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MONKS, Howard Hulse.

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A thesis entitled

CYCLOPOLYMERISATION STUDIES:

THE SYNTHESIS AND CHARACTERISATION OF SELECTED

DI-UNSATURATED MONOMERS AND A STUDY OF THEIR POLYMERISATION

presented by

HOWARD HULSE MONKS A.R.I.C.

in part fulfilment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

of the

COUNCIL FOR NATIONAL ACADEMIC AWARDS

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Howard H. Monks.

AUTHORS NOTE

The formulae occurring in the text are referred to in the form (1.I), (2.II), (3.III), (4.IV), etc. The arabic numeral refers to the Chapter, the roman numeral to the number of the formula in that Chapter. The charts found at the end of the thesis are lettered A to H inclusive and J to K inclusive. The formulae therein are referred to as (AI), (BII), (CIII), etc., the letter indicating the particular chart.

SYNOPSIS

The literature covering the cyclopolymerisation reaction is briefly surveyed with emphasis on the methods used to determine ring size in cyclopolymers.

Part 1 of this thesis describes the synthesis and polymerisation of N,N'-divinylureas of general structure:

$CH_2=CH-\underset{\displaystyle R}{\overset{|}{N}}-CO-\underset{\displaystyle R}{\overset{|}{N}}-CH=CH_2$, where $R=R=CH_3$ or C_6H_5 and $R+R=-CH_2-CH_2-$ or $-CH_2-CH_2-CH_2-$. The cyclic N,N'-divinylureas, 1,3-divinylimidazolid-2-one ($R+R=-CH_2-CH_2-$) and 1,3-divinylhexahydropyrimid-2-one ($R+R=-CH_2-CH_2-CH_2-$), gave insoluble, cross-linked polymers which confirmed the findings of Crawshaw and Jones[55]. The acyclic N,N'-divinylureas, 1,3-diphenyl-1,3-divinylurea ($R=R=C_6H_5$) and 1,3-dimethyl-1,3-divinylurea ($R=R=CH_3$), could not be polymerised under a variety of conditions. To explain the failure of the cyclic N,N'-divinylureas to cyclopolymerise, Crawshaw and Jones proposed a continuous coplanar overlap of the π orbitals of the vinyl and carbonyl groups with p_z orbitals on the nitrogen atoms. Evidence to support this proposal has been obtained from ultraviolet, n.m.r. and infrared spectroscopy. The failure of the acyclic N,N'-divinylureas to polymerise has also been explained on the basis of this overlap. Addition of a radical initiator to 1,3-diphenyl-1,3-divinylurea produces a resonance stabilised radical which does not homopropagate and which inhibits or retards the polymerisation of other monomers. A study of the copolymerisation behaviour of N,N'-divinylureas supports this proposal. Although 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one form copolymers with ethyl acrylate from which reactivity ratios and Q and e values have been determined, 1,3-diphenyl-1,3-divinylurea inhibits the polymerisation of these N,N'-divinylureas and ethyl acrylate and retards the polymerisation of styrene. For 1,3-dimethyl-1,3-divinylurea it is suggested that conjugation does not permit intramolecular cyclopolymerisation and that a steric effect prevents the intermolecular reaction. A study of the hydrolysis of N,N'-divinylureas to acetaldehyde and the corresponding urea is included.

Part 2 describes the synthesis and cyclopolymerisation of divinyl phenylphosphonate and divinyl methylphosphonate. ^{31}P N.m.r. spectroscopy is shown to be able to quantitatively determine phosphorus atoms in different chemical environments and is applied to the determination of

five- and/or six-membered rings in the cyclopolymers from divinyl phosphonates. Using this technique poly(divinyl phenylphosphonate) was found to contain both five- and six-membered rings and poly(divinyl methylphosphonate) only six-membered rings. Telomerisation of divinyl phosphonates gave di-adducts rather than cyclic mono-adducts.

CONTENTS

INTRODUCTION

The polymerisation of non-conjugated dienes produces either cross-linked insoluble polymers, linear polymers containing approximately one residual double bond in each structural repeating unit or cyclopolymers.

The term cyclopolymerisation has been introduced to denote a chain-growth mechanism involving alternating intramolecular and intermolecular steps (Figure 1). This mechanism was proposed by Butler and Angelo[1] to explain the formation of soluble, and hence linear, saturated polymers from diallyl quaternary ammonium salts.

Confirmation of the proposed structures for poly(diallylammonium bromide) and poly(diallyldimethylammonium bromide) involved degradation to products which could only be explained by assuming cyclic units containing a piperidinium ring[2]. After the initial investigations by Butler, it was soon found that symmetrical 1,5- or 1,6-dienes generally gave soluble fully saturated polymers, the repeating unit being proposed as a five- or six-membered ring, respectively. Marvel and co-workers [3-5] proposed cyclic structures for the polymers from hepta-1,6-diene and related compounds on the basis that partial dehydrogenation of the polymers gave products whose infrared and ultraviolet spectra were characteristic of meta-substituted aromatic rings.

