occurs. Chain scission of the crosslinked gel would give a wide range of linear and cyclic oligomers, but not necessarily just the 'simple oligomers' as suggested by studies of the linear MDM and other cyclic compounds. Crosslinking is considered to be a random process, provided no side-groups are present which assist crosslink formation. It can be assumed that the chain scission process is of a similar type; random cleavage of a randomly crosslinked gel. It was shown earlier (Chapter 3) that a siloxane end-group readily reacts by back-biting with itself to form low molecular weight species. By this process cleavage by  $\gamma$ -radiation of only one bond would be necessary to facilitate oligomer formation.

Between  $D_7$  and  $D_{11}$  a number of peaks other than cyclics were detected, which suggests the formation of additional compounds by two possible routes.

- a) addition of the unknown low molecular weight oligomers to the cyclic species;
- b) coupling of the unknown oligomers to form higher molecular weight siloxanes.

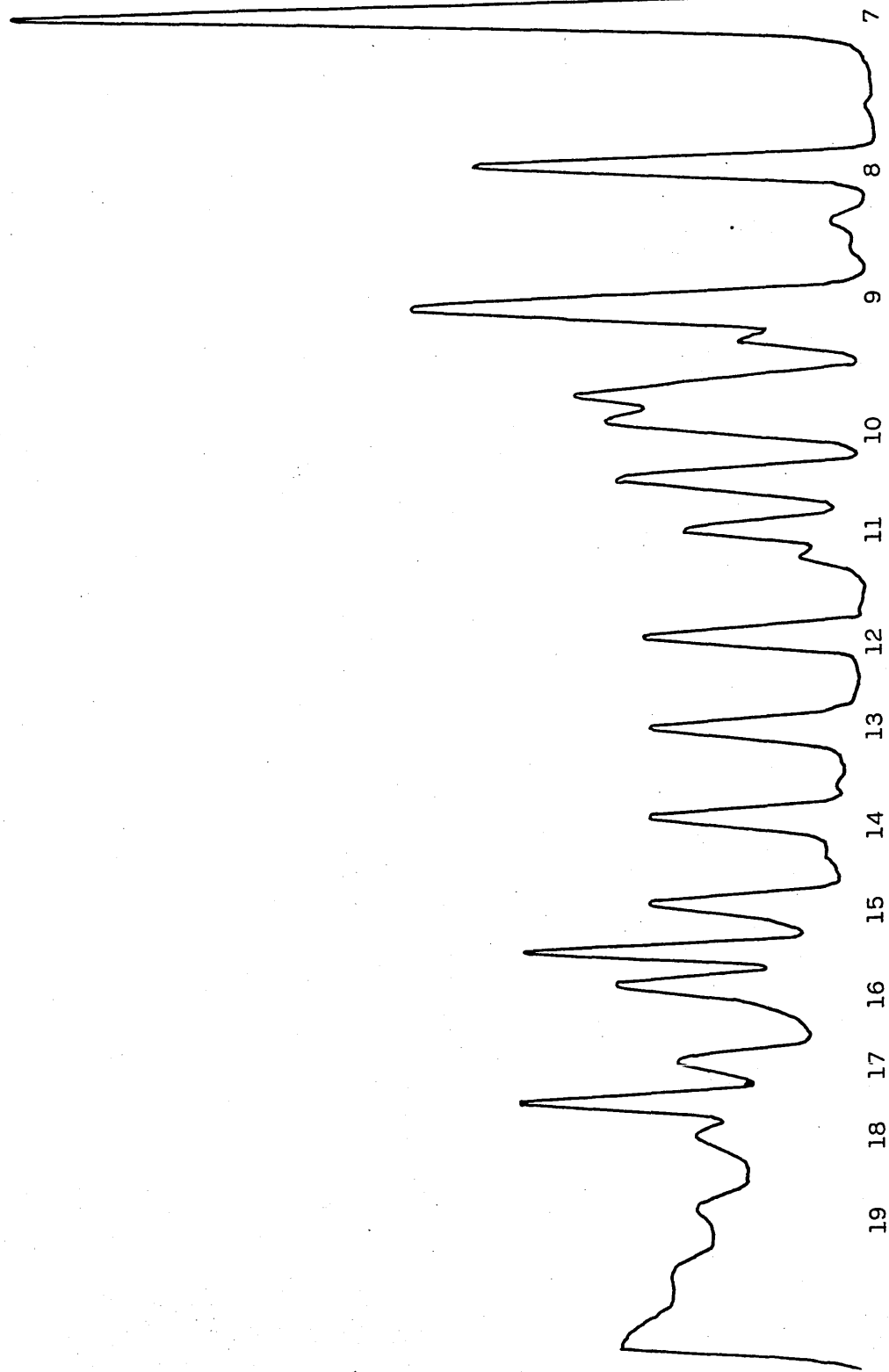
Consider the chromatogram of the 75 Mrad sample (Fig.4.24). It is clear that this is different from the chromatogram of the sample irradiated at 1.03 Mrads, in several respects. The previously "unknown peaks" in the low molecular weight range (less than the hexamer) have disappeared, whilst certain of the "unknown peaks" around  $D_7 - D_{11}$  have increased. Also, there are additional new peaks present.

It is clear that the absorption of a large amount of radiation results in a reduction of the amounts of low molecular weight unknown oligomers present, and increases the amounts of unknown species in the  $D_7 - D_{11}$  range. It would seem that increased absorption leads to further coupling of the low molecular weight oligomers leading to a range of compounds that have retention distances in the  $D_7 - D_{11}$  range.

One interesting point is the appearance of a very prominent new peak between  $D_{15} - D_{16}$ , which must be due to a radiation induced coupling reaction. This may have been brought about through reaction of the low molecular weight unknowns with themselves or with a cyclic oligomer possibly the  $D_{11}$  oligomer.

These results obtained from the GLC analysis of the sol fractions of irradiated samples show very clearly that  $\gamma$ -irradiation cannot be simply explained as a crosslinking and/or chain scission reaction. One fact is certain from this evidence, that reactions amongst the non-crosslinked species, be they linear or cyclic, take place even after the maximum gel is formed.

Fig.4.24 GLC trace of a sample extracted from irradiated polydimethylsiloxane (75 Mrads).



RADIATION STUDIES II

POLYMER BLENDS AND BLOCK COPOLYMERS

Polydimethylsiloxane was found to be susceptible to a radiation induced crosslinking reaction. The overall effect being the formation of a 3-dimensional gel network. The main aim of this work is to investigate the effect of incorporating a radiation resistant component into the polydimethylsiloxane. Polystyrene has been chosen as the second component, for production of blends or block copolymers with polydimethylsiloxane. Although theoretical considerations predict complete immiscibility for these components, from the thermal analysis of such blends and block copolymers, it was concluded that a small degree of miscibility does exist. It was suggested that this phenomena may occur in either of the following ways:

- a) a small degree of miscibility at the  
interphase region;
- b) limited intermixing of polymer chains  
within each phase boundary.

A number of blends were prepared using polystyrene with a molecular weight of 100,000 as described in Chapter 2. The samples were sealed and irradiated using exactly the same procedure as for the polydimethylsiloxane, and the analysis of the irradiated blends was carried out using the techniques of soxhlet extraction, swelling tests, a differential scanning calorimetry, and morphological studies by scanning electron microscopy. Results are discussed in this chapter, as well as those from limited study of the prepared block copolymers.

It is appropriate, however that results from the irradiation of polystyrene can be considered prior to those of the blends and block copolymers.

### 5.1 Radiation Behaviour of Polystyrene

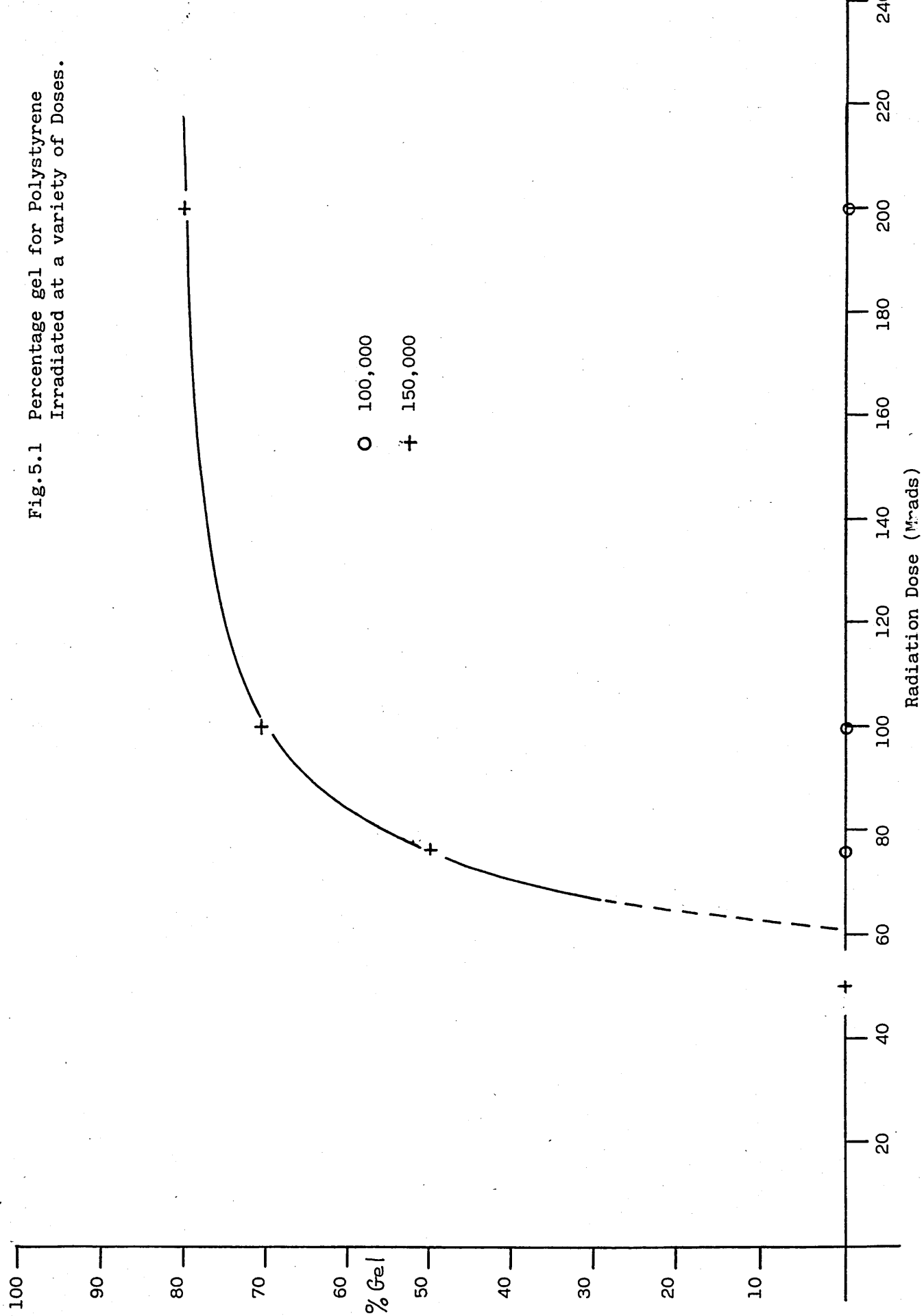
Two samples of polystyrene of different molecular weights (100,000 and 150,000) were irradiated and the G (crosslinking) value, determined for polystyrene. The results are given in Table 5.1 and Fig.5.1.

Table 5.1 Solubility data for Irradiated Polystyrene

Dose/Mrad	Percentage Gel	
	100,000 gmol <sup>-1</sup>	150,000 gmol <sup>-1</sup>
10	0	0
20	0	0
30	0	0
50	0	0
75	0	51.0 $\pm$ 0.5
100	0	73.0 $\pm$ 1.0
200	0	80.2 $\pm$ 0.6



Fig.5.1 Percentage gel for Polystyrene  
Irradiated at a variety of Doses.



It is seen that a 50% increase in molecular weight resulted in a much lower dose being required for the onset of gelation. This trend is expected; the gelation dose being inversely proportional to the molecular weight of the polystyrene chain. Extrapolation of the data (Fig.5.1) indicates a dose of 56-62 Mrads for rgel. Comparison of the gelation dose for polystyrene with polydimethylsiloxane of a similar molecular weight (using Fig.4.4) reveals that the siloxane undergoes gelation around 1.3 Mrads as compared to  $60 \pm 5$  Mrad for the polystyrene. This clearly emphasises the radiation resistance of the polystyrene.

Calculation of the crosslinking efficiency ( $G(x)$ ) gives a mean value of 0.028, which is in good agreement with reported results.<sup>5,40,42,222</sup> By simple comparison of  $G(x)$  values, it is seen that polydimethylsiloxane is 100 times more efficient in producing a crosslinking than polystyrene. Polydimethylsiloxane is a material in great demand because of its many technical features; however, it is far too efficient in terms of crosslink production. It is this property that needs to be reduced; it is essential that polydimethylsiloxane becomes more efficient in dissipating energy without the cleavage of a covalent bond.

The lower molecular weight polystyrene was the sample chosen for the second component, since in the dose range studied (up to 200 Mrads) it remains completely soluble. Thus, in subsequent irradiation studies it was anticipated that, within the blend, the polydimethylsiloxane would be the only species involved in any degree of crosslinking.

## 5.2 Solubility Study of Irradiated Blends

### using Soxhlet Extraction

#### 5.2.1 High Dose Irradiation

The first batch of blends that was irradiated contained 1-15% w/w polystyrene. From the published data on polystyrene and siloxanes with phenyl substituents, a range of irradiation doses were selected. With no directly comparable data available, the assumption was made that as the percentage polystyrene increases, then the resistance to crosslinking would increase. The results are presented in Table 5.2 and Fig.5.2.

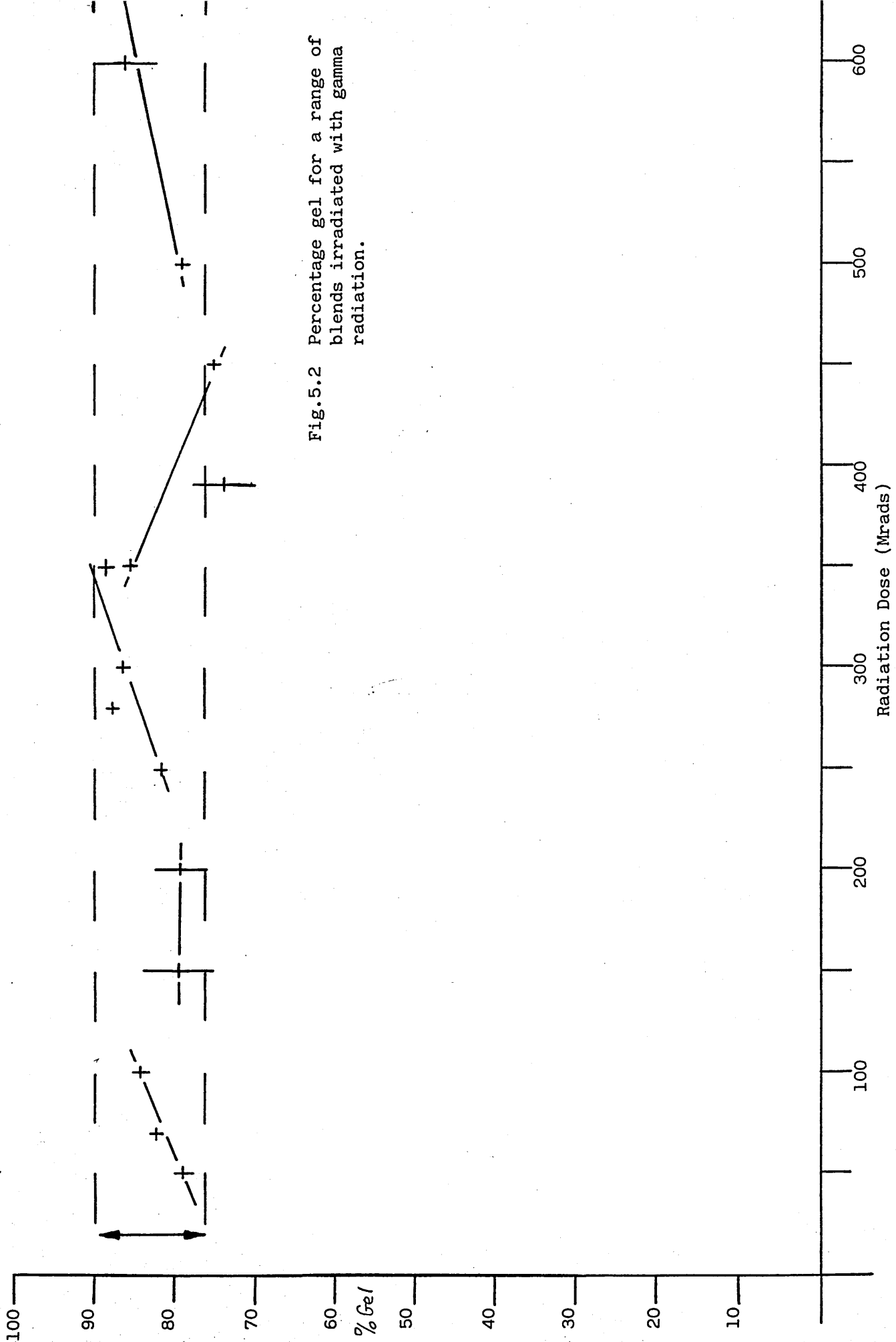
It is clear that the dose range investigated was far too high to observe a gradual increase in the percentage gel, which would have allowed the gelation dose to be determined. The experimental data, falls in the "plateau" region of the % gel vs dose plot. It is obvious that the "protective action" of the polystyrene was over anticipated, clearly a lower dose range needed to be investigated.

The gel content in each of these blends gives a value very similar to that of pure polydimethylsiloxane after a dose of only 10 Mrads. It would appear that even with a large increase in dose, no increase in crosslinking is observed and some 15-17% remains as a sol fraction. This would seem to confirm the view that this sol fraction is due to chain scission occurring simultaneously with the crosslinking reaction.

Table 5.2 Solubility Data for Polydimethylsiloxane-

Polystyrene Blends

% Polystyrene	Dose (Mrads)	% Gel
1	50	78.0 $\pm$ 2.0
	70	80.9 $\pm$ 1.0
	100	83.4 $\pm$ 2.0
3	150	78.8 $\pm$ 3.5
	200	77 $\pm$ 3
5	250	81.5 $\pm$ 0.5
	280	88.5 $\pm$ 1.0
	300	86.0 $\pm$ 0.5
	350	89.0 $\pm$ 1.0
7	350	85.7 $\pm$ 1.0
	390	73.4 $\pm$ 3.0
	450	74.2 $\pm$ 1.0
11	500	79.5 $\pm$ 0.5
	600	86.5 $\pm$ 3.0
	650	86.5 $\pm$ 1.0
15	800	77.2 $\pm$ 1.0
	900	82.0 $\pm$ 0.5



### 5.2.2 Low Dose Irradiation

A range of blends were subsequently irradiated at a much lower dose range, so that the dose for incipient gelation could be determined. The results are given in Table 5.3 and Fig.5.3 and 5.4. The data is also expressed as the percentage gel obtained from each blend for a constant radiation dose (Fig.5.5 a-f).

The Charlesby-Pinner relationship is used in Table 5.4 and selected data is illustrated in Fig.5.6. The gelation dose ( $r_{gel}$ ) has been obtained by extrapolation of curves in Fig.5.3 and 5.4, and by calculation of the gradient in the plot from the Charlesby-Pinner relationship (Fig.5.6). Gelation results are given in Table 5.5.

Table 5.3 Solubility Data for Irradiated Polydimethylsiloxane-

Polystyrene Blends

% Polystyrene in Blend	% Gel							
		Radiation			Dose/Mrads			
	0.5	1.00	1.55	3.28	4.7	8.06	10	20
0	23.2 +0.6	63.6 +2.0	(74.6 + 0.8)	(81.1 + 1.5)	(81.9 + 1.5)		83.5 +1.5	84.0 +1.0
3	0	0	49.5	77.8 +0.1	81.4 +0.8	81.6 +2.0	-	-
5	0	0	57.2 +2.0	74.7 +2.0	85.2 +0.1	85.3 +0.1	-	-
7	0	41.6 +3.0	82.1 +2.1	88.9	88.4	96.4	-	-
10	0	8.0 +2.0	61.1 +0.4	81.2 +0.6	94.5	88.7 +2.0	-	-
15	0	6.6	58.5 +3.0	68.4 +0.4	72.6 +0.2	71.6 +1.0	81.5 +0.2	-
20	0	50.6 +2.5	63.0 +0.3	72.8 +0.2	76.3	—	78.5 +2.0	-
25	0	0	30.1 +3.0	61.3 +1.5	61.4 +1.5	64.8 +1.7	69.7 +2.0	-
30	-	2.4	22.6 +4.0	49.1 +0.7	54.2 +2.5	51.6 +2.0	62.0 +2.0	65.5 +0.6
50	-	0	0	20.5 +3.0	30.9 +0.5	30.6 +1.0	41.6 +1.2	35.5 +0.2

Table 5.4 Solubility Data from Irradiated Polydimethylsiloxane-

Polystyrene Blends expressed in the form of the

Charlesby-Pinner Relationship

Dose/Mrad	1/Dose Mrad <sup>-1</sup>	Gel	Sol	$\sqrt{\text{Sol}}$	Sol + $\sqrt{\text{Sol}}$
3% Polystyrene					
0.5	2.0	0	1.0	1.0	
1.0	1.0	0	1.0	1.0	
1.55	0.645	0.495	0.505	0.7106	1.2156
3.28	0.305	0.778	0.222	0.471	0.693
4.7	0.213	0.814	0.186	0.431	0.617
8.06	0.124	0.816	0.184	0.429	0.613
5% Polystyrene					
0.5	2.0	0	1.0	1.0	2.0
1.0	1.0	0	1.0	1.0	2.0
1.55	0.645	0.572	0.428	0.654	1.082
3.28	0.305	0.747	0.253	0.503	0.756
4.7	0.213	0.852	0.148	0.385	0.533
8.06	0.124	0.853	0.147	0.383	0.530
7% Polystyrene					
0.5	2.0	0	1.0	1.0	2.0
1.0	1.0	0.416	0.584	0.764	1.348
1.55	0.645	0.821	0.179	0.423	0.602
3.28	0.305	0.889	0.111	0.333	0.444
4.7	0.213	0.884	0.116	0.340	0.457
8.06	0.124	0.964	0.036	0.190	0.226
10% Polystyrene					
0.5	2.0	0	1.0	1.0	2.0
1.0	1.0	0.08	0.92	0.959	1.879
1.55	0.645	0.611	0.389	0.624	1.013
3.28	0.305	0.812	0.188	0.434	0.622
4.7	0.213	0.945	0.055	0.235	0.290
8.06	0.124	0.887	0.113	0.336	0.449



Table 5.4 (contd.)