The possibility that some degree of cyclisation had occurred during the polymerisation of non-conjugated dienes was reported [6-13] before the work of Butler, however, the examples did not include any 1,6-dienes. Walling[6] commented that the gel points of some diene polymerisations occurred later than those predicted because the calculation failed to include factors accounting for occasional cyclisation. Simpson, Holt and Zetie[7] found 40% cyclisation in the polymerisation of diallylphthalate which agreed with the statistical calculations of Haward[8]. Owia and Ogota[10] later found that polymerisation of diallylphthalate in solution gave 80% cyclisation.

Since the original work on cyclopolymerisation the scope of the reaction has been extended to a wide variety of symmetrical, unsymmetrical and heterocyclic monomers. These reactions have been summarised in several reviews. Butler[14] in the U.S.A. and Matsoyan[15], U.S.S.R., have published reviews dealing mainly with chemical and structural investigations of cyclopolymers up to 1966. A review surveying the literature to 1972 has been published by Corfield[16] and one on the kinetics and mechanism of cyclopolymerisation by Gibbs and Barton[17].

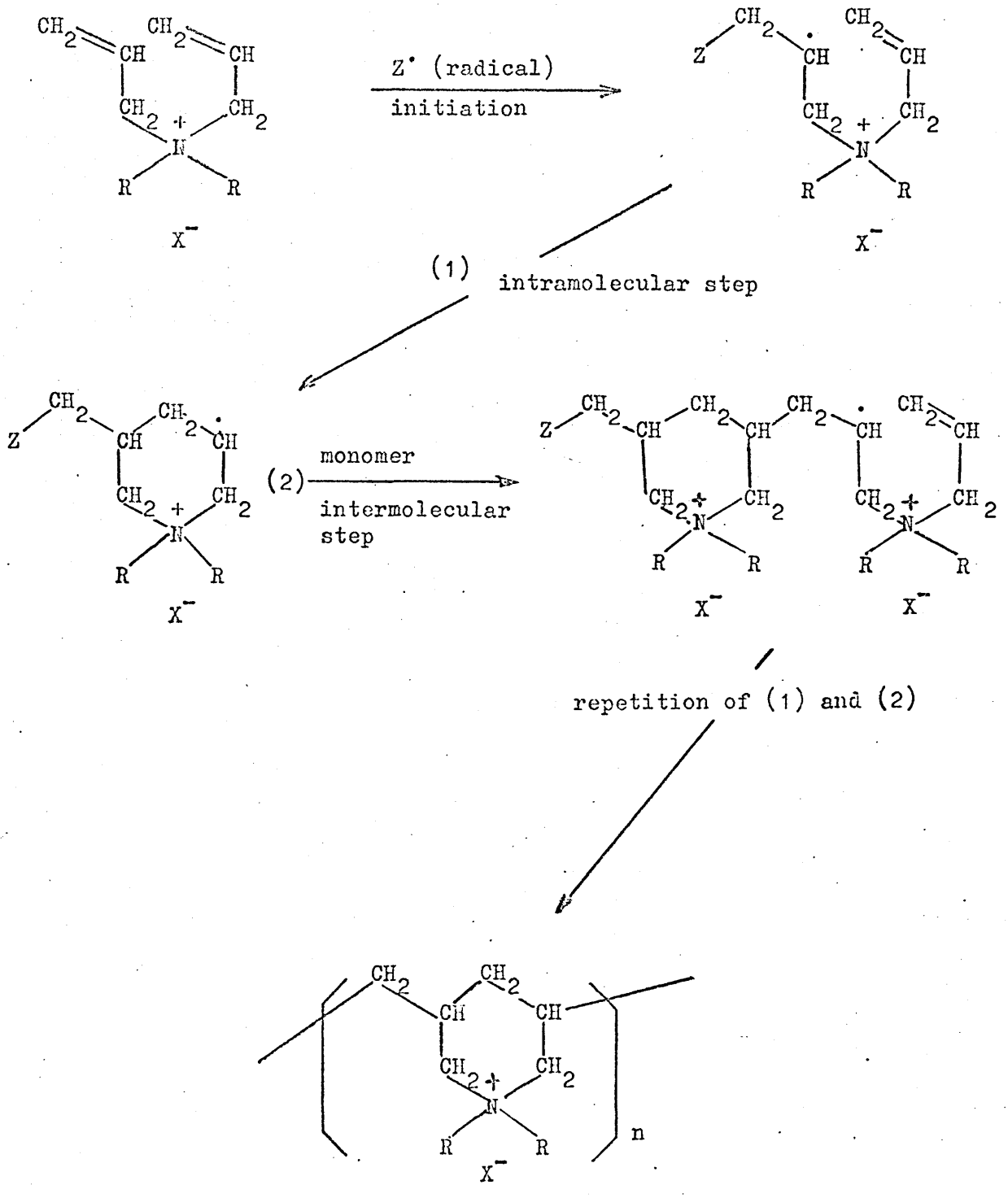


Figure 1.

Proposed mechanism for the cyclopolymerisation of diallyl quaternary ammonium salts.

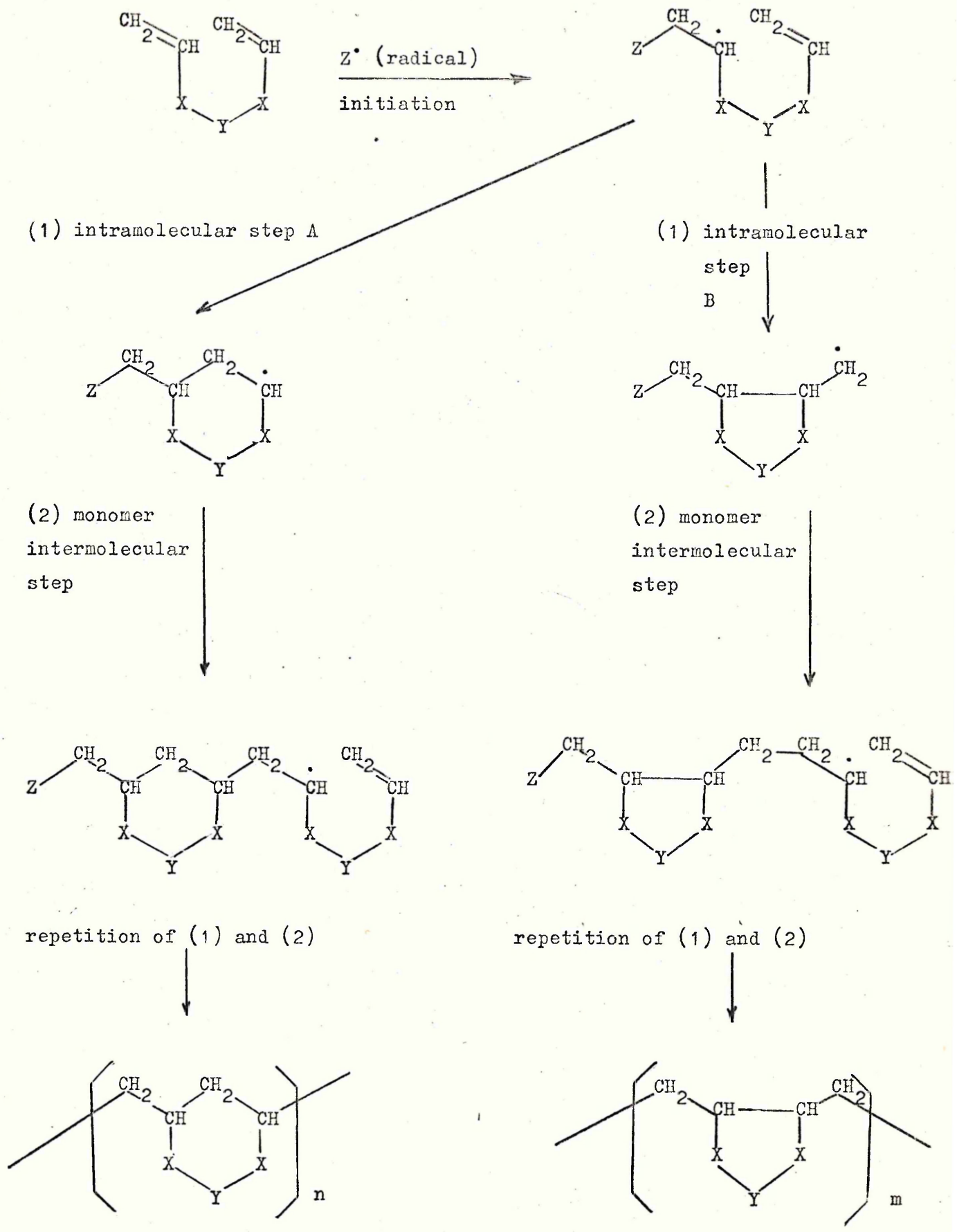
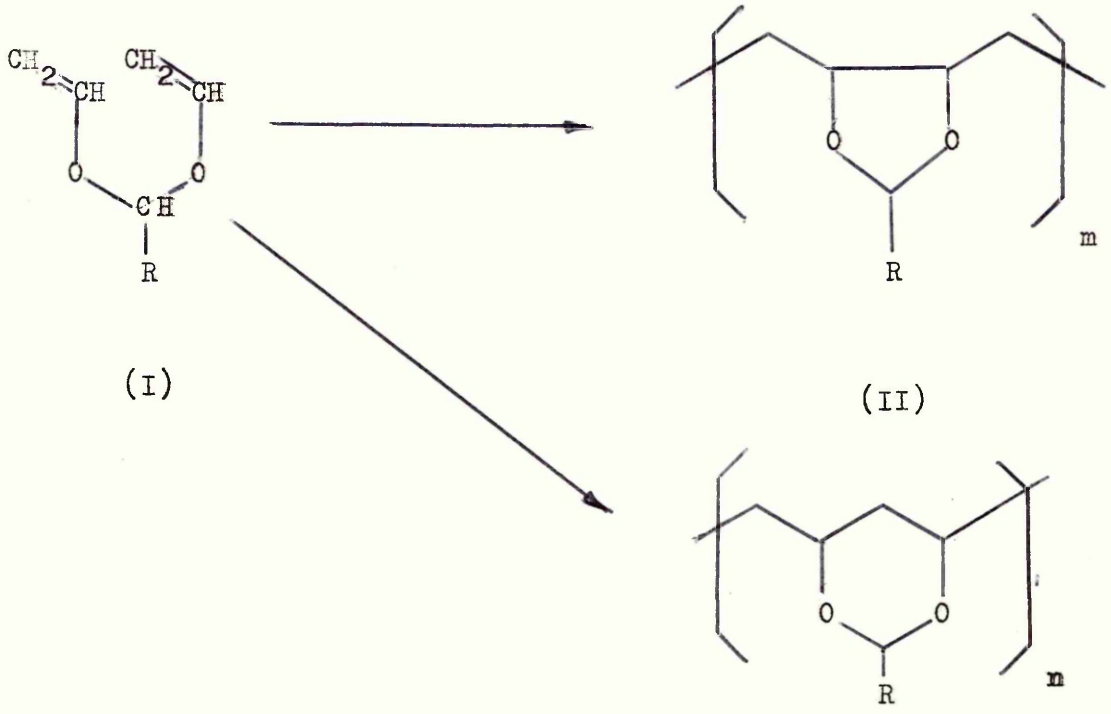