Dose/Mrad	1/Dose Mrad <sup>-1</sup>	Gel	Sol	$\sqrt{\text{Sol}}$	Sol + $\sqrt{\text{Sol}}$
15% Polystyrene					
0.5	2.0	0	1.000	1.000	2.000
1.0	1.0	0.066	0.934	0.966	1.900
1.55	0.645	0.585	0.415	0.644	1.059
3.28	0.305	0.684	0.316	0.562	0.878
4.7	0.213	0.726	0.274	0.523	0.798
8.06	0.124	0.716	0.284	0.533	0.817
10.0	0.100	0.815	0.185	0.530	0.615
25% Polystyrene					
0.5	2.0	0	1.000	1.000	2.00
1.0	1.0	0	1.000	1.000	2.00
1.55	0.645	0.301	0.699	0.836	1.535
3.28	0.305	0.613	0.387	0.622	1.009
4.7	0.213	0.614	0.386	0.621	1.007
8.06	0.124	0.648	0.352	0.593	0.945
10.0	0.10	0.697	0.303	0.550	0.853
30% Polystyrene					
1.0	1.0	0	1.000	1.000	2.000
1.55	0.645	0.226	0.774	0.879	1.654
3.28	0.305	0.491	0.509	0.713	1.222
4.7	0.213	0.541	0.459	0.677	1.136
8.06	0.124	0.516	0.484	0.696	1.179
10.0	0.100	0.620	0.380	0.616	0.996
50% Polystyrene					
1.0	1.0	0	1.000	1.000	2.000
1.55	0.645	0	1.000	1.000	2.000
3.28	0.305	0.205	0.795	0.892	1.687
4.7	0.213	0.309	0.691	0.831	1.522
8.06	0.124	0.306	0.694	0.833	1.527
10.0	0.100	0.416	0.584	0.764	1.348

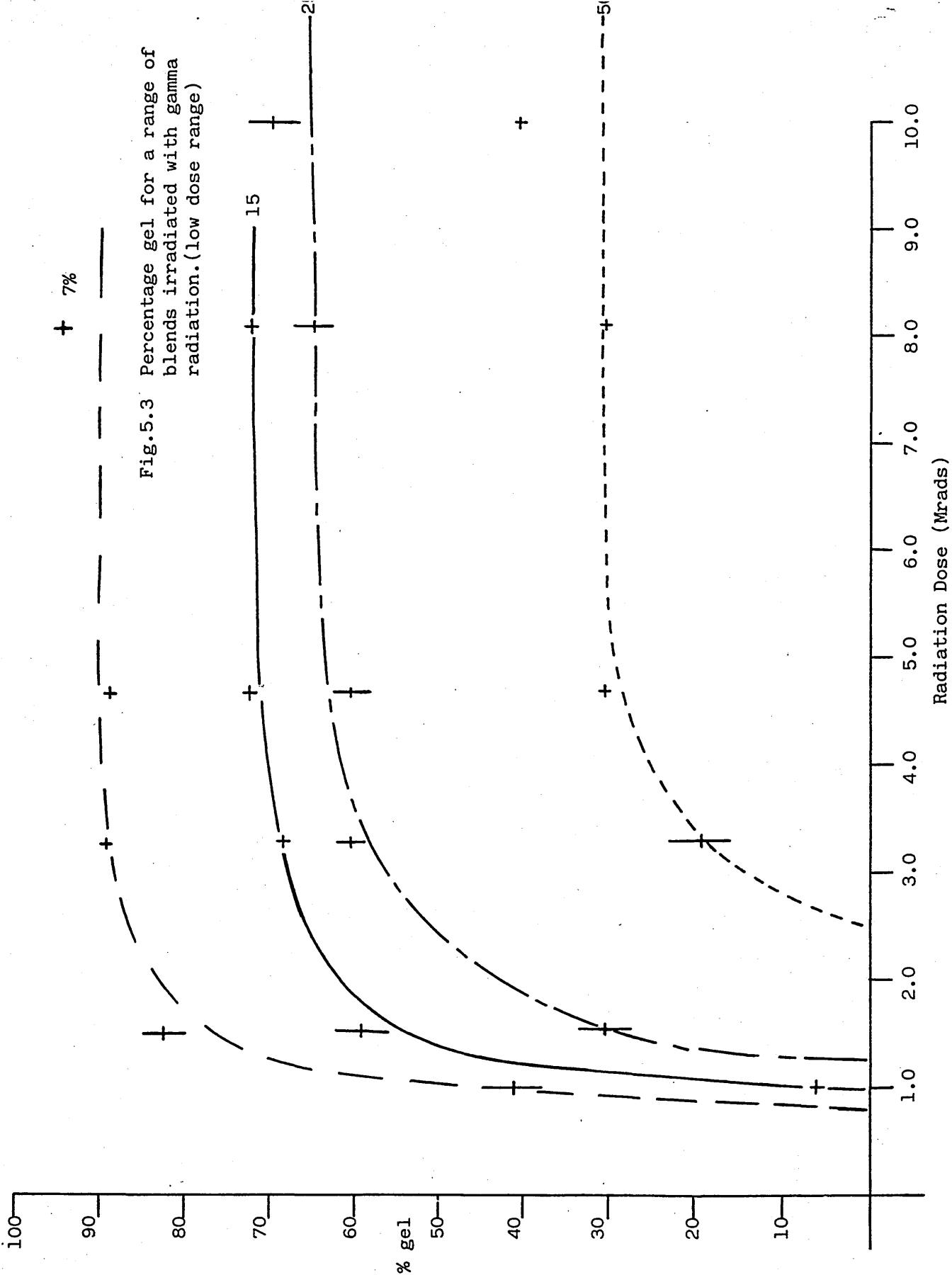


Fig.5.4 Percentage gel for an irradiated  
3% Polystyrene Blend.

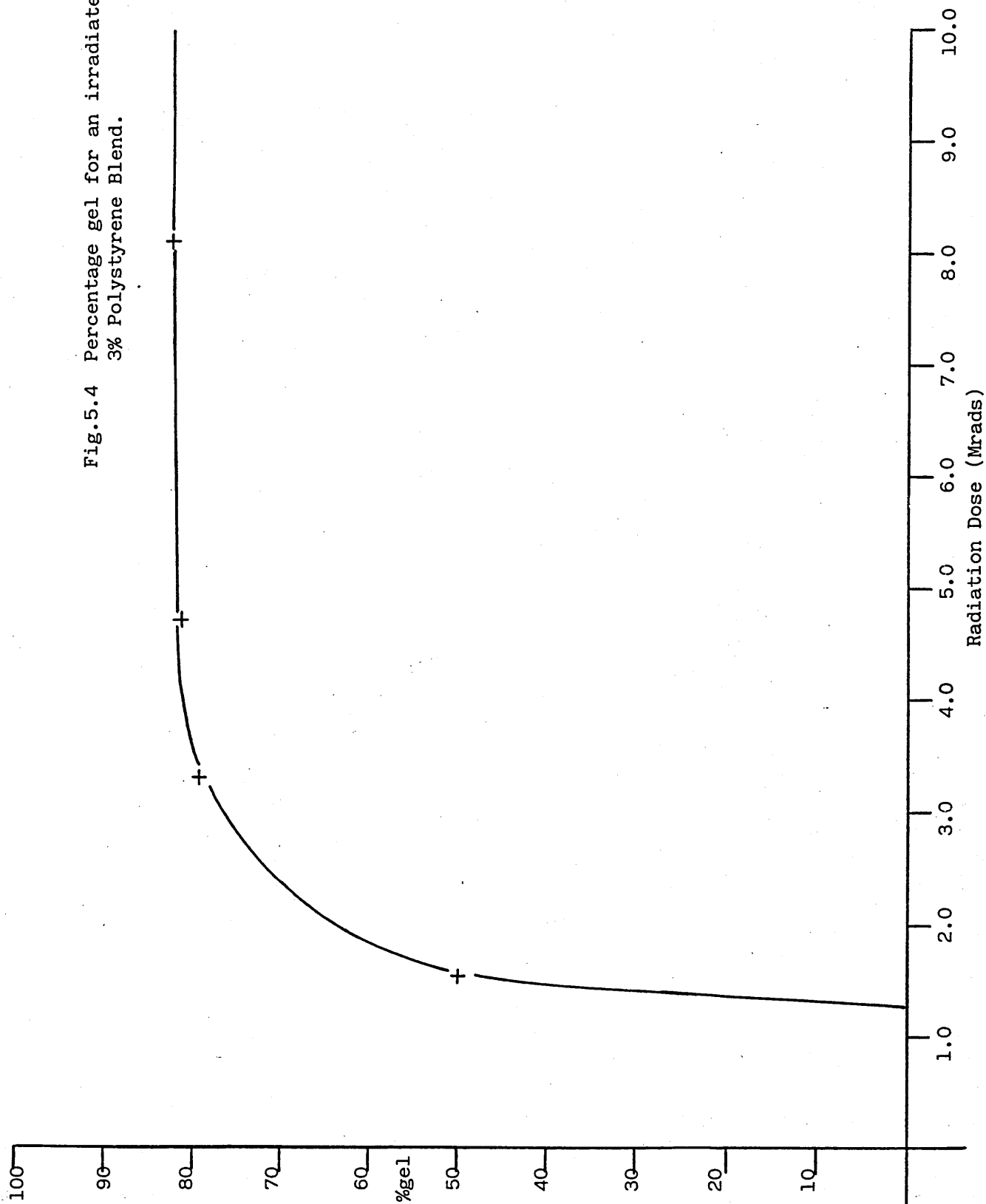


Fig.5.5a Percentage gel for a range of blends irradiated at 1 Mrad.

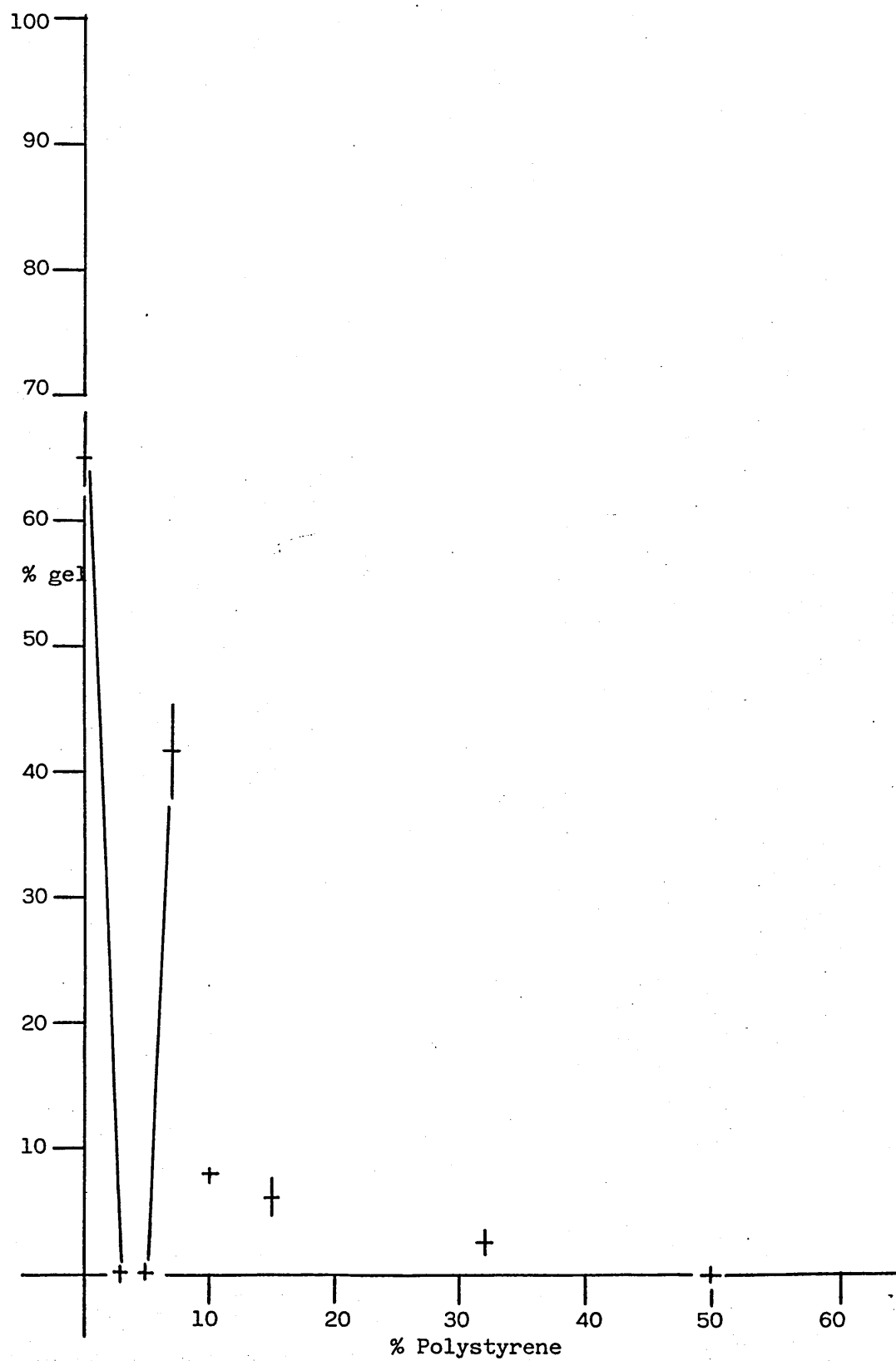


Fig.5.5b Percentage gel for a range of blends irradiated at 1.55 Mrads.

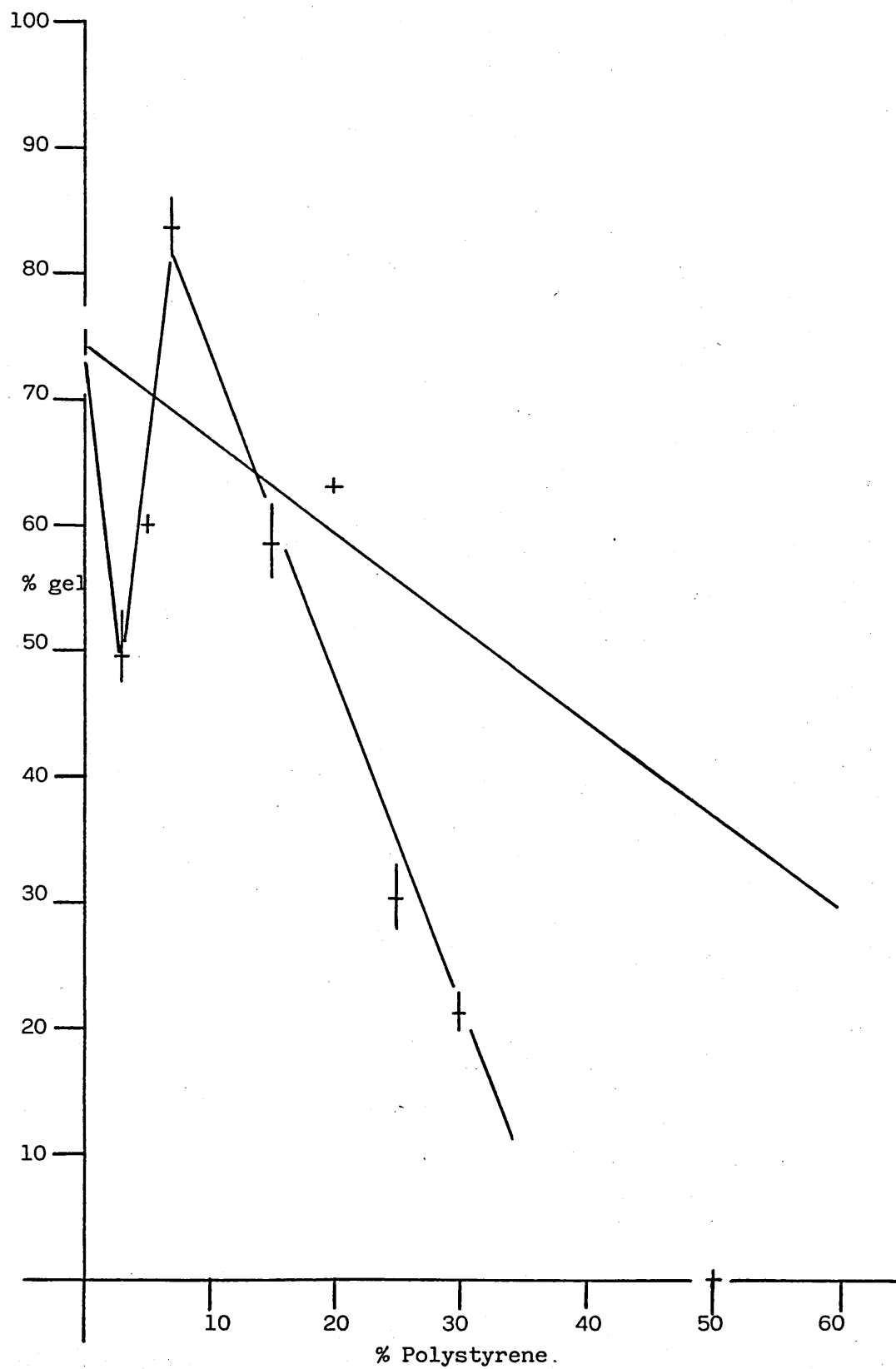


Fig.5.5c Percentage gel for a range of blends irradiated at 1.55 Mrads (expanded percentage gel).

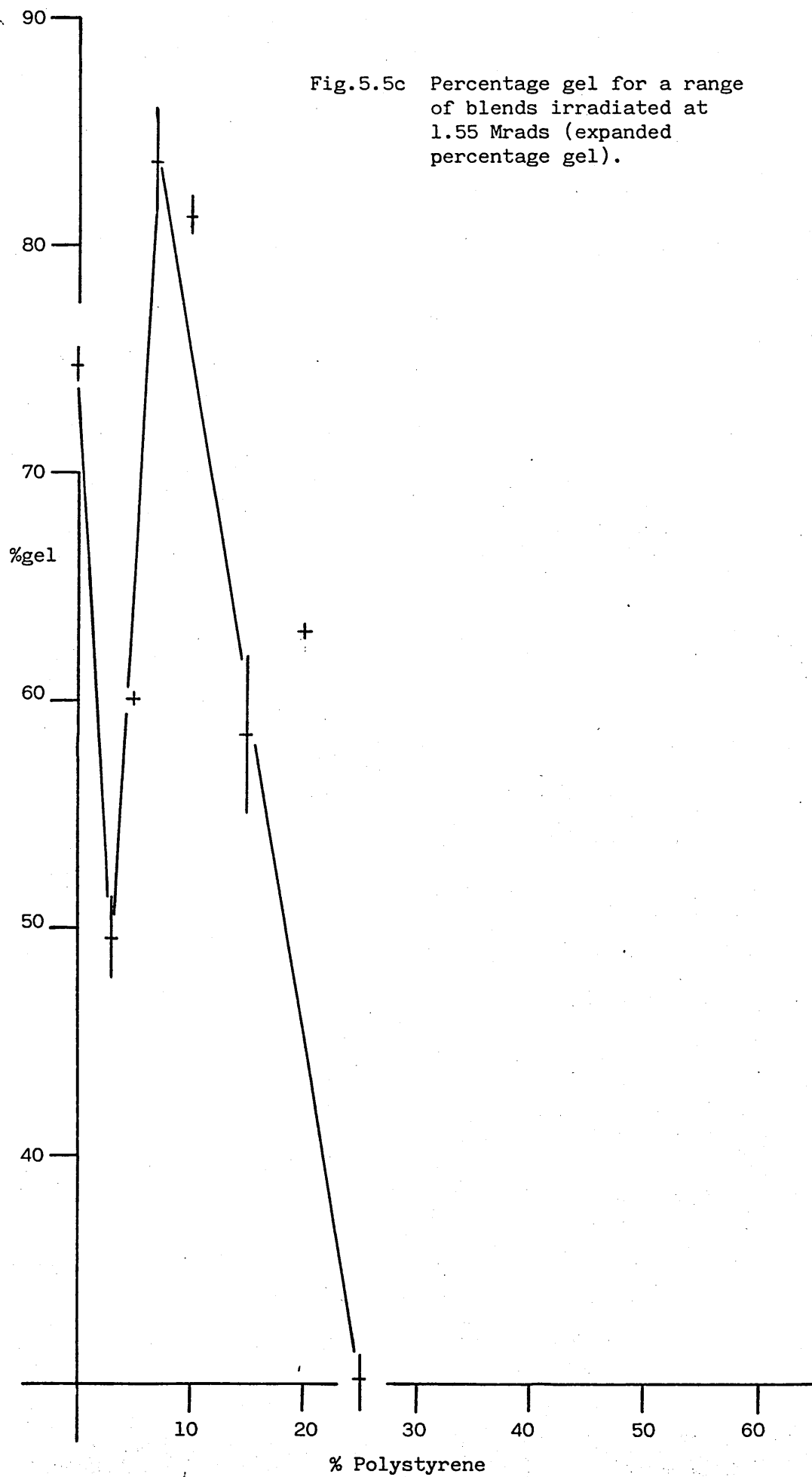


Fig.5.5d Percentage gel for a range of blends irradiated at 3.28 Mrads.