Figure 2.

Cyclopolymerisation of 1,6-dienes to polymers containing five- or six-membered rings.

Although a six-membered ring repeating unit has been proposed for the structure of cyclopolymers from 1,6-dienes[1-6,18,19], two different cyclic structures are possible; either a five- or a six-membered ring repeating unit (Figure 2). Arbuzova and Sultanov [20,21] found that the polymerisation of divinyl acetals (I) gave polymers containing both five- and six-membered rings, (II) and (III) respectively.

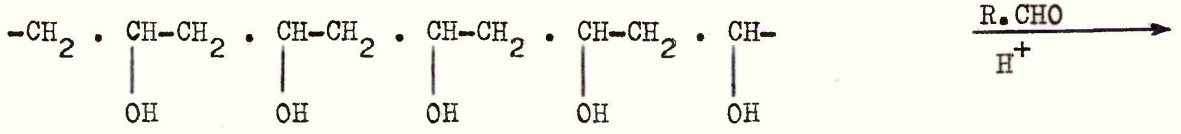


(I)

(II)

(III)

Poly(vinyl acetals) (V) are usually produced by the acid-catalysed condensation of poly(vinyl alcohol) (IV) with aldehydes[22]. Complete acetal formation does not take place since some hydroxyl groups become isolated and have no opportunity to form a cyclic acetal. Calculations show that 13.5% of the total hydroxyl groups should remain unreacted. However poly(vinyl acetals) prepared by cyclopolymerisation of divinyl acetals gave complete acetals containing no pendant unreacted groups [20,21,23-32].



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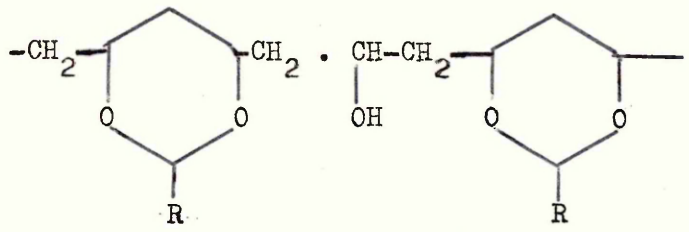
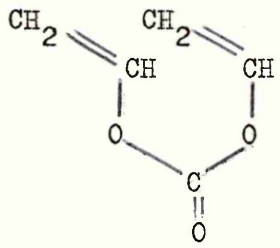


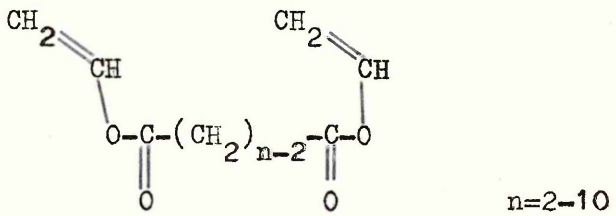
(V)

A direct determination of the distribution of five- and six-membered cyclic units in poly(vinyl acetals) prepared by cyclopolymerisation can be effected by hydrolysis of the cyclopolymer followed by analysis of the derived poly(vinyl alcohol) for 1,2- and 1,3-glycol content. The percentage of 1,2-diol units in poly(vinyl alcohol) can be determined from the consumption of periodate[33] or by viscometric methods[34] following cleavage. Since 1,2-glycols are derived from five-membered rings and 1,3-glycols from six-membered rings the analysis gives the five- and six-membered cyclic units in the cyclopolymer directly (Figure 3).

Matsoyan and co-workers[23-32] used this technique to determine the five- and six-membered cyclic units in a series of poly(vinyl acetals). Kikukawa[35-37] determined the 1,2-glycol content in poly(vinyl alcohol) derived from divinyl carbonate (VI) and divinyl esters of dibasic acids (VII) from the periodate consumption.



(VI)



n=2-10

(VII)

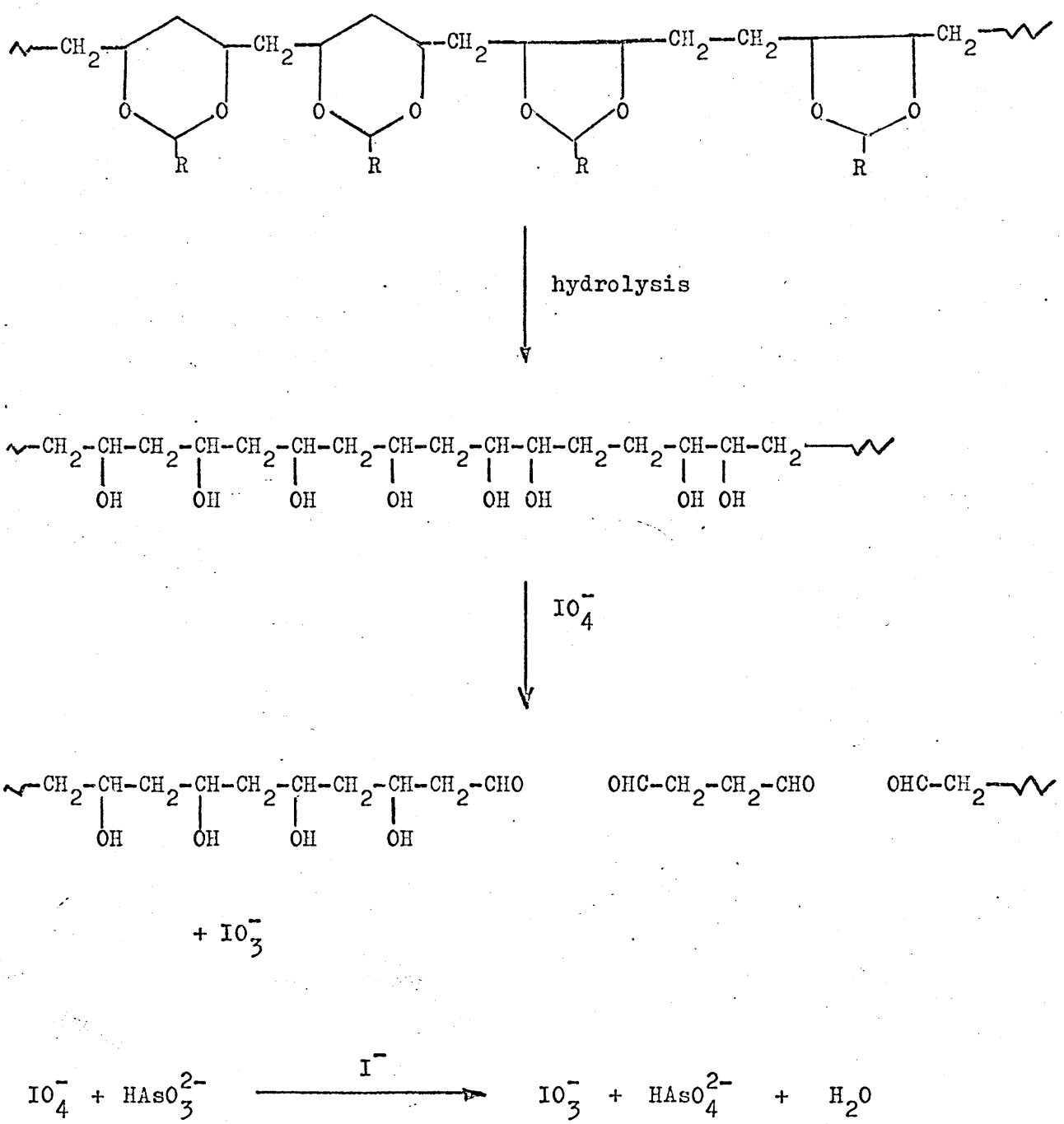
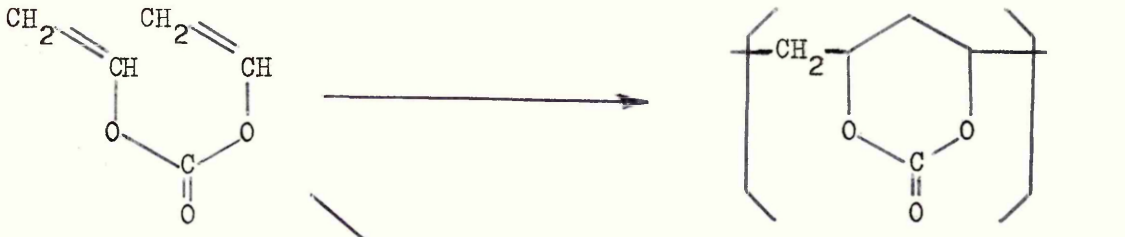


Figure 3

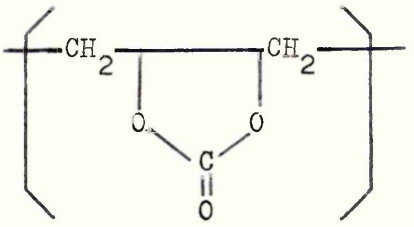
Reaction scheme for the determination of the 1,2-glycol content and hence 5-membered ring content in poly(vinyl acetals).