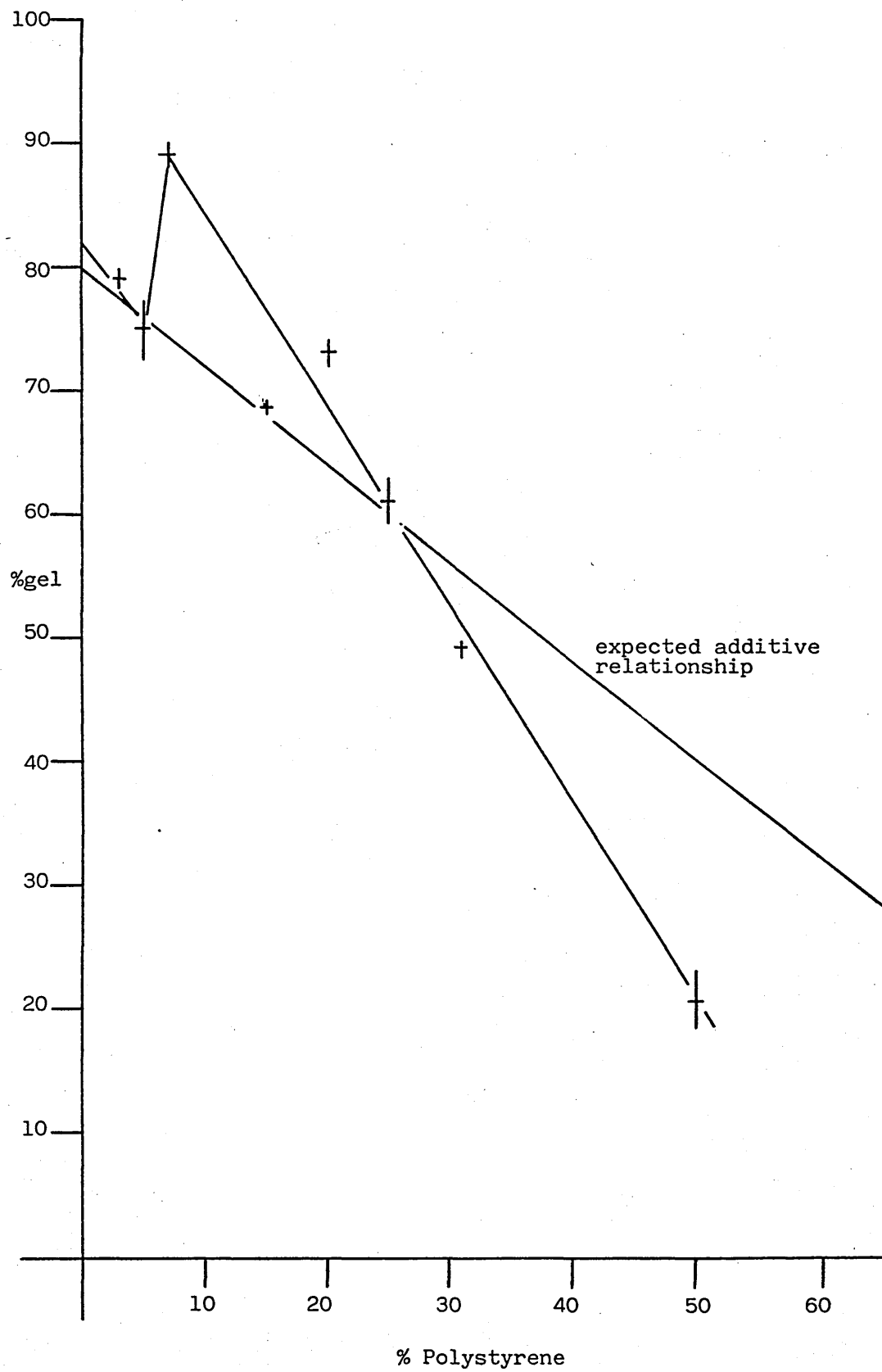


Fig.5.5e Percentage gel for a range of blends irradiated at 4.70 Mrads.

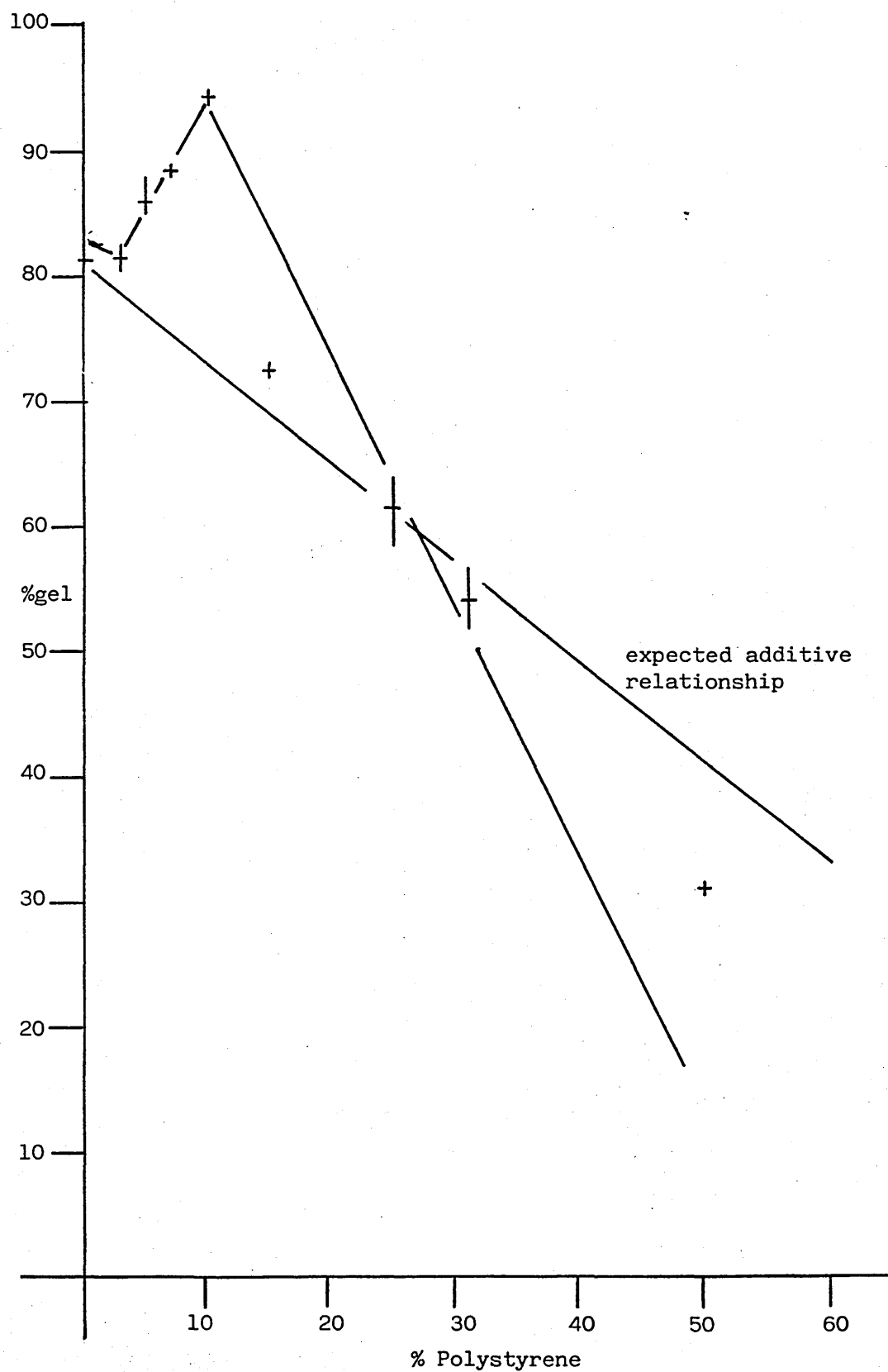
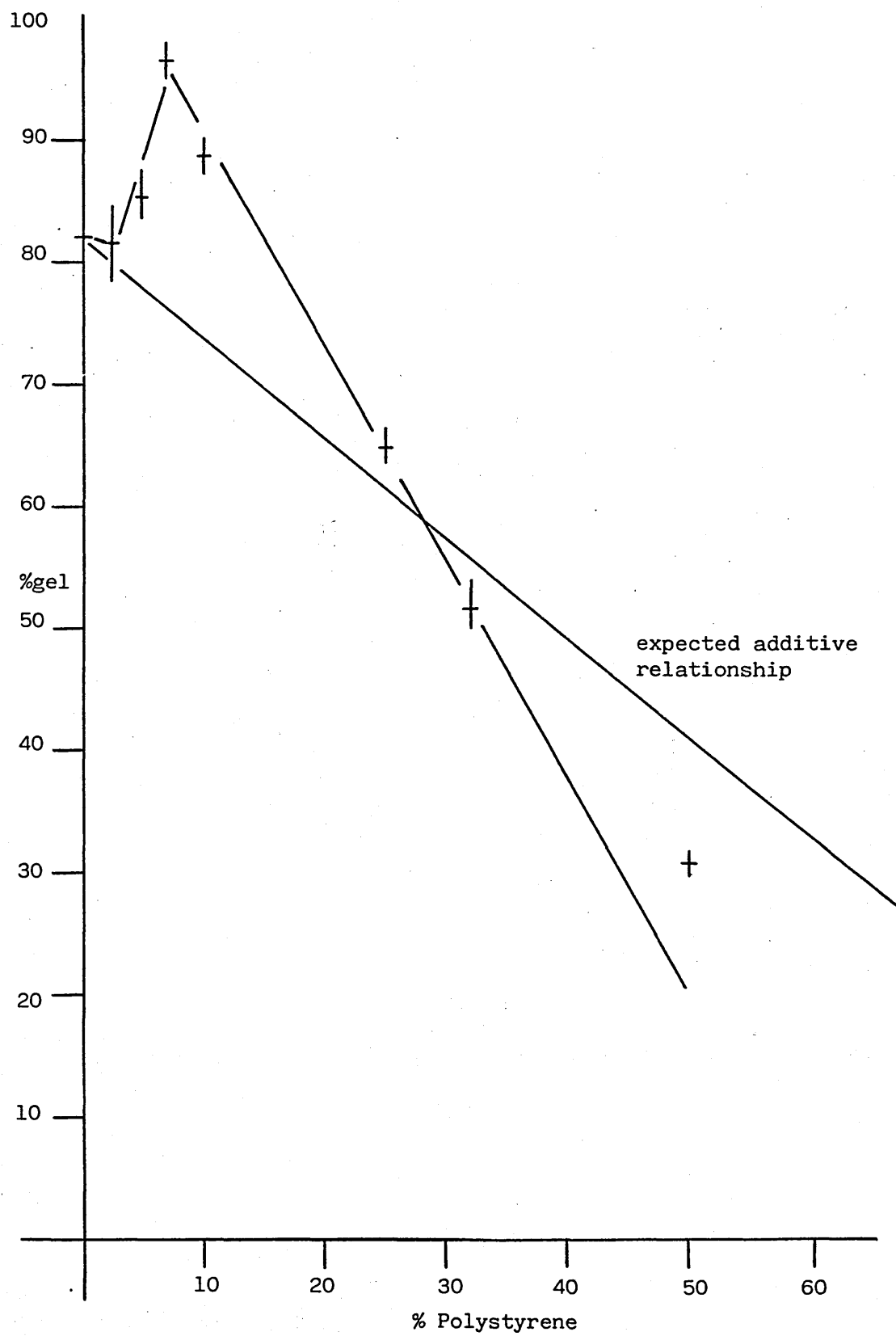
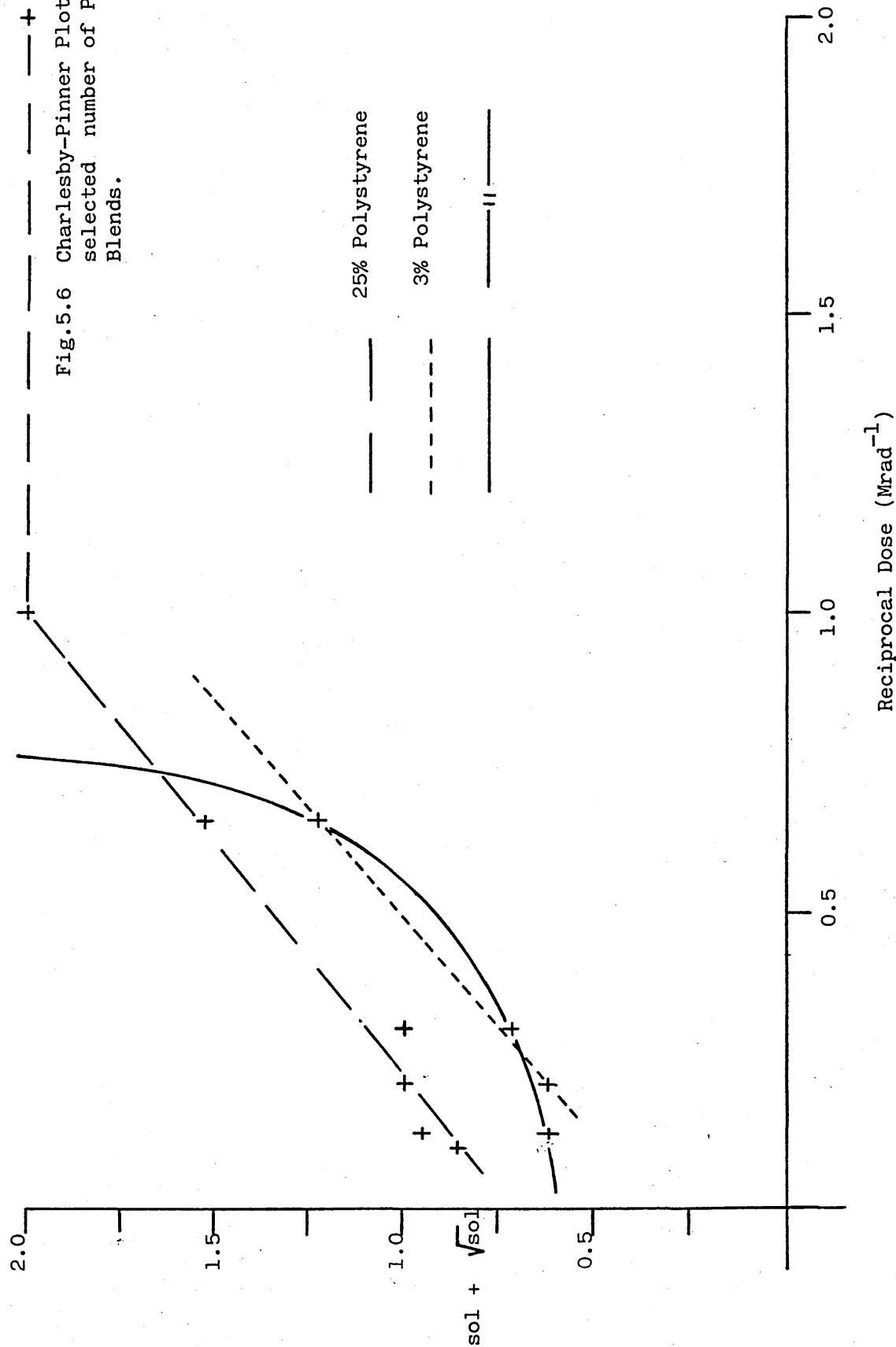




Fig.5.5f Percentage gel for a range of blends irradiated at 8.06 Mrads.





### 5.2.3 Discussion

The results obtained from the extraction of these two component system assume that:

- i) in the mixing of polymeric components, no chemical bonds have been formed between chains, hence the initial molecular weight of the siloxane is unchanged;
- ii) in the dose range investigated, it is only the polydimethylsiloxane that is involved in the crosslinking reaction;
- iii) all the polydimethylsiloxane chains which are not part of the gel network are removed on extraction.

In the Figs. 5.3 and 5.4, it is observed that there is a variation in the value of incipient gelation ( $r_{gel}$ ) for each blend sample. With increased styrene content the gelation dose appears to reach a minimum, then subsequently increases. This relationship is tabulated in Table 5.5. It is clear that the 3% w/w styrene blend requires the highest dose to bring about the onset of gelation; a value significantly higher than that required by pure polydimethylsiloxane. Also the gelation dose for the 3% w/w blend is higher than that for blends containing a larger amount of the radiation resistant component.

The data also reveals that the maximum % gel obtained from the blends decreases with a larger styrene content. This supports one of the above assumptions; that it is only the siloxane that is taking part in any interchain crosslinking reaction. With each successive increase in the styrene content, there will be less polydimethylsiloxane available to become part of the gel.

Table 5.5 Gelation values for Polystyrene-Polydimethylsiloxane Blends

% Polystyrene in Blend	Gelation Dose (Mrad)
0	0.30
3	1.30 - 1.40
5	1.0 - 1.1
7	0.75
15	0.95 - 1.0
20	0.65 - 0.75
25	1.25 - 1.3
50	2.5

Consideration of the gelation doses obtained by the Charlesby-Pinner relationship shows that they are not only different from the extrapolated values but in error. For the 25% w/w styrene blend, the gradient of the data gives a gelation dose of 0.38 Mrads, yet after a 1 Mrad dose the sample was completely soluble. The same is true for the 3% w/w styrene blend, where the gelation dose was calculated to be 0.68 Mrads, yet there is total extraction of a sample which had absorbed 1 Mrad.

It would appear that the polystyrene-polydimethylsiloxane blend system does not fulfil the specific requirements for use of the Charlesby-Pinner relationship. The best line through the data points would suggest a curve, rather than a linear relationship. The intersection of such a curve with the line  $S + \sqrt{S} = 2$  can also be used as a prediction for gelation dose, and this gives results which are closer to the experimentally observed results. The polydimethylsiloxane used to prepare the blends is exactly that from which results for pure polydimethylsiloxane were obtained; yet such a gross deviation from the Charlesby-Pinner relationship is observed. This leads to the conclusion that the presence of the polystyrene is interfering with the crosslinking and the chain scission reactions. If the best fit for the data from a 3% w/w blend is a curve, then at  $1/R = 0.8$  (1.25 Mrads), the curve suggests 0% gel, whereas if the Charlesby-Pinner relationship held true a 35% gel would be anticipated. It would appear that the polystyrene is interacting in such a way as to reduce the susceptibility of the polydimethylsiloxane to crosslink formation.

In Figs. 5.5 a-f, the solubility data, at various but constant doses for a number of polystyrene-polydimethylsiloxane blends of varying composition are shown. They all exhibit the same basic features.

At each dose, it is generally observed that an increase in styrene content gives a decrease in the % gel formed. It is also true that, for a particular blend, the amount of gel increases with increase in the absorbed dose.

However there are two departures from what can be termed the "Additive Effect"; one involving blends of low % polystyrene (<5% w/w) and the other in blends containing a much higher amount. The "Additive Effect" is simply the anticipated percentage gel at each dose, based on the amount of polydimethylsiloxane present in the blends. If, at 1.55 Mrads, the pure polydimethylsiloxane gives a 74.5% gel, then the 50% w/w polystyrene blend would be expected to give a gel of approximately 37%; however, no gel is observed.

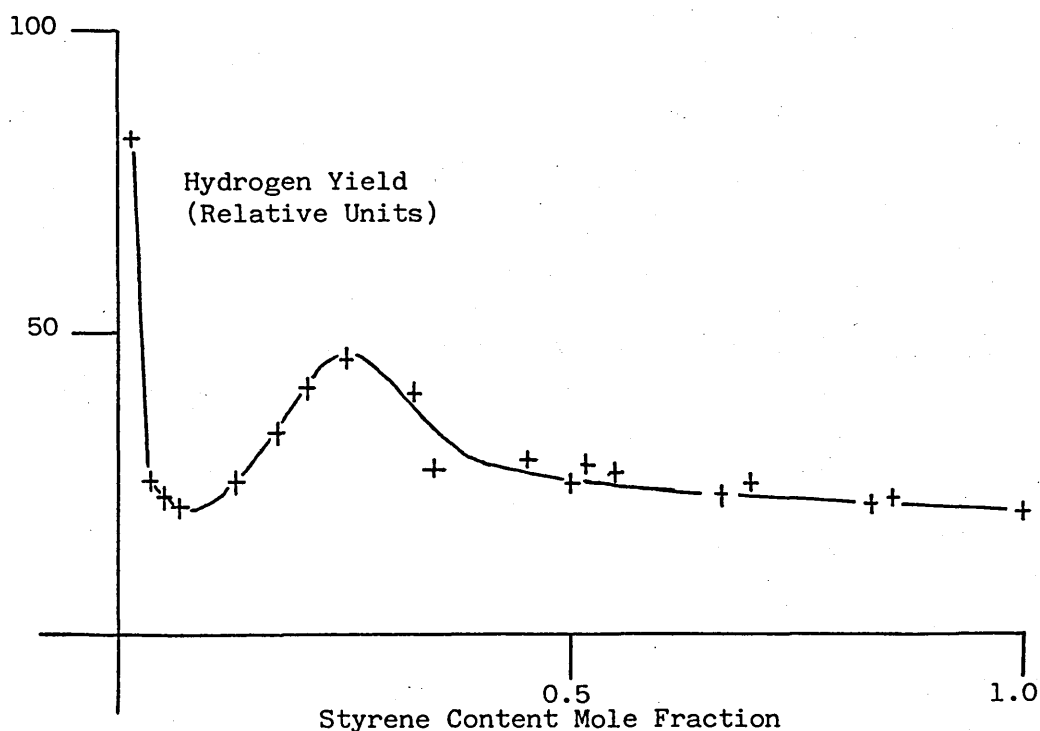
The above example illustrates that the gel produced is very much less than anticipated, which indicates once again that the number of crosslinks is very much reduced by the presence of the polystyrene. With increasing dose (1.55 — 3.28 — 8.0 Mrads) this departure decreases for the 30% w/w and 50% w/w blend, until at 10 Mrads, the % gel is exactly the same as expected by the additive effect. At a low dose absorption, the influence of the polystyrene in the 50% blend is rather marked, yet this influence appears to decrease with an increase in the dose absorbed. The prevention of crosslink formation can operate at low dose, but is reduced as more radiation is absorbed.

It is evident that, for doses up to 4.7 Mrads, the 3% w/w blend gives a % gel very much lower than would be anticipated. Not only is there a departure from additivity, but more importantly, the gel values are inconsistent with the 0, 5 and 7% w/w polystyrene blends. The polystyrene present in the 3% w/w blend clearly has a stronger influence in reducing the degree of crosslinking than in the 5% w/w sample. For a 3% w/w blend to acquire the same amount of gel as the

pure polydimethylsiloxane, it would be necessary to absorb twice the level of  $\gamma$ -radiation, such is the protective effect of the polystyrene. The protective effect decreases with increasing absorbed dose, until at doses of 4.7 Mrads and above it is no longer detected. This would suggest that there is a finite amount of available protection. This protection can only be ascribed to the presence of polystyrene, thus, if more protective species were present, in the appropriate way then a greater degree of protection may be observed.

A similar trend was observed by Weber and Heusinger,<sup>62</sup> when the protective action of styrene in a styrene-acrylonitrile copolymer was investigated (Fig.5.7).

Fig.5.7 Hydrogen yield<sup>a,b</sup> as a function of copolymer composition.<sup>62</sup>



- a. A minimum in the hydrogen yield is equivalent to a minimum percentage gel.
- b. Absorbed dose 31.7 Mrad.

In this case, a departure from additivity was observed throughout the whole blend composition range, but maximum protection was observed when the molar content of styrene in the copolymer was 0.05 (5%). At this value, the hydrogen yield is at a minimum, which is an indication of the reduced number of crosslinks formed. With a decreasing styrene content, the protective action is decreased, the acrylonitrile undergoes crosslinking before the absorbed energy, reaches the dispersed styrene units. No explanation being given as to why an increasing styrene content also decreases the protective effect.

In an earlier study, Witt<sup>59</sup> compared the crosslinking efficiency of styrene-butadiene copolymers with similar blends, to find that the styrene had a greater protecting effect in the copolymers than in the blends. In the blend system the polystyrene was said to act simply as a diluent, with no protective capacity. However, it must be pointed out that the lowest % styrene blend studied, was of the order of 16% w/w styrene. In the results obtained from Weber's study<sup>62</sup> and from this investigation, the protective effect was observed at a relatively low styrene composition.

The polydimethylsiloxane is the component that is the most susceptible to bond cleavage, and thus crosslinking yet the presence of polystyrene reduces the likelihood such a process taking place. The absorbed energy must therefore be diverted or dissipated before bond cleavage can take place. It is known that efficient energy dissipation by polystyrene renders that particular polymer resistant to irradiation. Two mechanisms to explain the protective effect of polystyrene, energy transfer or hydrogen abstraction, can be considered.



Interaction between the 'excited' siloxane units on the polydimethylsiloxane chain, with a nearby polystyrene unit may result in the absorbed energy being transferred to the polystyrene. The pendant aromatic rings of the polystyrene chain, involve electrons in a number of low energy levels. The transferred energy can be used to promote the delocalised electrons to higher energy states. As the electrons return to the ground state, it may be possible to detect the emitted energy as a fluorescence emission.

The protective effect of polystyrene may be similar to that of an 'antirad' or 'radical scavenger'. The aromatic group, can have a stabilising effect on free radicals, which allows it to act as a donor or acceptor of hydrogen radicals. Crosslinking can be explained by a hydrogen abstraction mechanism, as discussed in Chapter 1. The crosslinking in the polydimethylsiloxane will be reduced if the polystyrene acts as an acceptor or donor of radicals.

Whatever mechanism is involved in the protection of the siloxane, they both require an intimate degree of contact between the blend components. As the data indicates, the 3% w/w polystyrene blend provides the maximum protection to polydimethylsiloxane; it can be concluded therefore, that the morphology of this particular composition must be such that the contact between the components is at a maximum.

### 5.3 Swelling Behaviour of Irradiated Blends

A brief study of the swelling behaviour of a number of selected blends revealed some interesting results. A full treatment was not possible since certain pieces of information, needed for the calculations were not accessible. Despite this, the data, which is expressed as the mass of solvent absorbed  $\text{g}^{-1}$  sample, allows meaningful discussion.

#### 5.3.1 Results

Table 5.6 Swelling data for a Selection of Blends

% Polystyrene in Blends	Mass of Solvent absorbed $\text{g}^{-1}$ sample						
	0.5	1.0	Dose (Mrad)		4.7	8.06	10.0
3			11.11	5.12	4.63	3.72	
5			13.25	5.20	4.76	3.94	
7		22.43	7.98	5.94	4.64	3.91	
10		N.S <sup>a</sup>	21.09	9.77	5.13	4.41	
15		N.S <sup>a</sup>	12.43	7.15	5.89	4.79	3.84
20		19.94	12.42	6.77	5.76	4.89	4.03

a - No sample

The swelling data (Table 5.6) is illustrated in Fig. 5.8 and 5.9. Fig.5.8 is virtually the converse of the % gel v's dose plot (Fig.5.4), in that the amount of solvent absorbed  $\text{g}^{-1}$  sample is inversely related to the amount of gel present in the blend sample. Fig.5.9 is similar to Fig.5.5 where the data for each sample is expressed for a constant dose.

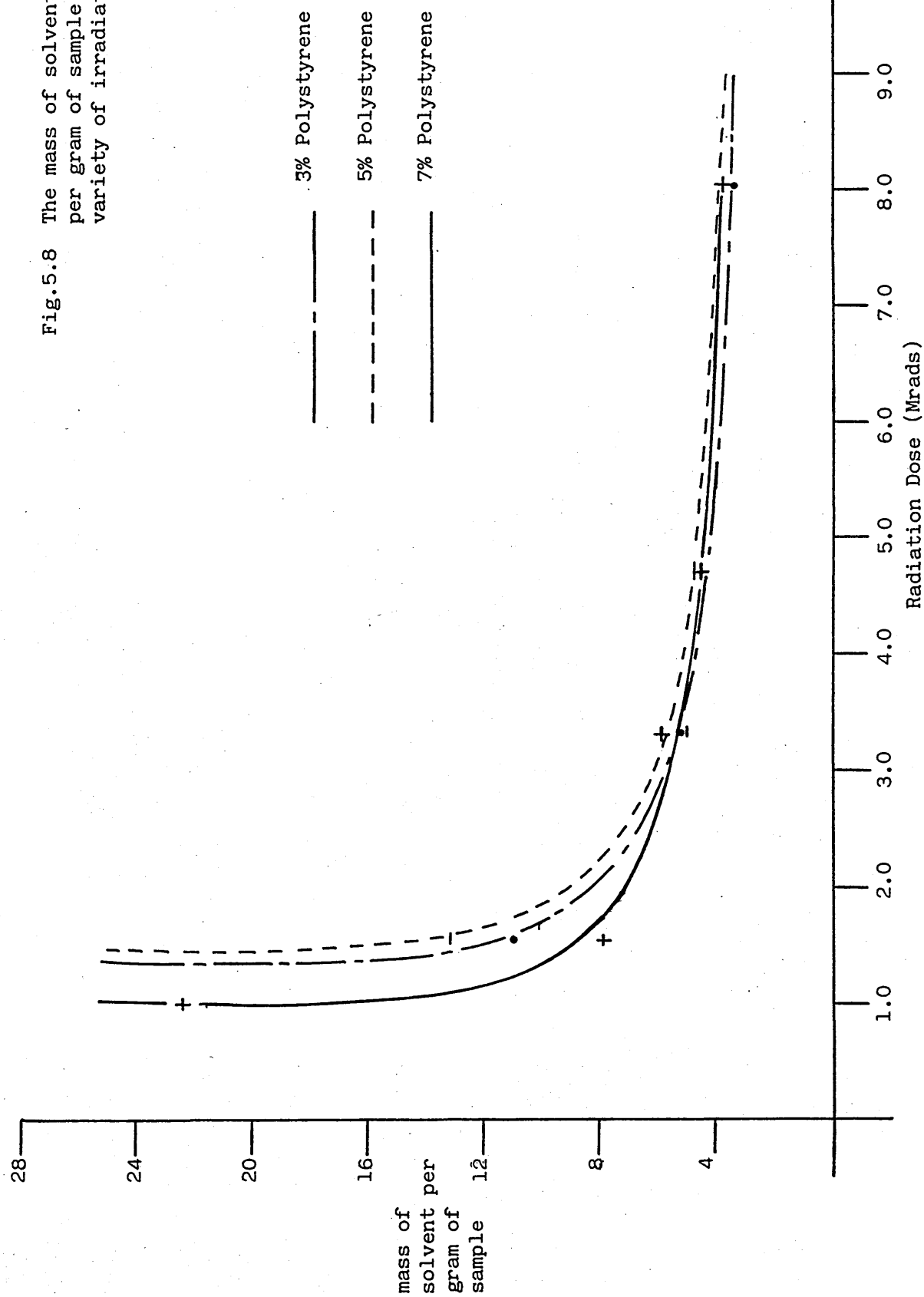
### 5.3.2 Discussion

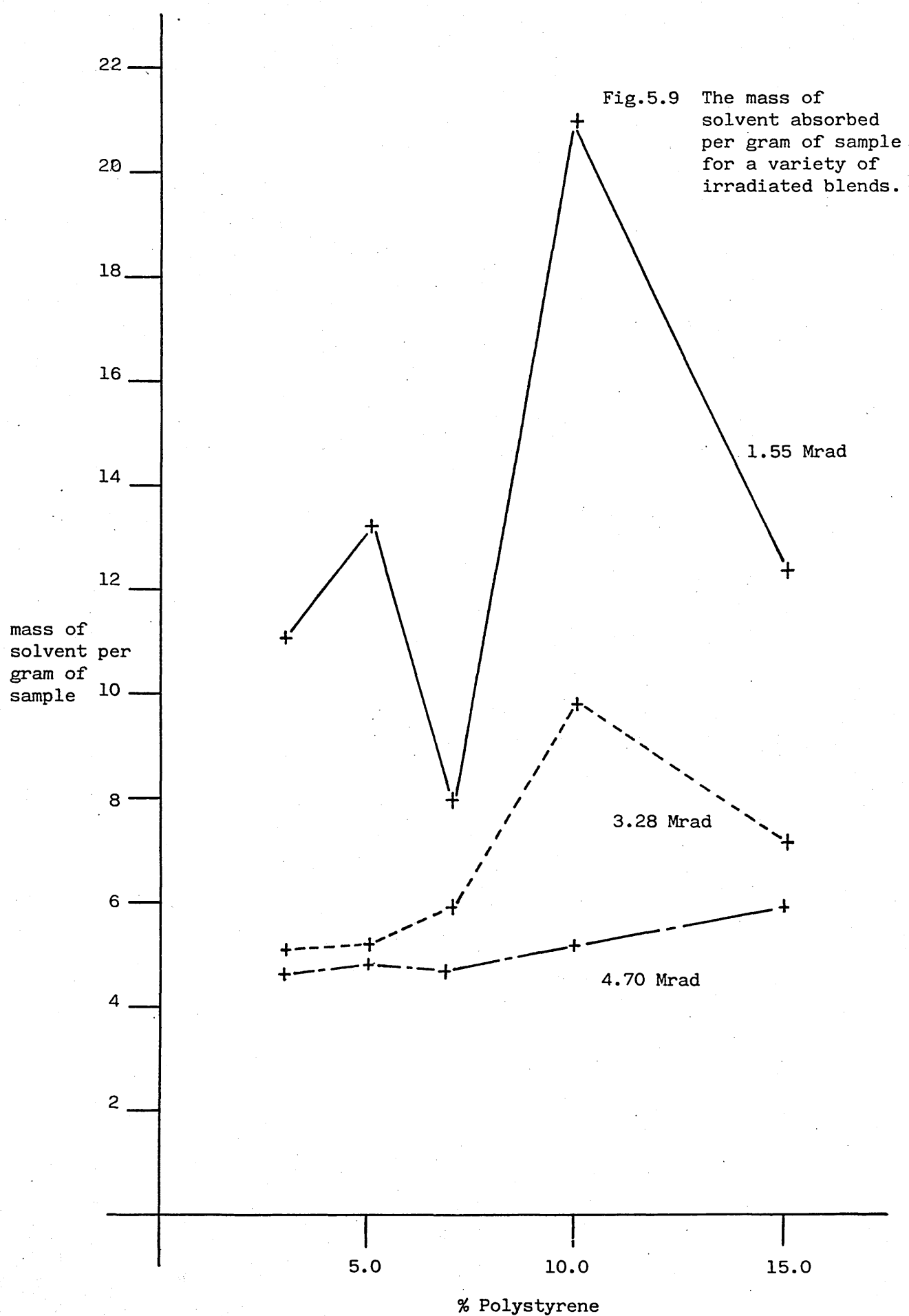
The swelling theory, developed by Flory and Renner, has been applied to many homopolymer systems, crosslinked either by the action of curing agents or the absorption of irradiation. It has been extended for use with tri-block copolymers, such as SBS, where the swelling agent specifically swells the elastomer phase but does not affect the incompatible thermoplastic domains.

Since a polymer blend is simply a physical entanglement of the two immiscible polymers, dissolution of the blend will rapidly occur when it is placed in an appropriate solvent. After irradiation the blend samples absorb solvent to a degree which is dependent on the dose received.

Fig.5.8 clearly indicates that the greater the dose absorbed, the smaller the amount of solvent absorbed. This is a consequence of an increased number of crosslinks introduced into the polymer matrix. We can therefore conclude that a small degree of swelling is indicative of a large number of crosslinks. We can only discuss the data in terms of the mass of solvent absorbed  $g^{-1}$  of sample, i.e. degree of swelling; since the polymer blend interaction parameter at each dose is unknown. However this should not detract from the discussion.

The 7% w/w polystyrene blend at 1.55 Mrad, would seem to support this view. This is a very high gel giving rise to a small degree of swelling. The 3% w/w sample does not follow what would be expected, in that it yields a lower percentage gel than the 5% w/w sample, yet gives rise to a smaller degree of swelling. How can a low percentage gel value be reconciled to a low degree of swelling? With an increased dose, the discrepancy is reduced, but the trend is still observable within the four blend samples. It would therefore appear that the morphology of the 3% w/w sample is an important influence on the introduction of crosslinks into the polymer matrix.





## 5.4 Thermal Analysis of Irradiated Blends

### 5.4.1 Results

A range of blends of differing compositions, irradiated at a fixed dose of 1.03 Mrads, were analysed by the procedure outlined earlier. The results of the thermal analysis are given in Tables 5.7 and 5.8.

### 5.4.2 Discussion

Each of the irradiated blends gives a polydimethylsiloxane glass transition temperature, in the region of  $-116^{\circ}\text{C}$  to  $-118^{\circ}\text{C}$ ; it does not appear to be composition dependent. This value is very much higher than the  $T_g$ , of the unirradiated blend samples, where the incorporation of the polystyrene component has a tendency to increase the transition temperature of the polydimethylsiloxane ( $-123.5^{\circ}\text{C}$ ) by  $1.0^{\circ}\text{C}$ , this being explained as being due to a small degree of miscibility of the two components.

The irradiation of pure polydimethylsiloxane increases the  $T_g$ , from  $-123.5^{\circ}\text{C}$  to  $-102.3^{\circ}\text{C}$  with the absorption of 1 Mrad of radiation. A comparison of the irradiated blends with pure polydimethylsiloxane for the same absorbed dose, indicates that the glass transition of the siloxane component in the blends has not increased by the same degree as the pure polydimethylsiloxane. It is clear that the presence of the polystyrene component, has prevented such a large increase in the glass transition of the polydimethylsiloxane.

With the absorption of radiation, crosslinks are produced within the polymer sample, the consequence of the crosslinking being a marked effect on the thermal properties of the polydimethylsiloxane. With an increase in the number of crosslinks,  $T_g$  was found to increase. It is

Table 5.7 Glass Transition data for a range of

Polydimethylsiloxane-Polystyrene Blends.<sup>a</sup>

% Polystyrene in Blend	T <sub>g</sub> °C	ΔT <sub>g</sub> °C
0	-102.3	5.5
3	-117	11.0
5	-118	10.0
7	Not Detectable	
15	-116	13.0
25	-116	18.0
30	-117	16.0
50	-116	14.0

a. 1.03 Absorption

Table 5.8 Exothermal and Endothermal data for

Polydimethylsiloxane-Polystyrene Blends.<sup>a</sup>

% Polystyrene in Blend	Exothermal		Endothermal	
	JG <sup>-1</sup>	Temperature °C	JG <sup>-1</sup>	Temperature °C
0	Not Present			
3	3.32	-99	29.8	-37.5
5	2.11	-96.8	29.75	-37.0
7	Not Present		27.3	-37.5
15	Not Present		26.95	-38.5
25	Not Present		23.05	-37.5
30	Not Present		20.95	-39
50	Not Present		15.81	-39

a. 1.03 Mrad Absorption

reasonable therefore to conclude that the increase in the glass transition is an indication of an increased crosslink density. Applying this to the results obtained from analysis of the blends, it appears that the presence of polystyrene has had the effect of reducing the number of silicone crosslinks.

When the range over which each glass transition takes place ( $\Delta T_g$ ) is examined, the unirradiated blends tend to show a value of 4-4.5°C, but the irradiated blends give a value which varies from 9-18°C. On the thermogram, the glass transition of the siloxane is no longer observed as a clear, sharp, well defined step, but as smoothed-out profile. The consensus opinion is that a broadening of the glass transition is due to miscibility of the two components within a polymer blend or within a heterogeneous block copolymer. Thus this broadening of the glass transition could be indicative of newly formed linkages between the dispersed polystyrene and the polydimethylsiloxane. Earlier results have suggested that a very limited degree of miscibility exists in the blends on absorption of  $\gamma$ -radiation it would seem that a greatly enhanced miscibility is apparent, as indicated by the increase in  $\Delta T_g$ .

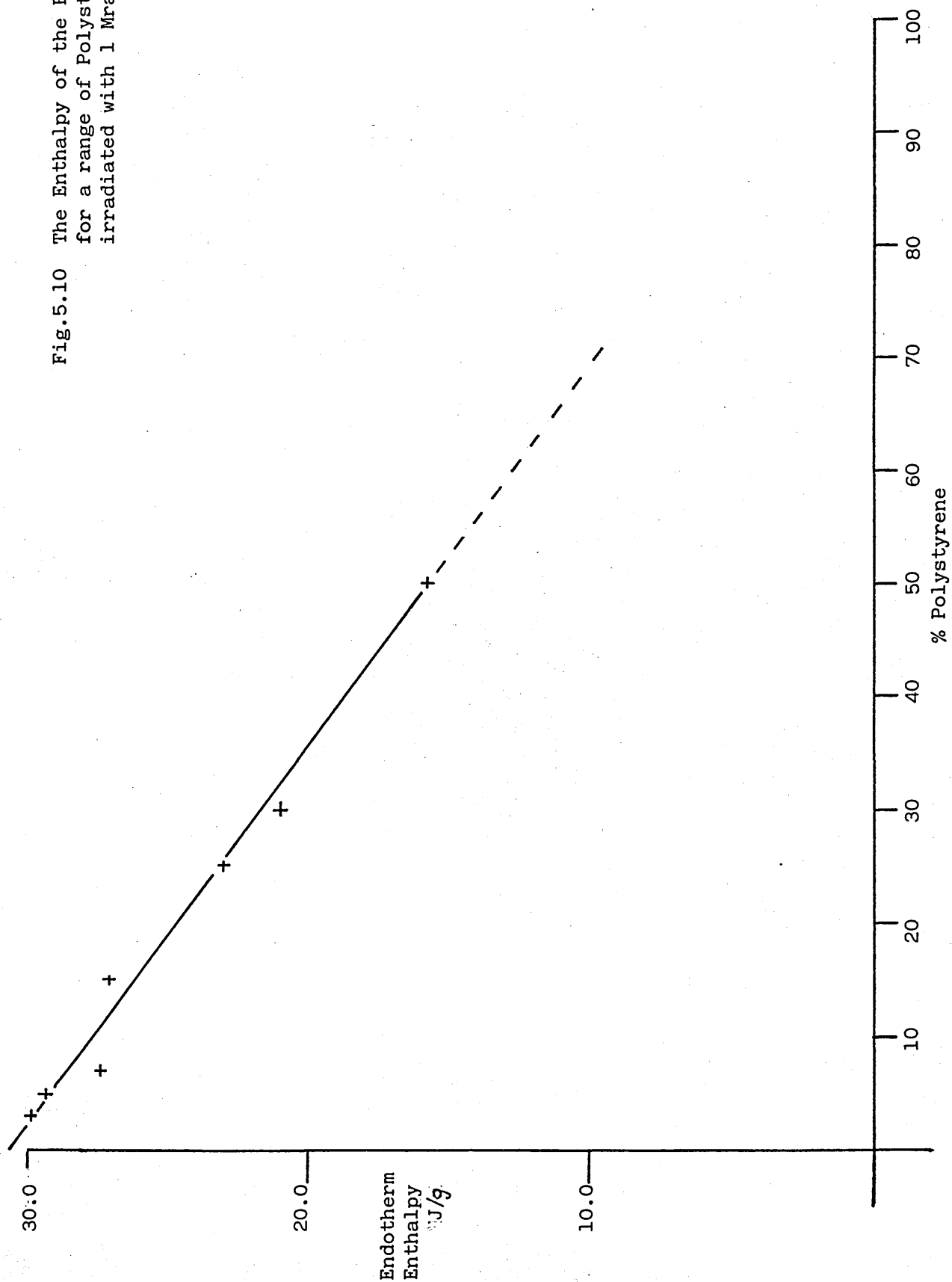
In each of the irradiated blends, the cold crystallisation exotherm of polydimethylsiloxane is a clear well defined peak, appearing at a different temperature to that of the unirradiated pure siloxane. It does not however, appear to be composition dependent. The presence of the polystyrene may have hindered crystal formation, resulting in a lower cold crystallisation temperature. The absorption of radiation by the pure polydimethylsiloxane, reveals that in the dose region correlating to incipient gelation, the cold crystallisation peak disappears (Fig.4.15). For pure siloxane this value is in the region of 0.25 - 0.3 Mrads. The data for the irradiated blends illustrates,



that at 1 Mrad, the peak is still observable, even though the enthalpy involved is only  $3.32 \text{ Jg}^{-1}$ . This would seem to fit with the solubility data, where the 3% w/w blend gave a gelation value of 1.3 Mrads. The exotherm peak would therefore seem to be present, right up to the commencement of gelation. (It would be expected that in the 1.55 Mrad sample the peak would not be present, but this has not been examined.) The existence of the cold crystallisation peak at 1 Mrads, suggests that there is a portion of siloxane remaining in the amorphous phase, after  $T_m$  has taken place. Since these results correlate with the solubility data, the sol fraction of the sample would seem to be this siloxane portion remaining in the amorphous phase. This data leads to the same conclusion as with the glass transition values in that the polystyrene prevents siloxane-siloxane crosslinks from being formed, hence a larger dose is needed to obtain the same level of gelation.

The polydimethylsiloxane endotherm ( $T_m$  peak) appears in each of the irradiated blends, the enthalpy of the transition being composition dependent (Fig.5.10). The enthalpy values are basically the same as those observed in the unirradiated blends. However, there is one difference in the nature of the peaks. In the unirradiated samples, a shoulder is observed at  $-41^\circ\text{C}$  on the main peak, which occurs at  $-38^\circ\text{C}$ . This being common to all the unirradiated blends. This shoulder is not detected in the samples of irradiated blends, but the tip of the main peak appears to be slightly broader. In the unirradiated blend samples the appearance of the shoulder suggests that at least two crystalline forms of polydimethylsiloxane are produced; the  $-41^\circ\text{C}$  form being due to slightly hindered siloxane chains. This particular form would appear not to be produced on the absorption of radiation. However another form may result, as exhibited by the broader peak. It

Fig.5.10 The Enthalpy of the Endotherm  
for a range of Polystyrene Blends  
irradiated with 1 Mrad.



can be concluded that, in the irradiated blends, the polystyrene is hindering crystalline formation, in a slightly different way than in the unirradiated samples. Hence, the nature of the peaks of the endotherm is altered. This effect may be due to a polystyrene-polydimethylsiloxane interaction, that occurs on the absorption of gamma radiation.