Divinyl carbonate (VI), a 1,6-diene, could give either five- (VIII) or six-membered rings (IX) on cyclopolymerisation.



(VI)

(VIII)

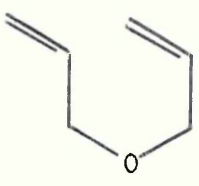


(IX)

Kikukawa[36] found values ranging from 6-23% of five-membered rings dependant on polymerisation time.

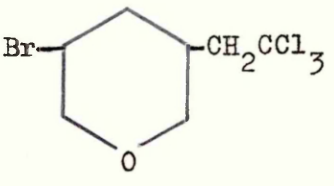
An indirect method of investigation of ring size in cyclopolymers is by the free radical addition of various addenda to the 1,6-diene monomer. However correlation of these telomerisation reactions with the precise structure of the cyclopolymers is far from satisfactory. The assumption is made that the ring size in cyclic monomeric products (telomers) is the same as in the cyclopolymerisation of the monomer, this may not always be the case.

Friedlander[38,39] reported the exclusive formation of six-membered cyclic monomeric products (XI) in the free radical addition of various addenda to 1,6-dienes (X). This work was in agreement with the findings of Butler[1] and Marvel[3-5] where soluble polymers were found from 1,6-dienes and from the evidence six-membered rings postulated as the repeating unit.



(X)

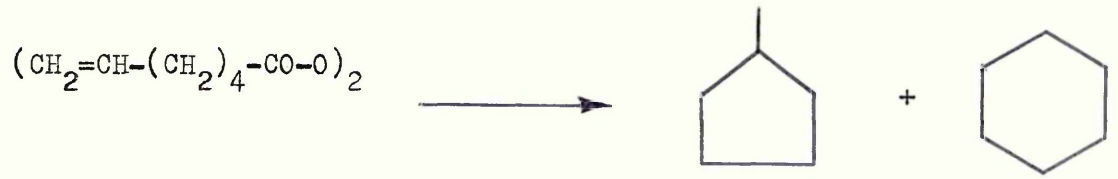
$BrCCl_3$ / ABIN →



(XI)

As a result of Friedlanders work, the structures of most new cyclopolymers from 1,6-dienes were given six-membered ring structures. In many cases no proof of structure was given or other ring size considered.

However, when Lamb, Ayers and Toney[40] observed predominantly five-membered rings in the thermal decomposition of 6-heptenoyl peroxide (XII) in toluene the question of ring size in radical addition reactions was reconsidered.



(XII) 94% 2.6%

Several workers then discovered that in free radical cyclisations where six-membered rings were expected mixtures of five- and six-membered rings or exclusively five-membered ring formation occurred.

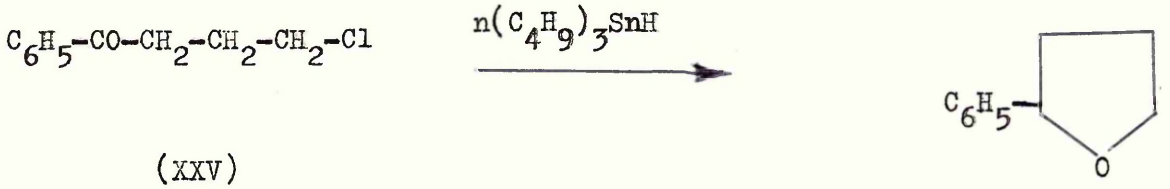
Brace[41] found that in cyclisations of 1,6-heptadiene (XIII) with perfluoroalkyl halides results were obtained which contradicted Friedlander's earlier work (XIV).

(XIII) cis and trans (XIV)

+ straight chain adducts.

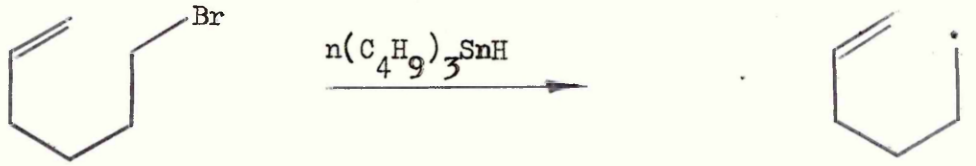
Brace then extended his work to include diallyl ether[42] (XV) where he again found that only five membered rings were formed (XVI). He suggested that the driving force of the reaction was the stability of the final product where the CH_2-I bond in a five-membered ring is 33 kJ mol^{-1} more stable than CH-I in a six-membered ring. Similarly studied were 1,6-heptadiene (XVII) with bromotrichloromethane, carbon tetrachloride and chloroform[43]; ethyl diallylacetate[44] (XVIII) with perfluoroalkyl halides or carbon tetrachloride and diall cyanamide[45] (XIX) with perfluoroalkyl iodides. In each case predominantly five-membered ring products were formed, (XX), (XXI) and (XXII) respectively.