## 5.5 Molecular Weight Studies of the Irradiated Blends

### Prior to Gelation.

#### 5.5.1 Results

A brief investigation was conducted to monitor the effect of  $\gamma$ -radiation on the molecular weight of the pure polydimethylsiloxane, and the polydimethylsiloxane in the blend with polystyrene (Table 5.9 and 5.10). Previous studies conducted on these blends have suggested that the 3% w/w polystyrene affords maximum protection against siloxane-siloxane crosslink formation.

#### 5.5.2 Discussion

A limited number of analysis were performed to monitor the behaviour of the molecular weight of the polydimethylsiloxane chains, the above results reveal a number of interesting points. After receiving only 0.01 Mrads radiation, a significant increase in the weight average molecular weight is observed, and with further absorption of radiation the increase continues rather dramatically (Table 5.9). The theoretical limit for this technique is the formation of a 3-dimensional gel network, so the molecular weight could be determined right up to the onset of gelation, where molecular weight immediately prior to gelation would be expected to approach infinity. However,

Table 5.9 Molecular Weight data of Irradiated Pure Polydimethyl-  
siloxane and that from the 3% w/w Polystyrene Blend

Dose (Mrads)	Molecular Weight (Mw)	
	Pure PDMS	PDMS from a 3% Blend
0	552,145	
0.01	604,378	587,806
0.05	639,876	567,980
0.1	935,946	569,666

Table 5.10 Molecular Weight data of the Extracted Sol<sup>a</sup> from a  
series of Polystyrene-Polydimethylsiloxane Blends

% Polystyrene in Blend	Molecular Weight (Mw) of PDMS	
	0.5 Mrad	1.0 Mrad
3	1,199,495	1,466,591
5	1,524,058	1,515,634
10	1,780,608	2,154,191

- a. Each of the above samples was extracted in the normal manner, only the 10% w/w blend, irradiated at 1 Mrad returned any gel.

practical difficulties in the GPC analysis prevents such a determination.

The average molecular weight of the polydimethylsiloxane chains within the 3% w/w blend, which received the same doses of radiation, remained constant (Table 5.9). The incorporation of polystyrene appears to have prevented a large increase in the average molecular weight from taking place, within the dose-range investigated.

The soluble fraction from a number of samples, mainly those with no detectable gel present, which received higher absorbed dose were also analysed by GPC (Table 5.10). There is a very clear relationship between the molecular weight and the increased styrene content for a constant dose irradiation. The larger the concentration of styrene present, the greater the molecular weight. The absorption of radiation, results in the siloxane chains undergoing crosslinking, increasing the average length of the siloxane chain. In the 3% w/w sample the molecular weight is the lowest; indicating that the increase in the length of the siloxane chains is retarded.

It would appear from the molecular weight data that the 10% w/w polystyrene blend, would be the first to give a detectable gel; since this sample shows the largest increase in molecular weight for the absorption of 0.5 or 1.0 Mrads. This is found to be the case. It appears that the 3% w/w polystyrene blend imparts the greatest protective action, in both the pre - and post-gel region, not only on the percentage gel produced but also in terms of the molecular weight of the growing chains.

## 5.6 Morphological Studies

It is generally accepted that the properties of a polymer blend system are closely related to the morphology of the two components. In Chapter 2, the concept of miscibility and that of compatibility were discussed in terms of the components constituting such a blend system. A two-component system may give rise to a 'compatible effect', which is normally achieved when a degree of miscibility exists between the two components. It was clear from the theoretical predictions, that the polystyrene-polydimethylsiloxane system would be expected to give rise to an immiscible blend. Thermal analysis of the blends indicated that a small degree of mixing may be possible, being indicated by a shift in the glass transition temperature of the polydimethylsiloxane in the blends. It is abundantly clear that, in terms of the radiation protection of polydimethylsiloxane, a compatible effect is observed.

This creates a dilemma; in that the two immiscible components seem to be interacting in such a way as to give rise to a compatible effect. We cannot explain this phenomena as being due to the miscibility of the two components; it must therefore be linked with the two phase morphology.

### 5.6.1 Experimental

Samples having undergone crosslinking by gamma irradiation were quenched in liquid nitrogen, and subsequently fractured by an applied force. The fractured surface was then prepared for mounting in a scanning electron microscope (SEM) by sputtering in a gold vapour atmosphere. Up to four prepared samples could be accommodated on the mounting stage, by attachment with a special adhesive. The fracture surface of the various samples were observed with a scanning electron microscope.

5.11a Scanning Electron Microscope Data for the

3% w/w Polystyrene Blend

Class Interval (x)	Frequency (F)	Percentage Frequency (% F)	xf	x <sup>2</sup> f
1.5	191	24.7	286.5	234.0
2.5	189	24.5	472.5	1181.3
3.5	141	18.3	493.5	1727.3
4.5	111	14.4	499.5	2247.8
5.5	47	6.1	258.5	1421.8
6.5	23	2.9	149.5	971.8
7.5	16	2.1	120.0	900
8.5	7	0.91	59.5	505.8
9.5	11	1.42	104.5	992.8
10.5	4	0.52	42.0	441
11.5	8	1.03	92.0	1058
12.5	4	0.52	50.0	625
13.5	6	0.78	81.0	1093.5
14.5	6	0.78	72.5	1261.5
15.5	2	0.26	31.0	480.5
16.5	1	0.13	16.5	272.3
17.5	1	0.13	17.5	306.3
18.5	3	0.39	55.5	1026.8
19.5	0	0	0	0
20.5	0	0	0	0
21.5	1	0.13	21.5	426.3
Total	772	100	2923.5	17209

5.11b Scanning Electron Microscope Data for the

10% w/w Polystyrene Blend

Class Interval (x)	Frequency (F)	Percentage Frequency (% F)	xf	$x^2f$
1.5	38	9.82	57	46.6
2.5	64	16.54	160	400
3.5	82	21.19	287	1004.5
4.5	66	17.05	297	1336.5
5.5	41	10.59	225.5	1240.3
6.5	18	4.65	117	760.5
7.5	5	1.29	37.5	281.3
8.5	6	1.55	51	433.5
9.5	6	1.55	57	541.5
10.5	6	1.55	63	661.5
11.5	7	1.81	80.5	925.8
12.5	4	1.03	50	625
13.5	8	2.07	108	1458
14.5	3	0.78	43.5	630.8
15.5	3	0.78	46.5	720.8
16.5	2	0.52	33	544.5
17.5	5	1.29	87.5	1531.3
18.5	7	1.81	129.5	2395.8
19.5	1	0.26	19.5	380.3
20.5	2	0.52	41	840.5
21.5	0	0	0	0
22.5	2	0.52	45	1012
23.5	1	0.26	23.5	552.3
24.5	3	0.78	73.5	1800.8
25.5	1	0.26	25.5	650.3
26.5	2	0.52	53	1404.5
27.5	0	0	0	0
28.5	0	0	0	0
29.5	1	0.26	29.5	870.3
30.5	0	0	0	0
40.5	1	0.26	40.5	1640.3
45.5	1	0.26	45.5	2070.3
Total	386	100	2327.0	26759



5.11c Scanning Electron Microscope Data for the

15% w/w Polystyrene Blend

Class Interval (x)	Frequency (F)	Percentage Frequency (%F)	xf	$x^2f$
1.5	44	18.49	66	53.9
2.5	52	21.85	130	325
3.5	30	12.61	105	367.5
4.5	24	10.08	108	486
5.5	9	3.78	49.5	272
6.5	11	4.62	71.5	464.75
7.5	7	2.94	52.5	393.75
8.5	8	3.36	68	578
9.5	3	1.26	28.5	271
10.5	4	1.68	42	441
11.5	4	1.68	46	529
12.5	4	1.68	50	625
13.5	5	2.10	67.5	911
14.5	4	1.68	58	841
15.5	6	2.52	93	1442
16.5	2	0.84	33	545
17.5	3	1.26	52.5	919
18.5	3	1.26	55.5	1027
19.5	0	0	0	0
20.5	1	0.42	20.5	420
21.5	1	0.42	21.5	462
22.5	0	0	0	0
23.5	1	0.42	23.5	552
24.5	1	0.42	24.5	600
25.5	3	1.26	76.5	1951
26.5	0	0	0	0
27.5	0	0	0	0
28.5	1	0.42	28.5	812
29.5	1	0.42	29.5	870
30.5	0	0	0	0
31.5	1	0.42	31.5	992
32.5	0	0	0	0
33.5	0	0	0	0
34.5	1	0.42	34.5	1190
39.5	1	0.42	39.5	1560
44.5	1	0.42	44.5	1980
46.5	1	0.42	46.5	2162
58.5	1	0.42	58.5	3422
Total	238	100	1656	27,466

5.1ld Scanning Electron Microscope Data for the

20% w/w Polystyrene Blend

Class Interval (x)	Frequency (F)	Percentage Frequency (% F)	xf	$x^2f$
1.5	51	16.5	76.5	62.5
2.5	44	14.24	110	275
3.5	39	12.62	136.5	477.8
4.5	38	12.29	171	769.5
5.5	27	8.74	148.5	816.8
6.5	11	3.56	71.5	464.8
7.5	11	3.56	82.5	618.8
8.5	13	4.21	110.5	939.3
9.5	5	1.62	47.5	451.3
10.5	4	1.29	42	441
11.5	4	1.29	46	529
12.5	2	0.65	25	312.5
13.5	11	3.56	148.5	2004.8
14.5	5	1.62	72.5	1051.3
15.5	2	0.65	31	480.5
16.5	4	1.29	66	1089
17.5	1	0.32	17.5	306.3
18.5	3	0.97	55.5	1026.8
19.5	2	0.64	39	760.5
20.5	5	1.62	102.5	2101.3
21.5	4	1.29	86	1849
22.5	2	0.64	45	1012.5
23.5	2	0.64	47	1104.5
24.5	1	0.32	24.5	600.3
25.5	2	0.64	51	1300.5
26.5	1	0.32	26.5	702.3
27.5	0	0	0	0
28.5	0	0	0	0
29.5	0	0	0	0
30.5	1	0.32	30.5	930.3
31.5	1	0.32	31.5	992.3
32.5	0	0	0	0
33.5	1	0.32	33.5	1122.3
34.5	1	0.32	34.5	1190.3
35.5	1	0.32	35.5	1332.3
41.5	1	0.32	41.5	1806.3
44.5	1	0.32	44.5	2070.3
45.5	1	0.32	45.5	2162.3
46.5	1	0.32	46.5	2256.3
47.5	1	0.32	47.5	2352.3
50.5	1	0.32	50.5	2652.3
52.5	1	0.32	52.5	2862.3
55.5	1	0.32	56.5	3192.3
57.5	1	0.32	58.5	3422.3
75.5	1	0.32	75.5	5852.3
Total	309	100	2522.5	49891.5

The samples were examined with magnification up to X1600; photomicrographs being taken within this range. For the results presented, and for the statistical analysis, the magnification was kept at approximately X400. The domain size distribution was computed using an electronic area counter.

#### 5.6.2 Results

Typical microstructures of the polystyrene-polydimethylsiloxane blends are illustrated by the SEM photomicrographs, presented in Figs. 5.11-5.16 and summarised in Tables 5.11a - 5.11d. A range of blends were analysed with several photographs being recorded for each sample, at a magnification of X400. The computation of the domain size is performed electronically. The photomicrograph is transposed to a visual display, which is divided into a large number of square units, called 'pixel'. The domains are located, then the size of each is determined as compared to these pixels. The computation is given as "the number of domains above 1 pixel unit", then the number of domains present with each successive increase in pixel size.

The limitation of such a technique is that:

- a) The apparatus does not record any domains below a size of 1 pixel unit, and
- b) the pixel units are of integral values.

This raw data has been converted to give the number of domains (frequency) occurring in a class group of an interval of 1 integral unit. In the presented results, (Table 5.11a - 5.11d) data from each photomicrograph for a particular sample, are simply added together, so that a brief statistical analysis can be performed. The percentage frequency of domain size is plotted in Fig. 5.17a - 5.17d. Table 5.12 summarises a number of derived statistical factors obtained from each blend sample.

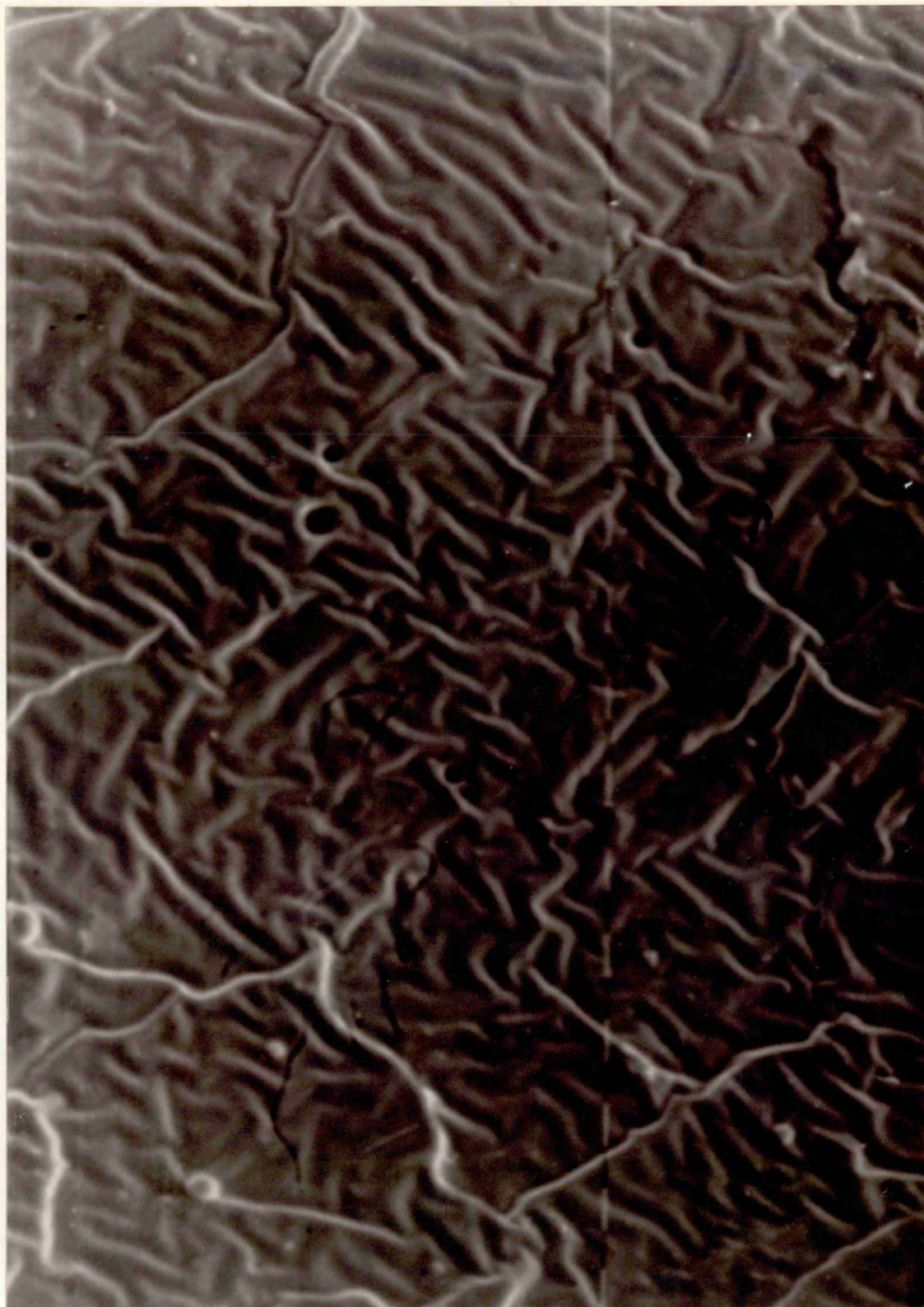


Fig.5.11 Photomicrograph of Polydimethylsiloxane



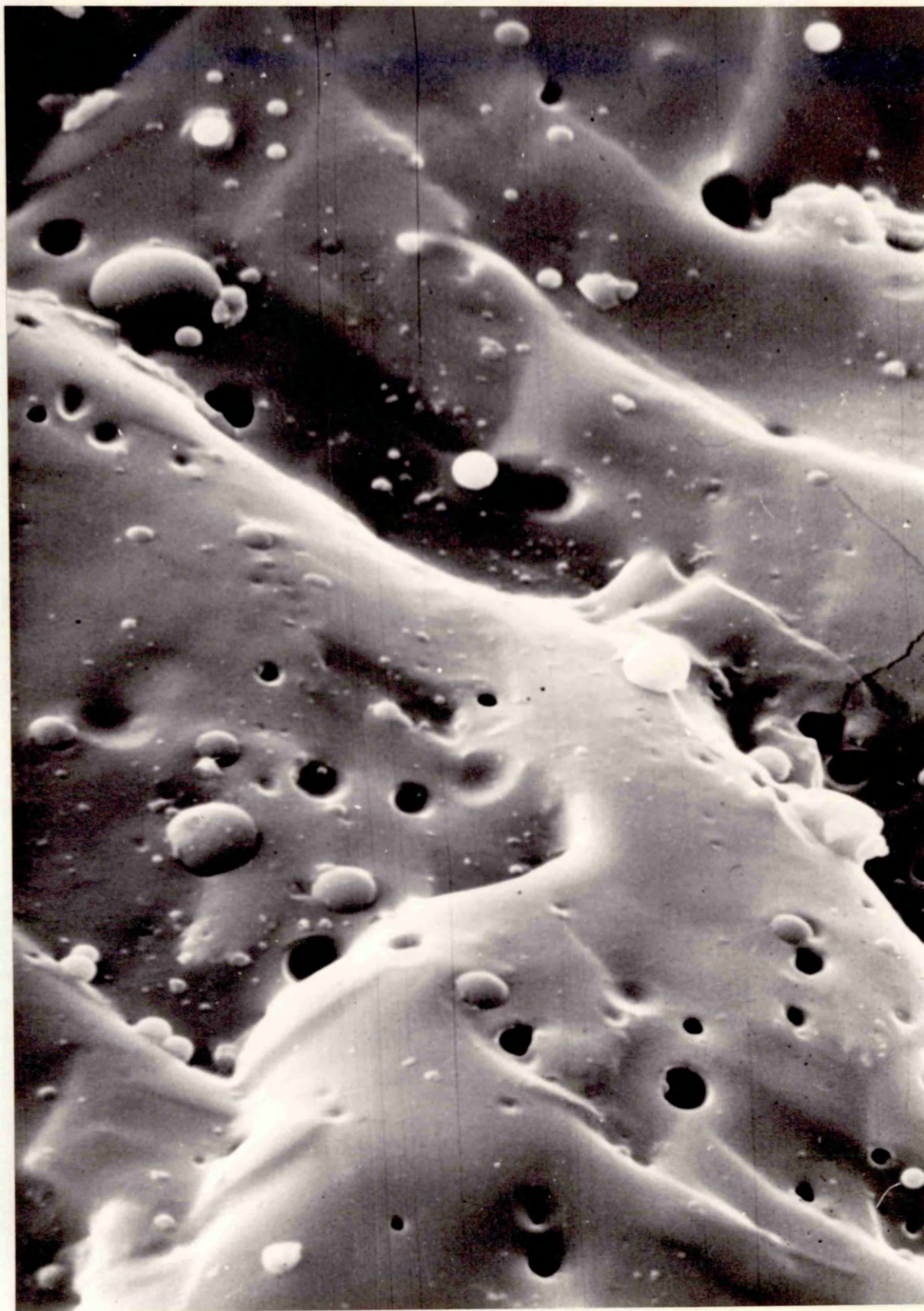


Fig.5.12a Un-extracted 10% w/w Polystyrene-PDMS Blend (x400)





Fig.5.12b Extracted 10% w/w Polystyrene-PDMS Blend (x800)

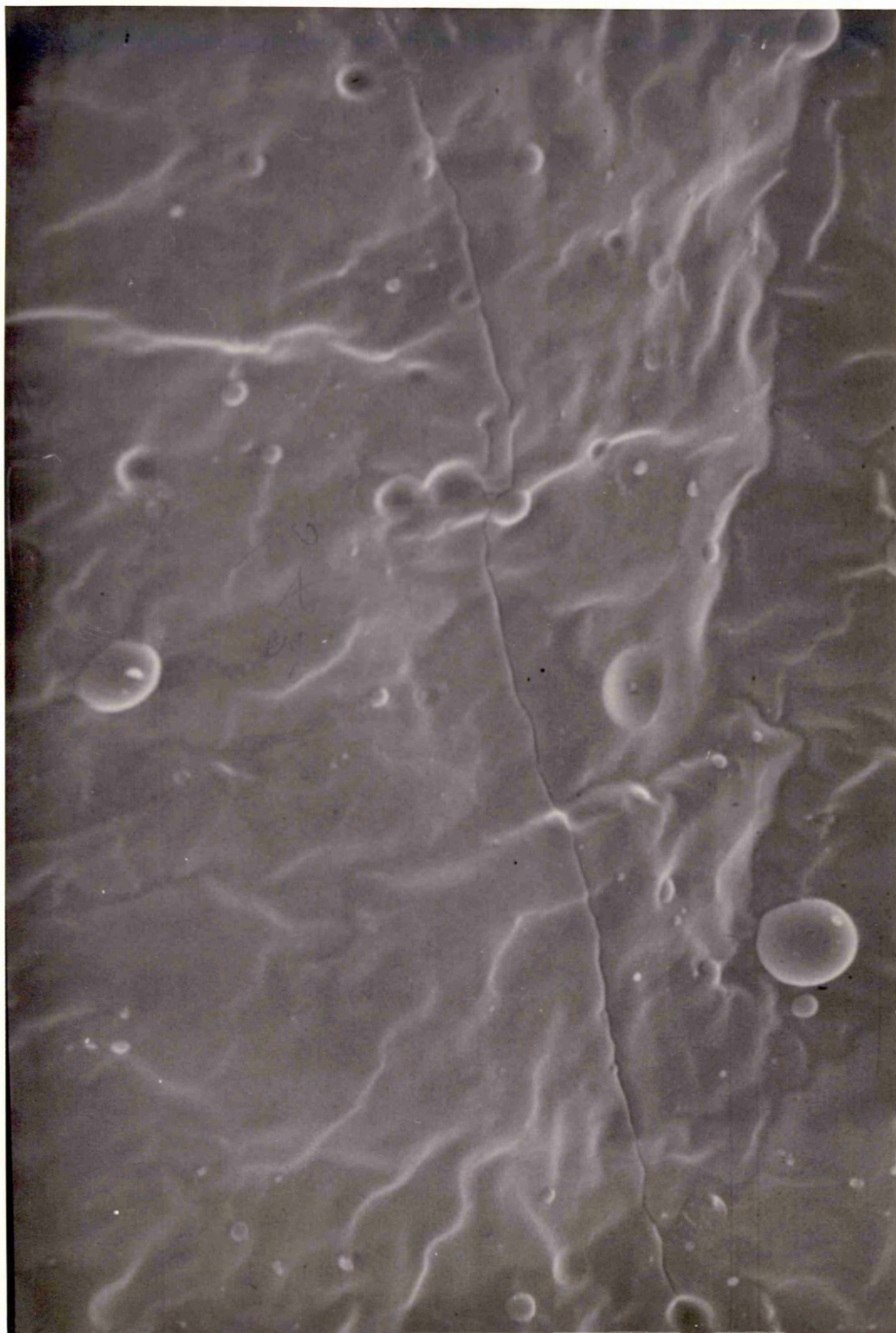


Fig.5.13 3% w/w Polystyrene-PDMS Blend (x400)





Fig.5.14 10% w/w Polystyrene-PDMS Blend (x400)



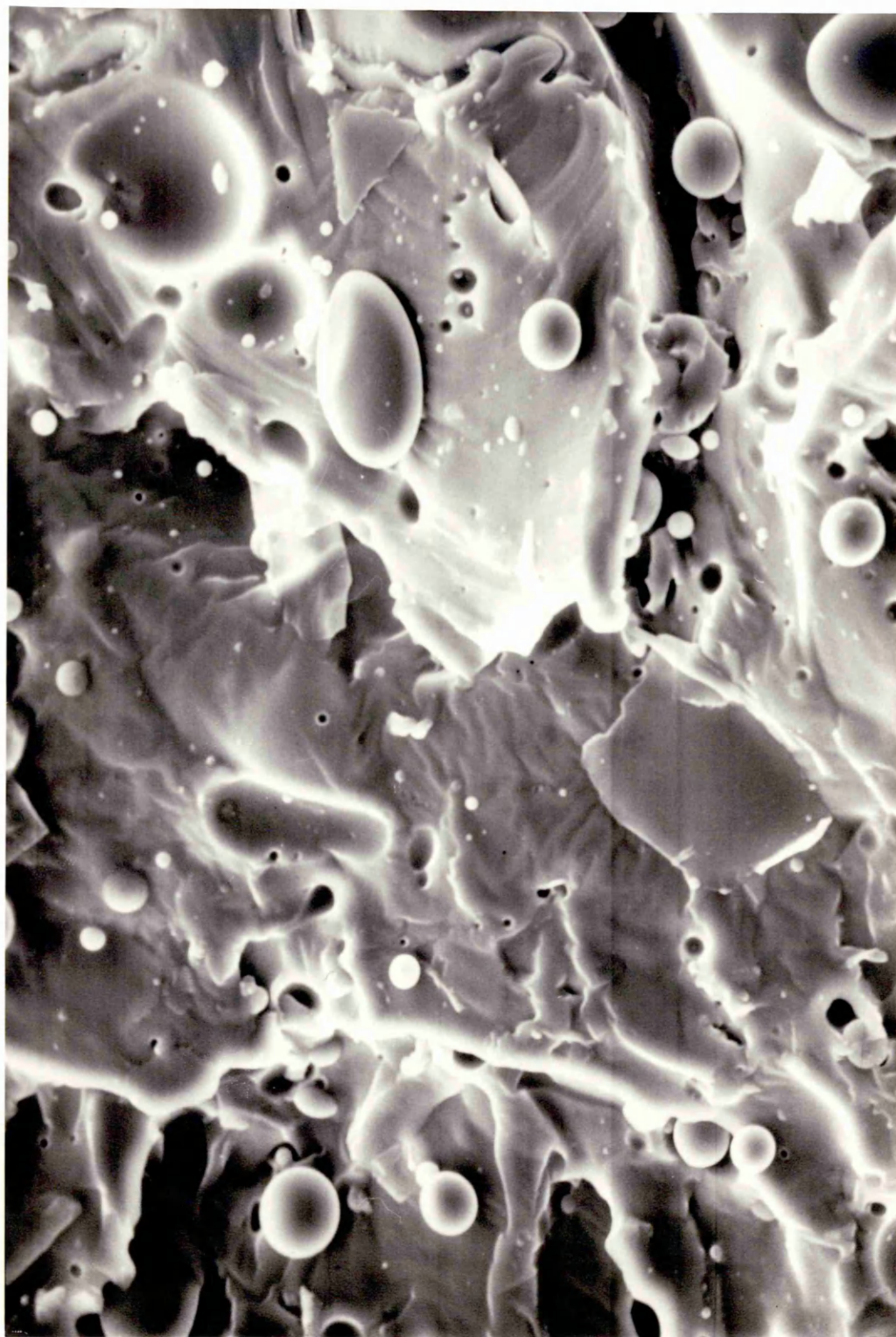


Fig.5.15 25% w/w Polystyrene-PDMS Blend (x200)



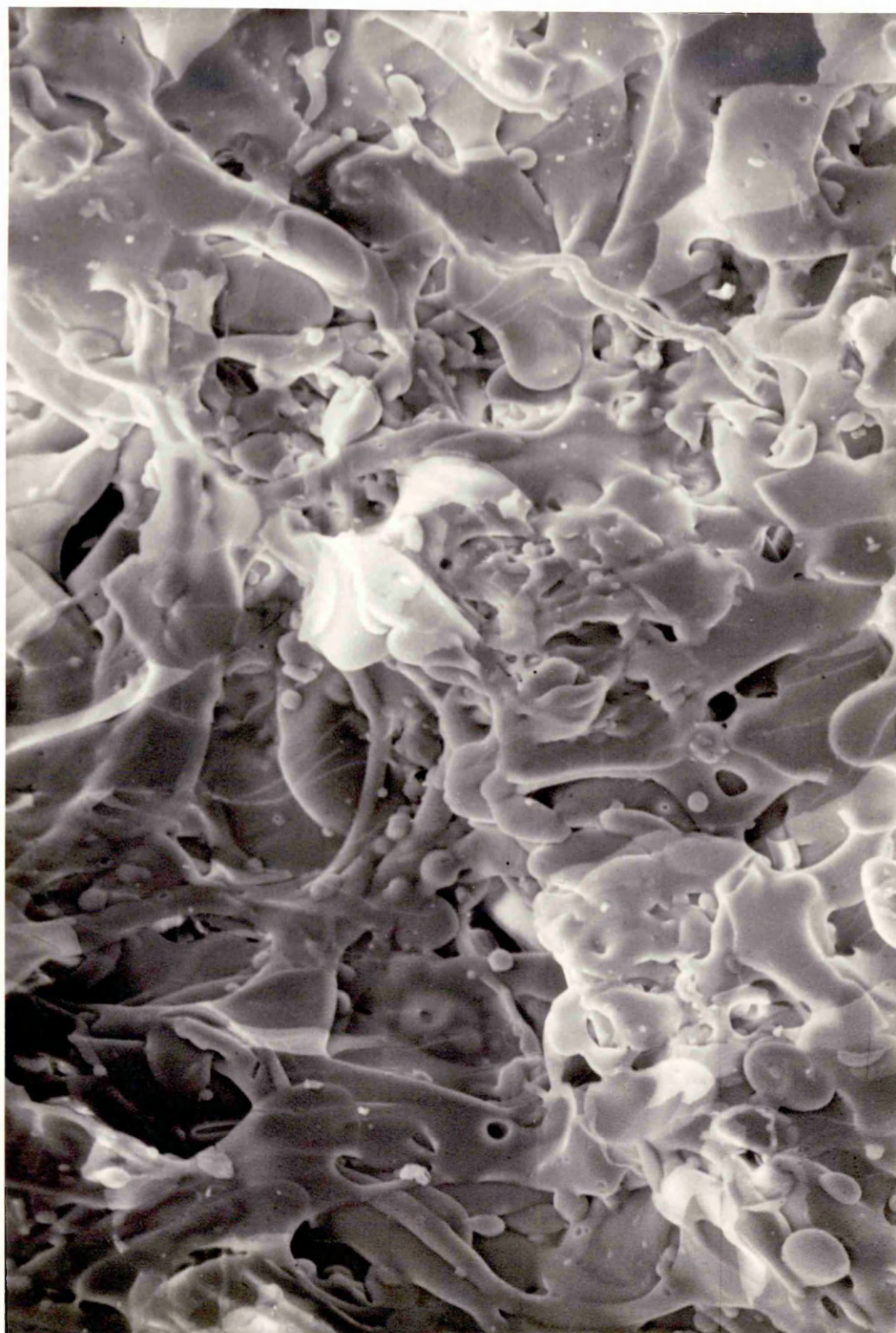


Fig.5.16 50% w/w Polystyrene-PDMS Blend (x100)

Table 5.12 Statistical Factors relating to the

Morphological Analysis

Sample Blend (% Polystyrene)	Mean (Pixel Units)	Mode	Standard Deviation
3%	3.86	1.5	22.3
10%	6.2	3.5	69.1
15%	7.0	2.5	115.4
20%	8.2	1.5	161

5.6.3 Discussion

Prior to polystyrene addition the morphology of the pure siloxane is such that a, 'rippled effect' is observed, which is illustrated in Fig.5.11. Addition of a small amount of polystyrene results in the appearance of domains, which tend to be spherical in nature, with some having an 'elipsoidal shape. It is evident that these domains are the second component, (i.e. polystyrene) since samples containing a larger amount of polystyrene, have a morphology of not only an increased number of domains, but domains of a larger size. Figs. 5.12a and 5.12b illustrate this point rather clearly. In the comparison of a 10% w/w polystyrene blend (Fig.5.12a) with a sample (Fig.5.12b) that has undergone soxhlet extraction it can be seen that the second component has been removed, leaving behind a number of spherical 'holes'. It is clear that, in general terms, the polystyrene-polydimethylsiloxane system forms a two-phase polymer blend, with the siloxane as the matrix, and the polystyrene forming microdomains.

In the observation of the fracture surface, it is assumed that

Fig.5.17a Percentage frequency of domain size for a 3% Polystyrene Blend.

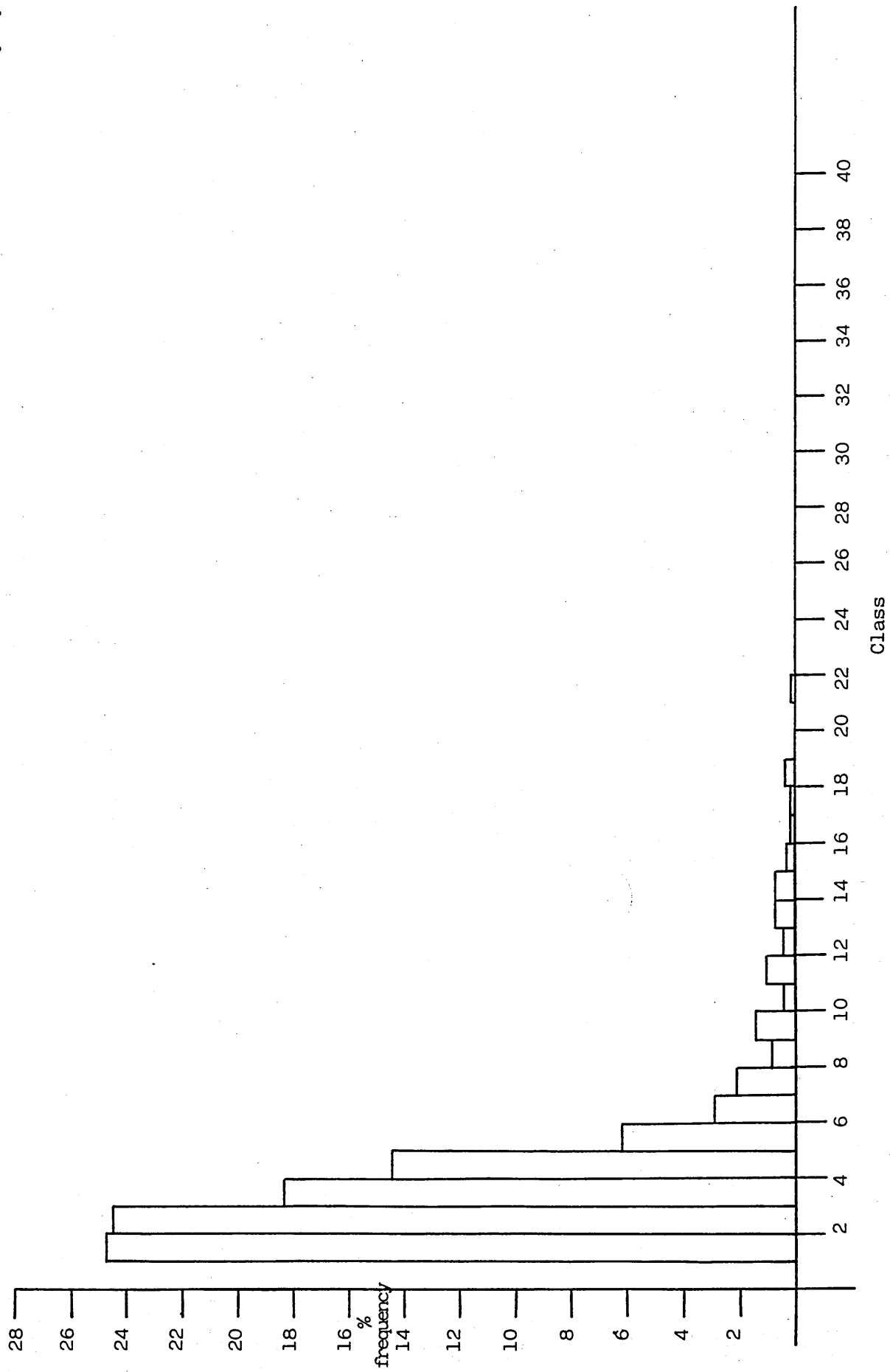


Fig.5.17b Percentage frequency of domain size for a 10% Polystyrene Blend.

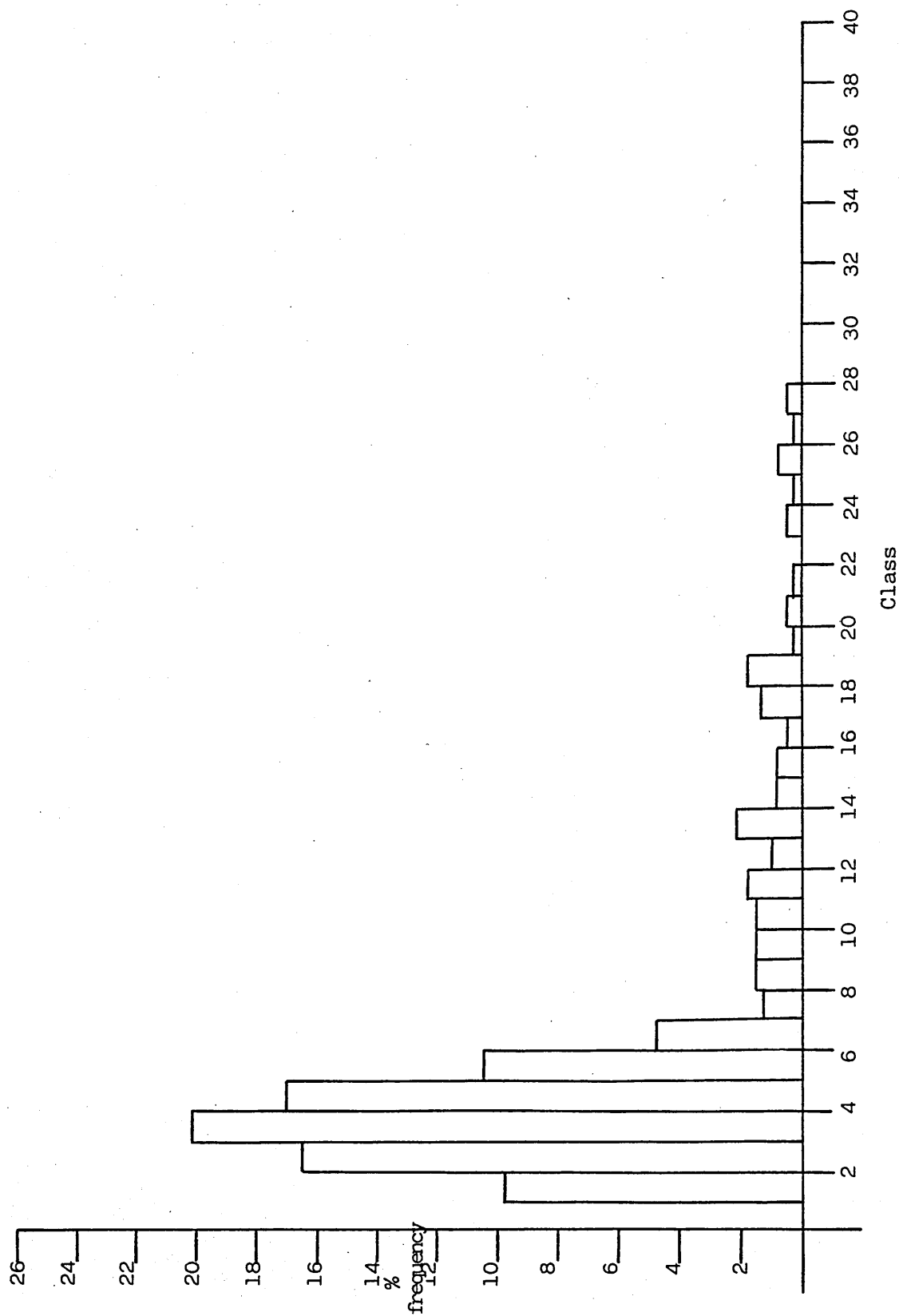


Fig.5.17c Percentage frequency of domain size for a 15% Polystyrene Blend.

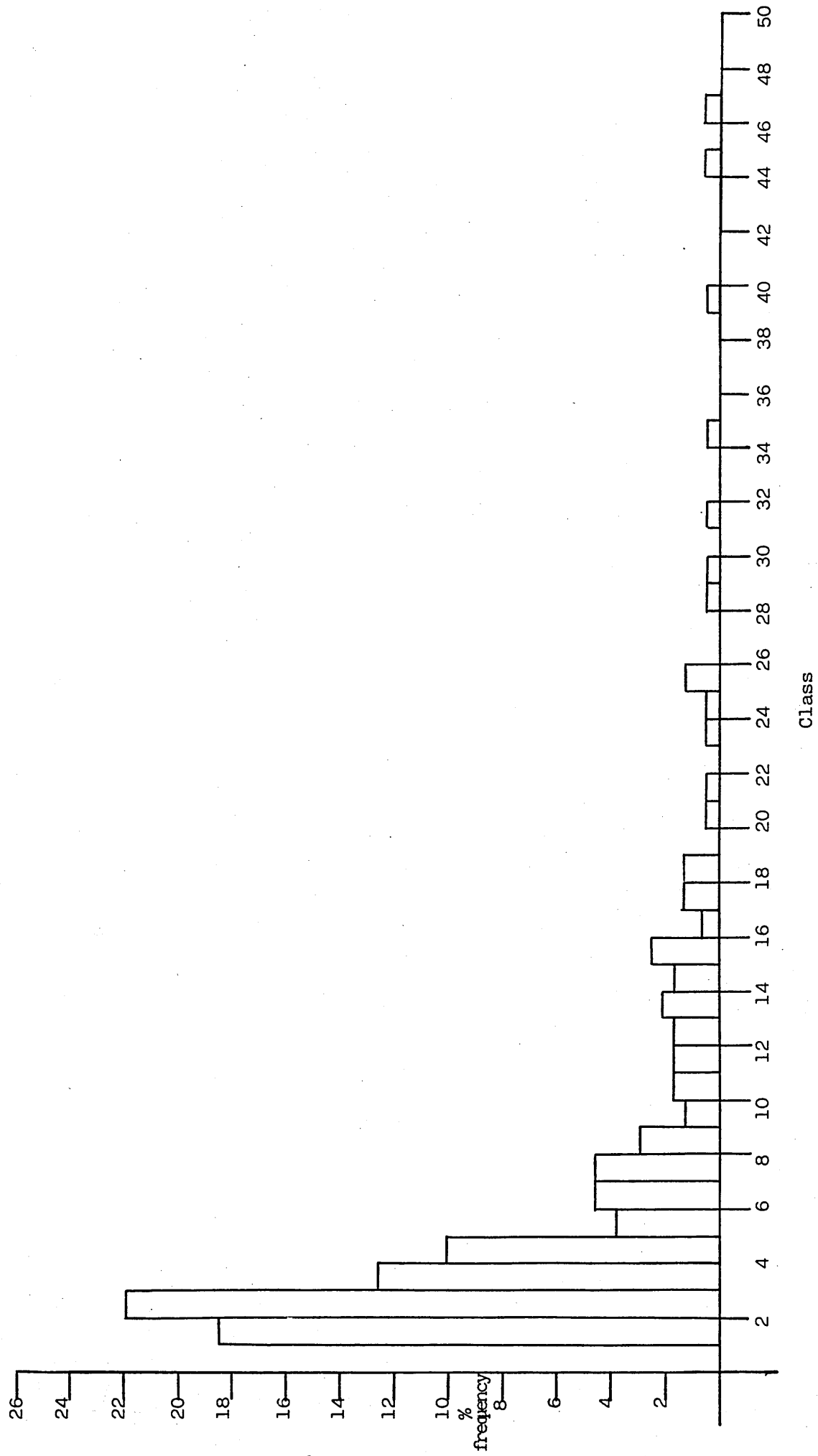
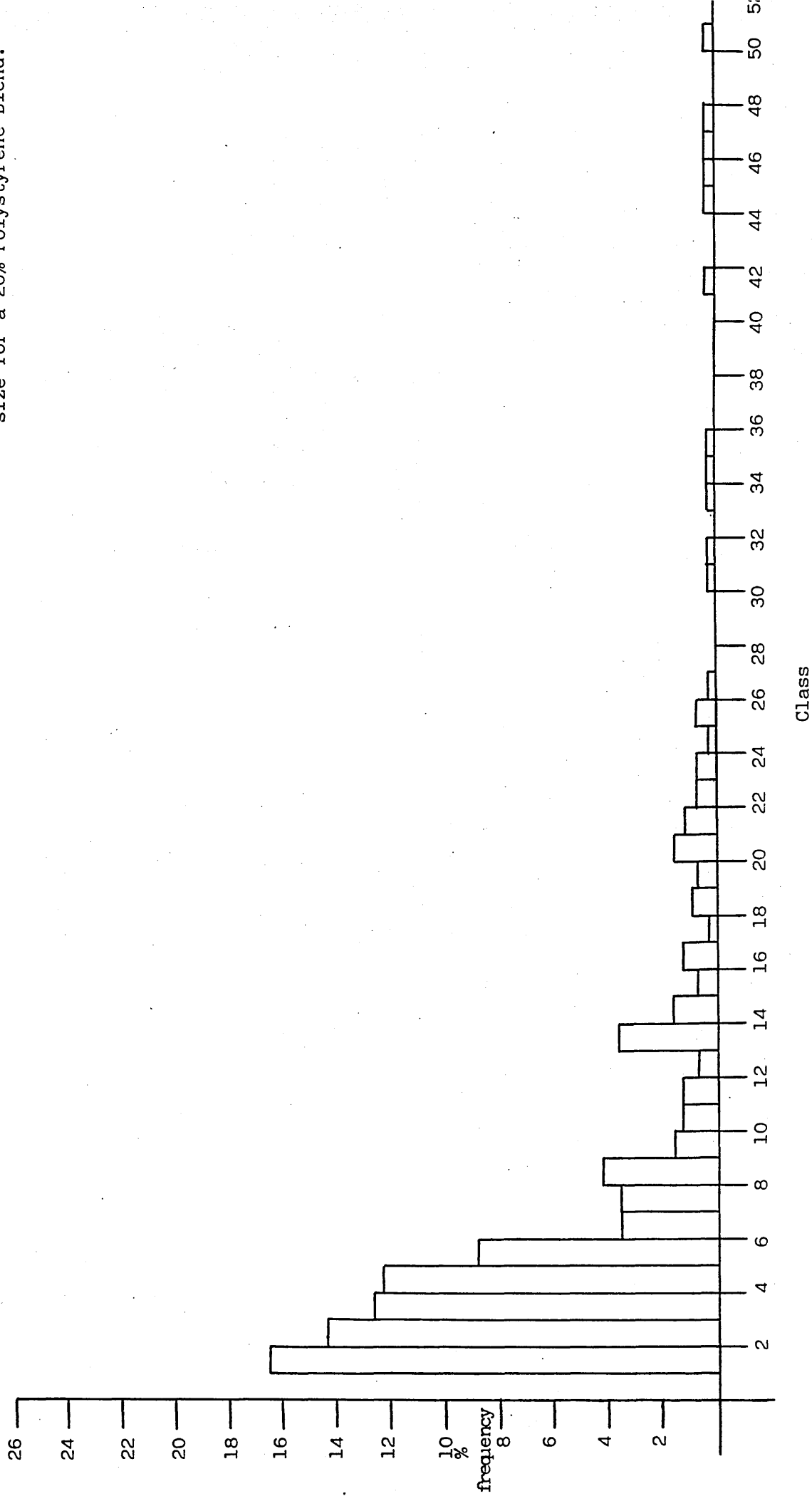