Aso[46,47] investigated the cyclisation of diallyl ether and divinyl formal (XXIII) observing five-membered rings (XXIV). Kuivila[48] was the first to report the use of organotin hydrides as a method to effect free radical cyclisation. The reduction of 3-chlorobutyrophenone (XXV) gave a five-membered ring product, 2-phenyltetrahydrofuran (XXVI).



(XXV) (XXVI)

Walling[49] and co-workers also used tri-n-butyltin hydride as a means of producing radicals (XXVIII) from 6-bromo-1-hexene (XXVII) and other alkenyl halides.



(XXVII) (XXVIII)

They found that five-membered ring closure was the preferred reaction even in the case of α,β-unsaturated esters where the six-membered ring would be favoured by the formation of a highly resonance-stabilized radical (Table 1).

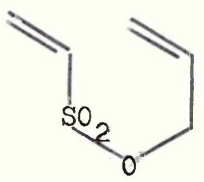
Table 1

Ring closures of alkenyl halides by tributyltin hydride[49]

Halide	Products (%)
6-Bromo-1-hexene	1-hexene (7), methylcyclopentane (78), cyclohexane (trace)
2-Bromoethylallyl ether	ethylallyl ether (4), 3-methyltetrahydrofuran (84)
6-Bromo-6-methyl-1-heptene	6-methyl-1-heptene (35), 1,1,3-trimethylcyclopentane (47), 1,1-dimethylcyclohexane (0.6)
2-Bromoethyl crotonate	ethyl crotonate (35), α-ethyl-γ-butyrolactone (13)
Di(2-bromoethyl) maleate	α-carboxymethyl-γ-butyrolactone (-)

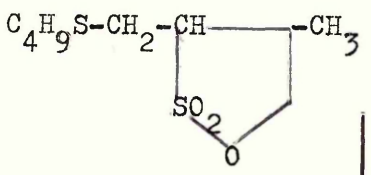
Mercaptans and other thio-compounds have been extensively used as free radical addenda to double bonds[50]. De-Witte and Goethals[51] used butyl mercaptan in cyclotelomerisation reactions with allyl ethenesulphonate (XXIX) finding only five-membered sultones (XXX) and sulphonium salts (XXXI). Previously in the cyclopolymerisation of allyl ethenesulphonate and allyl allylsulphonate[52-54] they proposed only six-membered rings despite the possibility of five- and seven-membered rings being formed respectively.

$$R^{\bullet} + C_4H_9SH \longrightarrow RH + C_4H_9S^{\bullet}$$

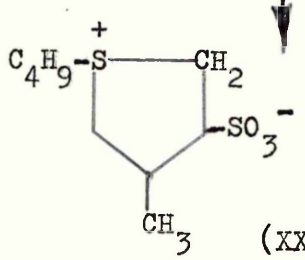


(XXIX)

$C_4H_9S^{\bullet}$



(XXX)



(XXXI)

Thus from the telomerisation studies of 1,6-dienes it may be concluded that the repeating units in cyclopolymers probably contain at least some, if they are not all five-membered rings. However, it remains to be proved that cyclotelomerisation and cyclopolymerisation reactions of non-conjugated dienes are related. It would be desirable therefore to study further the cyclotelomerisation of dienes which can be cyclopolymerised to polymers in which the ring size of the cyclic units can be determined directly.

In Part 1 of this thesis a study of the structure and polymerisation of N,N'-divinylureas is described. This work was carried out to try and understand why these compounds (1,6-dienes) failed to cyclopolymerise and only produced cross-linked polymers[55].

Part 2 describes one approach toward a method which would enable a comparative study of cyclotelomerisation and cyclopolymerisation reactions to be carried out. The work illustrates how ^{31}P n.m.r. can be used to determine directly the ring size in telomers and cyclopolymers from certain phosphorus containing 1,6-dienes.