Fig.5.17d Percentage frequency of domain size for a 20% Polystyrene Blend.



the two components are homogeneously mixed throughout the sample; so any photomicrographs obtained are considered to be representative of that sample. If this is so, it is axiomatic that the point of fracture in the sample occurs completely at random; that is there is no inducement for that point of fracture due to the polymer composition. This is simply another way of restating the basic assumption of homogeneity.

A wide range of photomicrographs were obtained, of differing composition, at various magnifications Figs.5.11-5.16. In the analysis of the size distribution of the polystyrene domains, a number of points need to be made.

- i) Each of the samples analysed, had been subjected to the same radiation dose (1.0 Mrads).
- ii) The method of recording surface observations, was conducted in a rather random manner. Although there was no rigorous adherence to a sampling theory, the photomicrographs were chosen such that they did not overlap in any way.
- iii) Only a limited population of photomicrographs were taken. Despite this 6-8 photomicrographs of reasonable quality were obtained for each sample, which allowed a brief statistical analysis. From the data, a number of statistical factors have been derived which are presented in Table 5.12.



- iv) The electronic counting apparatus registers domains above 1 pixel unit. There is no account of any domains below this value, hence the frequency distribution in certain of the figures (Fig.5.17) give the impression of being half a distribution curve. If analysis were conducted at a higher magnification, then this difficulty may be somewhat reduced.
- v) The class interval registered by the counter is of 1 integer unit, which serves the analysis more than adequately.

It is realised that, in statistical terms, a greater number of photomicrographs, would have allowed a fuller and more detailed analysis. However it is clear that, from the data a number of trends are observed.

It has long been recognised in immiscible systems that the size of the domains can be related to the degree of mixing, in that the smaller the domains the more compatible the system.<sup>223,224</sup> This has been noted by Tsukahara et al<sup>225</sup> in studies of polystyrene-poly(t-butyl acrylate) diblock copolymers. They found that dynamical interactions between the two phases was greater in diblock copolymers, than in blends. This was due to smaller domains occurring in the diblock copolymers which give rise to a larger surface area (SA) to volume ratio (SA/vol. ratio).

The theoretical prediction of miscibility, encountered in Chapter 2, involved the consideration of the molecular weights of the two components. The larger the molecular weight of the polystyrene, the greater the degree of immiscibility. In theoretical terms, the molecular weight of polystyrene that would be required to give a miscible system was calculated;

any sample greater than this specified value would result in a two phase system. A much larger molecular weight sample would then move further away from the one-phase miscible system, which would be observed as an increase in the segregation of the two phases. Ward et al,<sup>226</sup> in a study of poly( $\alpha$ -methylstyrene-dimethylsiloxane) found that the size of the domains tended to increase with the molecular weight of the blocks, indicating a higher degree of aggregation within the domains. It can therefore be concluded that in our particular blend system, a higher molecular weight polystyrene component would tend to give domains of a larger size.

With an increase in the weight % of polystyrene, Fig.5.17 and Table 5.12 clearly indicates that there is an increase in the size of the domains encountered. In the 3% w/w blend the highest domain is of 22 units, 31 units for the 10% w/w sample, 47 units for 15% w/w, and 75 units for the 20% w/w. This is perhaps best observed in the standard deviation for each sample, where there is a vast increase in the range of the size of the domains. Another way of observing such a trend, is by noting the percentage of the domains that occur below 4 pixel units. In the low % polystyrene blend (3% w/w) almost 68% of the domains occurs below 4 pixel units, whereas in the 20% w/w sample, 43% are below that integer value. It is evident that with an increase in the weight percentage of the polystyrene component, there is a higher percentage of domains occurring of a larger size. The calculated value of the "mean" domain size, increased by more than a factor of 2, for the samples analysed.

We can therefore conclude that as the concentration of polystyrene increases, there will tend to be a greater aggregation of that component. This being observed by the occurrence of larger domains.

It is expected that this increase would be observed until the point is reached when the polystyrene actually forms the matrix and the siloxane the domains. This conclusion appears to be very similar to that reached by Ward et al;<sup>232</sup> molecular weight increase being synonymous with weight percentage increase. Conversely, it is then expected that with a decrease in the percentage polystyrene, the domain size will decrease.

The mean domain size of the 3% w/w sample is less than half the size of the 20% w/w sample; hence there will be a greater surface area to volume ratio (SA/volume ratio) for the 3% w/w polystyrene blend.

These results suggest that the morphology of the blends can provide an explanation for the previously discussed experimental observations, which were attributed as resulting from the radiation protection of polydimethylsiloxane by polystyrene. It may be that, due to an increase in the interfacial contact between the two phases, in a blend with a low percentage of polystyrene present, a greater proportion of the polydimethylsiloxane chains may be protected from intra - and inter - molecular crosslink formation. This protection being observed as a decrease in the amount of gel produced in an irradiated sample.

## 5.7 Analysis of Irradiated Copolymers

A number of the prepared copolymers, were irradiated and analysed by soxhlet extraction. The copolymers were generally different in physical texture to the blends, however this presented no difficulty for the sealing of ampoules nor for their subsequent analysis.

### 5.7.1 Results

Table 5.13 Characterisation of the Copolymers

		Copolymer		Sample	
		PSS 9.1	PSS 10.2	PSS 23	PSS 25
Polymerisation Method		Condensation		Anionic	
Styrene Block					
	Mn	12,851	7,099		
	Mw	29,700	33,800		
Siloxane					
	Mn	50,000	2,000		
Copolymer	Mn	unknown	unknown	25,300	19,200
	Mw			62,300	42,800

Samples analysed and their molecular weight data are given in Table 5.13. Results obtained from soxhlet extraction after irradiation at various doses given in Table 5.14.

Table 5.14 Solubility data for Irradiated Copolymers

Dose (Mrads)	Copolymer Sample % Gel			
	PSS 9.1	PSS 10.2	PSS 23	PSS 25
15	30 $\pm 2$		53 $\pm 0.5$	33.3 $\pm 1.5$
25	37.3 $\pm 0.5$		64.5 $\pm 0.5$	58.2 $\pm 0.6$
30	41.8 $\pm 0.1$	44.9 $\pm 1.0$	68.3 $\pm 3.0$	59.5 $\pm 1.5$

### 5.7.2 Discussion

The two components in these copolymers are expected to form a two-phase structure. Thermal analysis of the copolymers indicated that this is the case; although there was certain evidence which suggested a degree of molecular mixing.

The irradiation behaviour of the copolymers was compared with that of pure polydimethylsiloxane of similar characteristics. The cross-linking efficiency  $G(x)$ , for polydimethylsiloxane is in the range 2.6 - 2.8; and this value appears to be independent of the molecular weight. If we assume the value to be 2.8, and substitute this into a rearranged form of the Charlesby equation, the theoretical incipient gelation dose ( $r_{gel}$ ) can be obtained.

$$G(x) = \frac{4.83 \times 10^5}{M_w \cdot r_{gel}}$$

$$r_{gel} = \frac{4.83 \times 10^5}{M_w \cdot G(x)}$$

This gives for:

$$\text{PSS 23} = 2.8 \text{ Mrads}$$

$$\text{and PSS 25} = 4.0 \text{ Mrads}$$

assuming that they are mainly comprised of poly<sup>d</sup>imethylsiloxane.

A plot of gel content and absorbed dose for PSS 23 and 25 (Fig.5.18) gives extrapolated rgel values in the range 5-6.5 and 11-12 Mrads, respectively.

The results are summarised in Table 5.15.

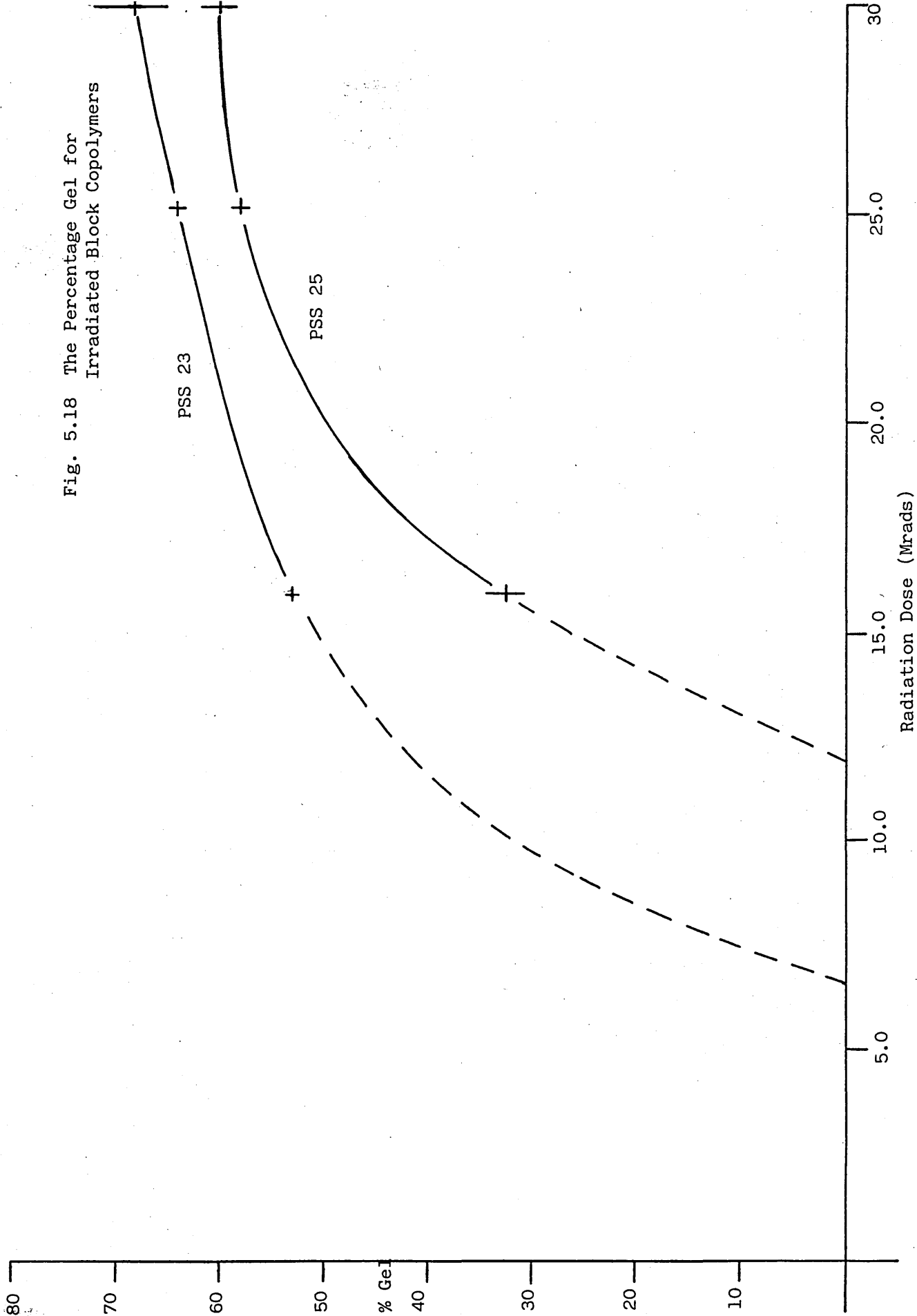
Table 5.15 Theoretical and Extrapolated values of the Incipient Gelation

Sample	Incipient Gelation (Mrads)	
	Theoretical	Extrapolated (Experimental)
PSS 23	2.8	5 - 6.5
PSS 25	4.0	11 - 12

In each polymer the extrapolated value is well above that which would be obtained if the polymer was completely polydimethylsiloxane. One fact is clear, when a portion of the polymer is polystyrene, a greater amount of energy needs to be absorbed before there is an average of 1 crosslink/molecule. The extrapolated values are 2-3 times greater than the theoretical gelation values.

The replacement of a segment of the siloxane within the polydimethylsiloxane chain, with a polystyrene block, would effectively reduce the molecular weight of the siloxane component, hence the number of potential crosslinking sites. The NMR spectra of PSS 23 and 25 show their siloxane composition to be 68% and 70% respectively. If we then assume that these percentages of the overall copolymer chain is composed of polydimethylsiloxane, we can then assess any protection that may be offered by the polystyrene to that portion of the chain, e.g. PSS 23.

Fig. 5.18 The Percentage Gel for  
Irradiated Block Copolymers



Molecular weight - 62,300

If it is composed of 70% polydimethylsiloxane,

the molecular weight of the siloxane component = 43,600

Using the rearranged Charlesby equation,

$$r_{gel} = 3.9 \text{ Mrads.}$$

Table 5.16 gives a theoretical gelation dose, for pure polydimethylsiloxane of the same chain length as that within the block.

Table 5.16 Theoretical and Extrapolated values of the  
Incipient Gelation

Sample	Molecular Weight (Mw)		Gelation Dose (Mrads)	
	Copolymer	Siloxane Component	Theoretical	Extrapolated
PSS 23	62,300	43,610	3.9	5 - 6.5
PSS 25	42,800	29,400	5.9	11 - 12

The calculated (theoretical) values give gelation doses which are somewhat smaller than the experimentally observed (extrapolated) values.

In PSS 9.1 and PSS 10.2, which are essentially ABA block copolymers polystyrene is coupled to both ends of a siloxane block. The morphology of ABA block copolymers are similar to AB blocks, the styrene components forming the 'hard block' domains.

The gel data follows the expected trend, an increase in dose resulting in a higher gel value. In all these irradiations it is to be expected that the styrene component does not give rise to any crosslinks, hence there would be no gel contribution from the polystyrene component.



For sample PSS 9.1, it was found that at 15 and 30 Mrads, the percentage gel is approximately half that obtained for pure polydimethylsiloxane. Here a substantial reduction in gel is observed when polystyrene is present.

It would appear that the polystyrene component in these copolymers is exerting a "protective effect" on the polydimethylsiloxane, by preventing crosslink formation. The morphology of the sample, would seem to facilitate such a phenomena, in very much the same way as proposed in the blends. Even with such a large proportion of polystyrene present, the molecular dimensions of the 'hard block' component must be such that a degree of miscibility is possible. This may involve a region at the domain interface, or dispersal of low molecular weight chains throughout the system.

CONCLUDING REMARKS

At the outset of this programme of work, it was anticipated that by manipulation of polydimethylsiloxane, either through physical mixing with, or chemical attachment of an appropriate second component, increased resistance to gamma-induced crosslinking reactions could be obtained. In addition to the prospect of gaining such a compound, it was presumed that further information that would lead to a greater understanding of gamma-induced reactions would arise from this study. Chapters 2 and 3, described the preparation of polymer systems that could fulfil these criteria, using polystyrene as the radiation resistant second component.

Polydimethylsiloxane was irradiated initially and analysed by a variety of techniques which revealed a number of interesting results. It was found that there was excellent agreement with literature values for the crosslinking efficiency parameter,  $G(x) = 2.8$ . The slight deviation from theory observed in the Charlesby-Pinner plot being explained as due to the polydispersity of the polydimethylsiloxane sample.

The swelling behaviour of the irradiated polydimethylsiloxane gave results that were expected, the degree of swelling being indirectly proportional to the absorbed dose. Further, the molecular distance between each crosslinking site, decreased with increasing absorption of radiation, until a rigid three-dimensional network was obtained. In a comparison of solvent extracted and unextracted samples, it was seen that at low doses quite large differences in swelling behaviour were observed, whilst with the higher dose samples no differences were apparent. Within an open 3-dimensional network, a greater proportion

of solvent can be accommodated after extraction of uncrosslinked material, whereas in the more lightly held structure, the removal of the sol does not increase such an absorption.

The thermal analysis results confirmed the information that had been obtained by solvent extraction and swelling methods, that the absorption of radiation had a profound effect on the molecular behaviour of the polymer chains. The glass transition of polydimethylsiloxane was found to increase on irradiation, but more importantly, at the onset of gelation the exotherm peak was found to disappear. Within experimental error, this occurred at the same dose, as that obtained from the soxhlet extraction studies. Further investigation of this observation is required, but this could offer many advantages over the extraction procedure as a method for the determination of the incipient gelation. Toxic solvents are not needed, nor prolonged extraction of a sizeable mass of sample.

Analysis by gas-liquid chromatography of the uncrosslinked portion (sol) of the siloxane, after irradiation indicated that a large number of reactions had taken place, the nature of which were determined by the absorbed dose.

Soxhlet extraction of the irradiated blends revealed a discontinuity in the amount of gel obtained. A plot of the Charlesby-Pinner relationship clearly indicated gross deviations, indicative of a non-random introduction of crosslinks within the polymer system. The presence of polystyrene would seem to be interfering with the crosslinking reactions of polymethylsiloxane, and it is evident that with 3% w/w polystyrene present a significant radiation protection is occurring.

Results obtained from the thermal analysis of the blends revealed that the shift in the glass transition of the siloxane is not as great as that incurred with a sample of pure polydimethylsiloxane. If the

assertion is true that the increase in glass transition is due to the formation of siloxane-siloxane crosslinks, then the results from the blends indicate a decreased number of crosslinks. The presence of an exotherm peak in the thermograms of blends containing 3 and 5% w/w polystyrene reinforces the view that a lower number of crosslinks are present for the same absorbed dose. However, with the blends the temperature range over which the glass transition takes place greatly increases on irradiation compared to that of irradiated pure polydimethylsiloxane, or of the unirradiated blends. This phenomena is generally ascribed to an increase in the miscibility of two components. It would therefore appear that on the absorption of radiation, some degree of interaction between the two components takes place, thereby increasing the glass transition range.

The two sets of data obtained from the molecular weight study, show that the presence of polystyrene (3% w/w), greatly retards any increase in molecular weight, especially in the dose range prior to gelation. In this particular range the molecular weight of the pure polydimethylsiloxane increases to almost double that of the siloxane which is blended with 3% w/w polystyrene. The 3% w/w sample also gives a siloxane molecular weight much lower than that of samples containing greater amounts of polystyrene. Again this would seem to suggest that within the 3% w/w polystyrene sample, maximum resistance to the introduction of crosslinks is obtained.

Theoretical predictions, discussed in Chapter 2, clearly pointed to the immiscibility of polydimethylsiloxane and polystyrene. Scanning electron micrographs clearly illustrated such a morphology, of a siloxane matrix interspersed with polystyrene domains. A brief statistical study revealed that the mean size of the polystyrene spheres increases with a higher polystyrene composition. It is well established in the

literature, that domain size can be used to indicate the extent of mixing, and that the smaller the domains the more "compatible" the system. The polystyrene-polydimethylsiloxane components are immiscible, yet under certain circumstances a "compatibility" is observed. It would seem that the observed effects in the solvent extraction, swelling and molecular weight studies are due to the "small" mean size of the polystyrene domains, that is the greater compatibility of the polystyrene.

Two main conclusions follow from this work:

- i) the presence of polystyrene reduces the extent of crosslinking of polydimethylsiloxane upon irradiation; and
- ii) the size of the polystyrene domains (its compatibility) greatly affect such a phenomenon

It is axiomatic that if in the presence of polystyrene there is a reduced number of siloxane crosslinks, then the polystyrene must be responsible for such a lowering. The origin of this protection is rather uncertain. At the present time, proposed theories can be classified as (a) energy transfer or (b) hydrogen abstraction mechanisms.

These ideas were discussed briefly in Chapter 4. But most publications usually conclude with a bland, rather vague statement, that the protection is due to

"the ability of the terminal aromatic group to dissipate the incident energy, without any internal molecular changes taking place."

Whilst one would acknowledge such a statement could be true it is equally important to note that the polystyrene can donate and receive hydrogen radicals, and yet remain stable. It would appear therefore, that the two mechanisms may be responsible for such protection.

However, prior to a discussion of the protection mechanism, it is pertinent to consider where the protection actually takes place. There are again two possibilities:

- i) dispersion of low molecular weight chains of polystyrene within the polydimethylsiloxane matrix;
- ii) a surface interaction between the polystyrene domains and the surrounding polydimethylsiloxane matrix.

The first possibility would suggest that with an increased amount of the polystyrene component present there would be a larger number of the low molecular weight chains dispersed within the siloxane, and subsequently an enhanced protection would be observed. However, this was not found by experiment.

It is possible that surrounding each polystyrene domain there is an annular region where a small amount of miscibility is present. At the magnification used, the photomicrographs do not indicate any such region. The use of EDAX at higher magnifications could possibly be used to confirm the presence of polystyrene outside the visually observed domains. The existence of such a region would explain the results obtained from the thermal analysis of the unirradiated blends, which clearly suggests a small degree of miscibility.

Of the mechanisms that have been proposed to explain the nature of radiation-induced reactions, no one theory seems sufficient to explain the various pieces of experimental data obtained in this study. The transfer of incident energy to the polystyrene probably contributes to the observed protection. If a small amount of gamma radiation is absorbed by the blend and transfer was very efficient, some styrene units would achieve an 'excited state'. The lifetime of this excited state would then determine whether fluorescence or phosphorescence could be observed. However, the energy emitted would be expected to be of a lower energy than the incident radiation, and no internal bond rearrangements would occur with internal molecular and vibrational relaxations accounting for the energy difference. In a very simple way, the sample would be able to absorb the gamma radiation without incurring any internal bond rearrangements.

Now if the absorption of energy is of a level that cannot be efficiently dissipated by the polystyrene, that is, the 'protection process' is swamped, crosslinks can take place within the siloxane matrix. Extraction of a lightly crosslinked network should remove the uncrosslinked siloxane chains, and all of the polystyrene. However, it has been found that even in a very lightly crosslinked network, which allows a high degree of swelling, a portion of the polystyrene component still remains after extraction. This may be simply due to physical entanglement of the chains, although prolonged extraction still results in a white opaque sample, indicative of the presence of polystyrene. This would appear to suggest that the polystyrene is 'bound' within the crosslinked network as a result of the absorption of radiation. It was found that polystyrene can be completely removed from an unirradiated blend.

If such a chemical reaction is possible, then this would explain the large broadening, of the glass transition of the polydimethylsiloxane within the blend sample. The absorption of radiation appears to lead to an enhanced degree of miscibility, possibly through formation of a covalent bond between the polydimethylsiloxane and some polystyrene.

A substantial body of opinion accepts that a radical mechanism plays the major role in the irradiation crosslinking of polymer chains; the hydrogen radical being the species responsible. The addition of a radical scavenger, or the presence of an external hydrogen pressure, does prevent such a process from taking place. It is likely that the polystyrene blended within polydimethylsiloxane may act in a number of ways:

- a) accept hydrogen radicals which have been cleaved from the polydimethylsiloxane chains, thereby preventing further crosslinking by the mobile H ;
- b) donation of hydrogen to a radical site on polydimethylsiloxane, thus preventing this position being a potential crosslinking site;
- c) combine, after donation of hydrogen, with radical sites on the polydimethylsiloxane chain.

In step (c) the energy is utilised, without a siloxane - siloxane crosslink being formed. The percentage gel would be less than is expected but this protection mechanism only involves the chains surrounding the polystyrene domains. Hence the morphology of the sample would be of paramount importance, in that many spheres of a small size could offer a greater degree of protection through an increased surface area/volume ratio.



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POSTGRADUATE COURSES/CONFERENCES ATTENDED

1. Polymer Analysis Module, a unit of the MSc Instrumental Analysis (Sheffield City Polytechnic).
2. Advanced Statistics, and Design of Experiments, provided by Department of Mathematics and Statistics, Sheffield City Polytechnic.
3. Research Colloquia, Sheffield City Polytechnic.  
3 years Attendance.  
2 Presentations.
4. Attendance at Meetings of the 'Macro Group', and Industrial Division of the Royal Society of Chemistry.
5. RAPRA Conference, 'GPC Applications'.
6. Attendance at the Annual Conference of the Royal Society of Chemistry.  
Aston University 1982.  
Lancaster University 1983.

### PRESENTATIONS

1. American Chemical Society, St. Louis, Missouri,  
April 1984. Dr. G. C. Corfield.
2. Society of Polymer Science Japan,  
International Polymer Conference Kyoto, Japan 1984.  
Dr. G. C. Corfield.
3. Research Colloquia. Sheffield City Polytechnic.  
D. T. Astill.

### PUBLICATIONS

1. Polymer Preprints vol.25, No.1. April 1984.
2. 'Materials for Microlithography' ACS Symposium  
Series, No.266.

## Radiation Stability of Silicon Elastomers

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Silicones form a class of chemical materials intermediate between organic polymers and inorganic glasses. The silicon-oxygen backbone provides good thermal stability, allowing unusually high operating temperatures (up to 270°C) as well as flexibility at low temperatures (down to -70°C). However, in general polysiloxanes are inferior to other elastomers in radiation resistance (1,2). On irradiation polydimethylsiloxane (PMDS) rapidly hardens, due to cross-linking, with evolution of ethane, methane and hydrogen. The introduction of aromatic substituents into the siloxane structure is found to increase resistance to cross-linking (3-6). The relative ease with which cross-links form in a series of polysiloxanes being:

- Si(Me)<sub>2</sub>O -            20
- Si(Ph)(Me)O -        2
- Si(Ph)<sub>2</sub>O -            1

In polymethylphenylsiloxane, cross-linking does occur through the aromatic moiety as well as through the methyl group, but to a much lesser extent. When aromatic groups having greater conjugation are present, such as biphenyl or naphthyl, even greater stability is observed.

In copolymers having both a readily cross-linked structure and an aromatic component, such as styrene-butadiene copolymers, it is found that radiation protection is greatest when the aromatic units are randomly dispersed in the copolymer rather than in segregated units, as with a block copolymer (7,8). In polysiloxanes, the methyl group receives the greatest protection when an aromatic component is attached to the same silicon atom (9).

This study is investigating the possibility of obtaining a silicone polymer having good radiation resistance, with retention of elastomeric properties. The main area of interest is the resistance to radiation of blends and block copolymers in which an aromatic component can form a separate microphase

from the elastomeric silicone component. The influence of this type of morphology upon radiation resistance in silicones has not been studied to date, although the effect of related morphological features and crystallinity have been investigated in some other cases (10,11). In this paper we report preliminary results on the irradiation behavior of blends of polystyrene (PS) and PDMS.

### Experimental

Blends of various compositions of PDMS ( $M_w$ , 650,000;  $M_n$ , 253,000) and PS ( $M_w$ , 100,000) were prepared by dissolution of the homopolymers in tetrahydrofuran, mixing the solutions and then rapidly removing the solvent using a freeze-drier. Blends were dried in a vacuum oven at 55°C, sealed in glass tubes under a nitrogen atmosphere and irradiated, using a  $^{60}\text{Co}$  source, with an absorbed dose rate of 0.2 Mrad  $h^{-1}$  (0.56 Gy  $s^{-1}$ ) at 30°C.

Soxhlet extraction, with toluene as solvent, of the soluble fraction from the cross-linked gels produced by irradiation, was used as a method to determine the radiation cross-linking efficiency,  $G(X)$ , for the homopolymers and blends under investigation. Samples were extracted to constant weight and two or three replicate extractions were carried out.

### Results and Discussion

**Homopolymer PDMS.** Results obtained from the extractions of irradiated samples of the homopolymer PDMS are given in Table I and Figure 1.

Extrapolation of this data yields a value for the incipient gelation ( $r_{\text{gel}}$ ) of 0.3 Mrad. Substitution of this value into Equation 1 gives  $G(X) = 2.48$ .

$$G(X) = \frac{4.83 \times 10^5}{M_w \times r_{\text{gel}}} \quad (1)$$

Use of the Charlesby-Pinner relationship (Equation 2) with this data (Table II, Figure 2) gives  $G(X) = 2.86$

$$S + \sqrt{S} = \frac{2r_{\text{gel}}}{r} \quad (2)$$

Table I. Percent Gel after Soxhlet Extraction of Irradiated PDMS

Dose/Mrad	% Gel
0.55	23.3 ± 0.6
0.99	63.6 ± 2.1
1.67	74.6 ± 0.8
3.41	81.1 ± 1.5
5.03	81.9 ± 1.5
10.1	83.5 ± 0.1
20.2	84.0 ± 1.0

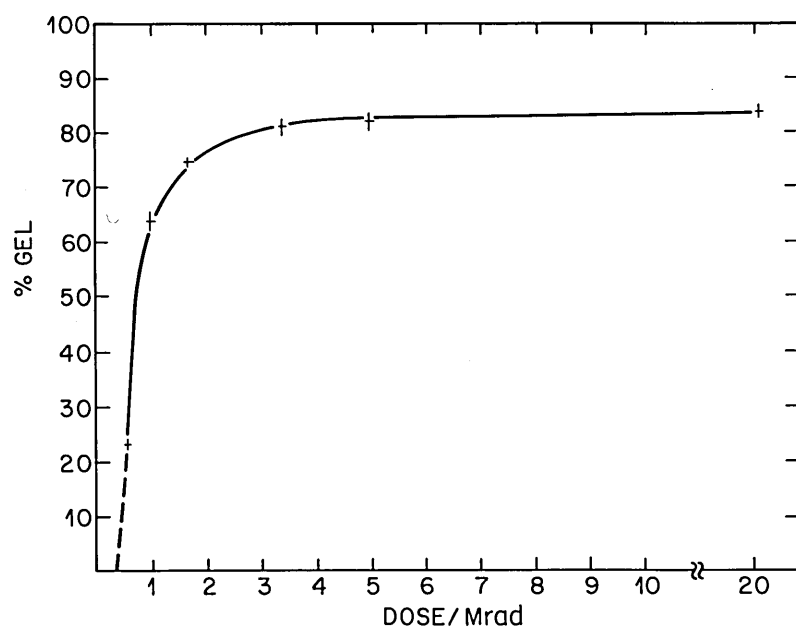
*Figure 1. Irradiation of PDMS*

Table II. Charlesby-Pinner Data for PDMS

Dose/Mrad	$\frac{1}{r}$	Gel Fraction	Sol Fraction (S)	$\sqrt{S}$	$S + \sqrt{S}$
0.55	1.818	0.233	0.767	0.876	1.643
0.99	1.010	0.636	0.364	0.603	0.967
1.67	0.600	0.746	0.254	0.504	0.758
3.41	0.293	0.811	0.189	0.435	0.624
5.03	0.199	0.819	0.181	0.425	0.606
10.0	0.100	0.835	0.165	0.406	0.571
20.1	0.049	0.840	0.160	0.400	0.560

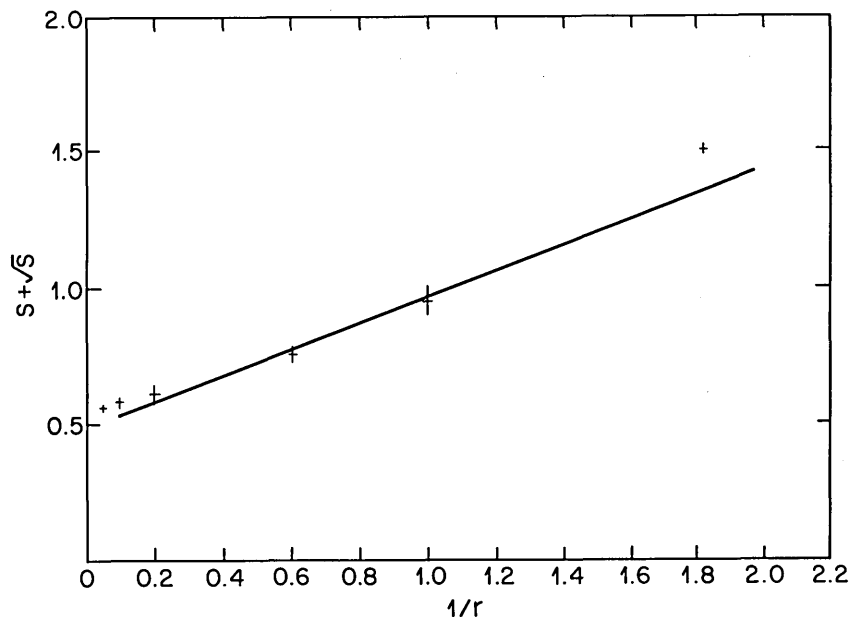


Figure 2. Charlesby-Pinner plot for PDMS

These results for  $G(X)$  in PDMS are in good agreement with other reported values which range from 2.5-2.8 (12).

The Charlesby-Pinner relationship is regarded as empirical, applicable in polymers that have a random molecular weight distribution, and where the cross-link density is proportional to dose. When the distribution is broader than the random value, the plot deviates from linearity (13,14). For the PDMS under investigation  $M_w/M_n = 2.57$ , and a deviation from linearity is evident. If irradiation is continued to high doses, a linear relationship is observed. The gradient in the high dose region has been used to calculate  $r_{gel}$ . Extrapolation of the data to  $\frac{1}{r} = 0$  have an intercept at  $S + \sqrt{S} > 0$ . This deviation of the intercept from zero is generally taken as an indication of simultaneous main chain scission in addition to cross-linking.

**Homopolymer PS.** In contrast to PDMS, for doses up to 200 Mrad the PS sample under investigation remained completely soluble (Table III), emphasizing the resistance to irradiation of PS compared to PDMS. Calculation of  $G(X)$  from samples of a PS of higher molecular weight ( $M_w$ , 150,000) gave a value of 0.028 which is in agreement with other reported results (12). In the blends produced from these homopolymers it would be expected that the component to undergo cross-linking would be the polysiloxane.



Table III. Solubility Data For Polystyrene

Dose/Mrad	% Gel After Extraction	
	$M_w = 100,000$	150,000
10	0	0
20	0	0
30	0	0
50	0	0
75	0	$51.0 \pm 0.5$
100	0	$73.0 \pm 1.0$
200	0	$80.2 \pm 0.6$

*Blends of PS and PDMS.* Irradiation of blends of PS and PDMS revealed interesting results. As expected  $r_{\text{gel}}$  increased, hence  $G(X)$  decreased as increasing amounts of PS were incorporated into the blends. This is attributed to protection of the PDMS by PS. However, at low % PS an enhanced protecting effect was observed (Table IV).

Further, when blends of various compositions were irradiated at a constant dose, the results indicated that the components do not act independently, i.e. they depart from an "additive" behavior.

For example, irradiation of blends at 1.55 Mrad shows that at compositions of >7% PS, gel formation decreases with increasing PS content, but not as predicted by an additive rule (Table V, Figure 3). At compositions of <7% PS a significant decrease in gel formation is observed.

Table IV. Variation of  $r_{\text{gel}}$  and  $G(X)$  With Polymer Composition

Polymer	$r_{\text{gel}}/\text{Mrad}$	$G(X)$
PDMS	0.3	2.48
3% PS blend	1.4	0.53
5% PS blend	1.1	0.67
7% PS blend	0.9	0.82
20% PS blend	0.6	1.24

Table V. Gel Formation In Blends Irradiated at a Constant Dose (1.55 Mrad)

Polymer	% Gel	% Gel if "Additive"
PDMS	74.5	74.5
3% PS blend	49.5	72.5
5% PS blend	60.0	71.0
7% PS blend	83.5	69.5
15% PS blend	58.5	63.5
25% PS blend	30.5	56.0
31% PS blend	21.0	52.0
50% PS blend	0	37.5
PS	0	0

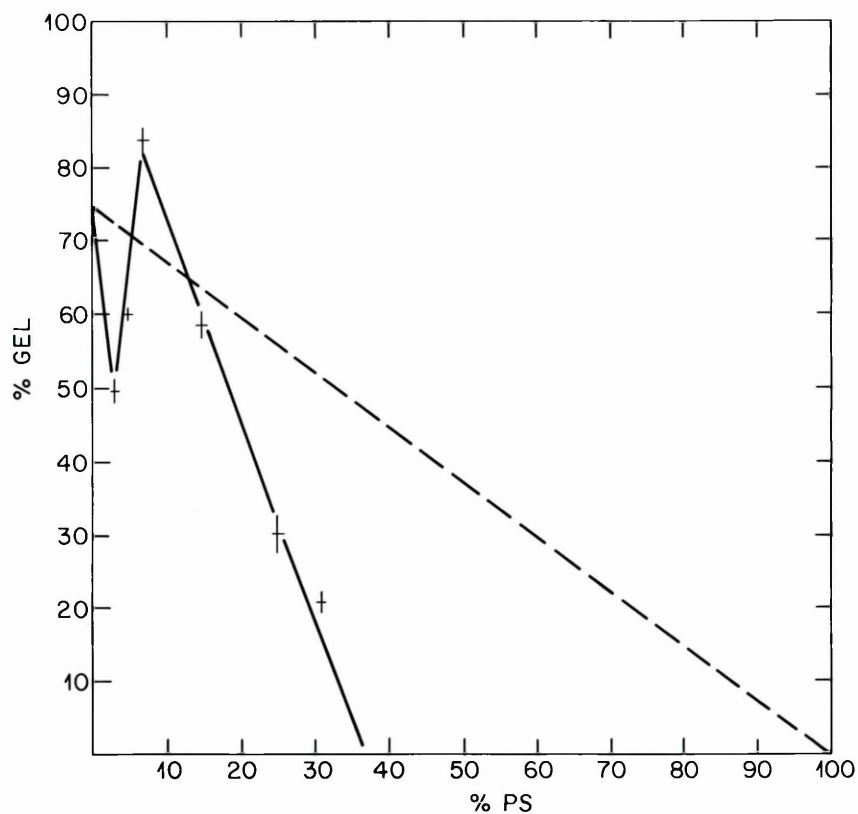


Figure 3. Irradiation of PS/PDMS blends at 1.55 Mrad. Experimental data (—); "additive" line (---)

This effect is observed at other low absorbed doses (Figure 4) and in each case a minimum of gel formation occurs at around 3% PS. However, it is noticeable that as the absorbed dose is increased the extent of this protective effect decreases.

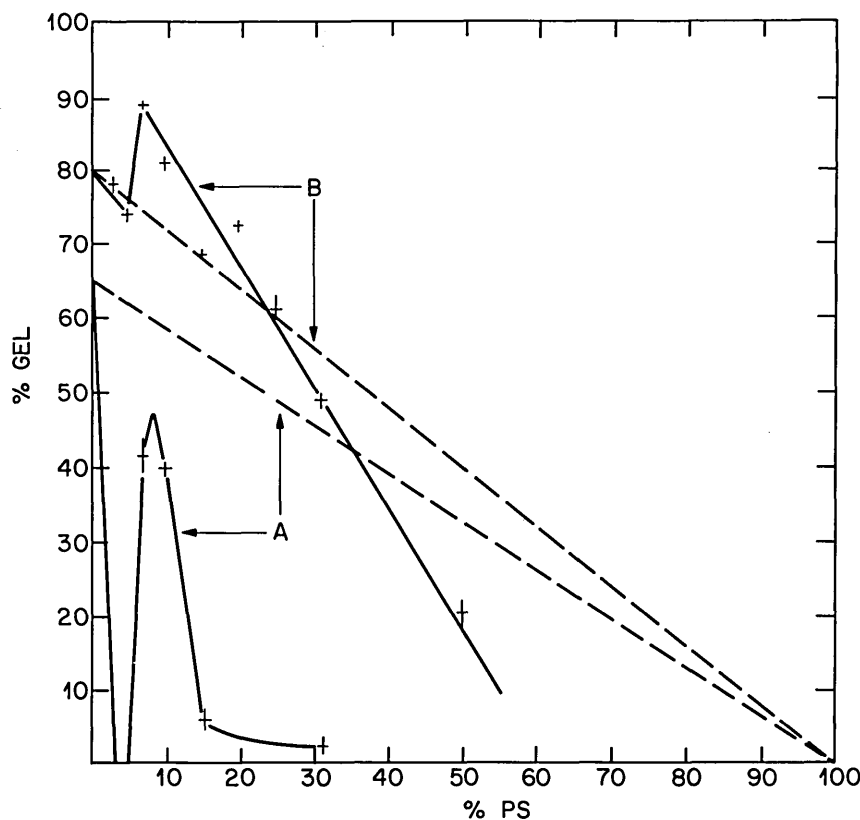


Figure 4. Irradiation of PS/PDMS blends at: A, 1.0 Mrad; B, 3.28 Mrad. Experimental data (—); "additive" line (---)

Also, it is apparent that the gel content of irradiated blends can be higher than that expected if the gelation was entirely due to the reaction of homopolymer PDMS. We can eliminate the possibility that PS is responsible for this deviation since previous results indicate that gel formation in the PS used does not take place below 200 Mrad. There are two possible explanations; the first is that some PS is "trapped" (not bound) within the PDMS gel, and cannot be extracted from the matrix. The other is that the PDMS is undergoing a higher degree of cross-linking, as a result of a reduction in chain scission.

The considerable stabilizing effect observed at low % PS, possibly is related to the compatibility of the components in the blends. From scanning electron microscopic studies, it is clear that all compositions, a two phase

system exists with PS dispersed in the PDMS matrix as very small regular spheres. Initial observations suggest that as the PS content increases, the PS spheres initially increase in number, then increase in size. It is possible that the enhanced protective effect at low % PS is due to either (a) stabilizing chemical reactions occurring at the interface of the two phases, or (b) mixing of low molecular weight PS within the siloxane matrix, or both.

Morphological investigations and comparisons with block copolymers are in progress to gain further understanding of the radiation protection of silicone elastomers.

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