RESULTS AND DISCUSSION

PART 1

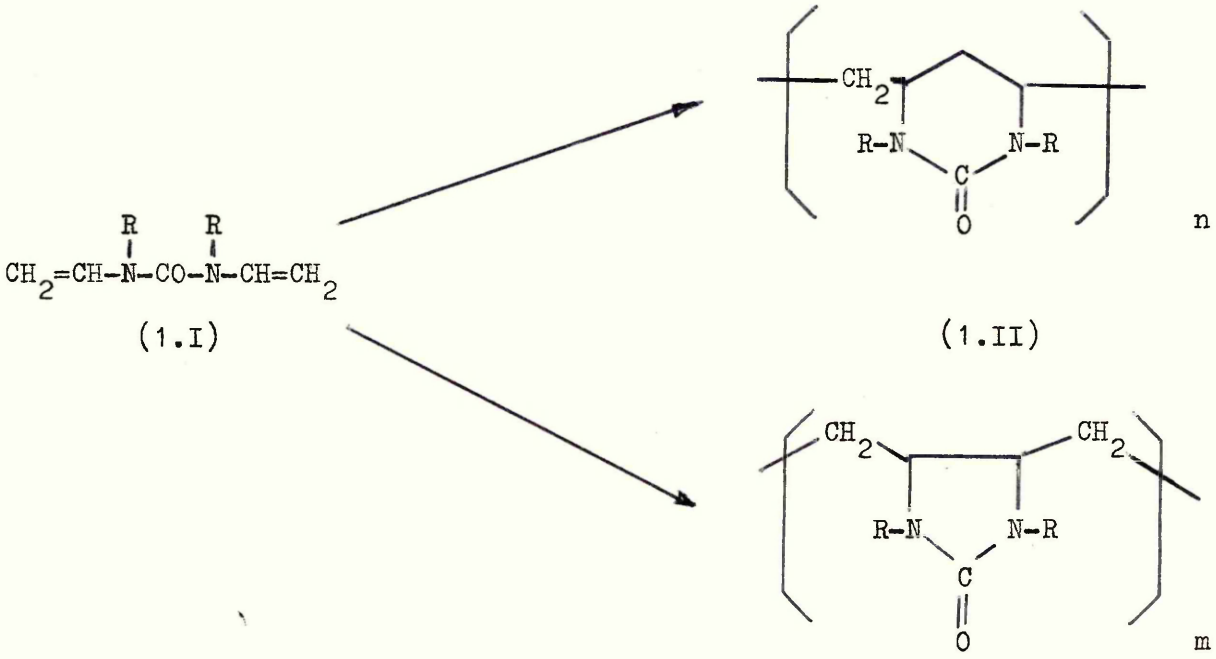
The Synthesis, Polymerisation and Structural Investigation of N,N'-divinylureas

CHAPTER 1

Monomer Synthesis and Homopolymerisation.

1.1 Introduction.

N,N'-divinylureas (1.I) are examples of 1,6-dienes and as such might be expected to yield linear polymers by the cyclopolymerisation mechanism, under suitable conditions. By analogy with 1,6-dienes, the cyclopolymers would be expected to contain repeating units consisting of six-membered cyclic ureas (1.II), five-membered cyclic ureas (1.III) or a mixture of both.

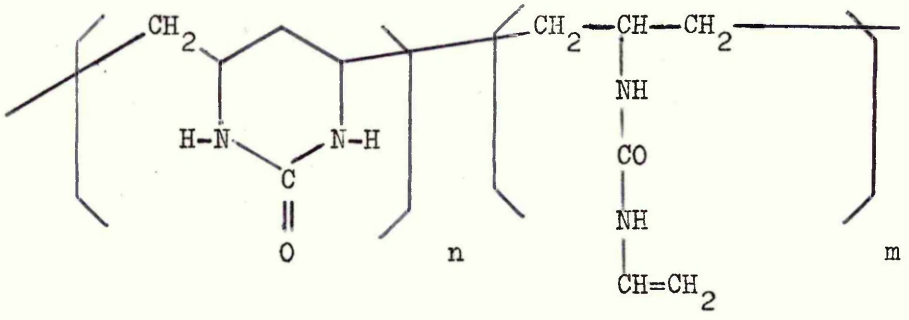


(1.I) (1.II)

(1.III)

With such repeating units, the polymers would be fully saturated, soluble and fusible; typical properties of cyclopolymers.

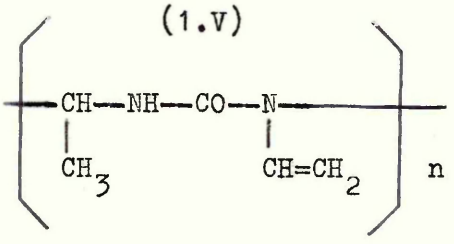
However, the results reported for N,N'-divinylurea polymerisations indicate that soluble polymers are not readily formed. Overberger and Ishida[56] reported that free-radical initiated polymerisations of N,N'-divinylurea gave insoluble polymers, (presumably cross-linked), but that their infrared spectra indicated a dominant cyclic structure with some pendant vinyl groups (1.IV).



(1.IV)

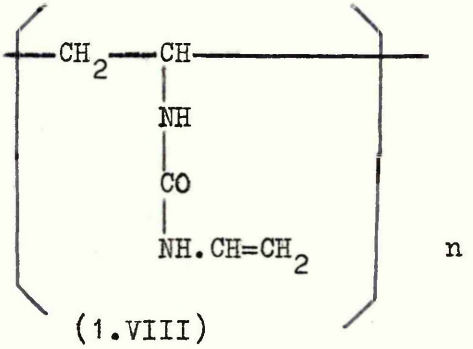
Overberger, Montaudo and Ishida later reported that acid-catalysed polymerisation of N,N'-divinylurea gave a soluble polymer[57], which reverted to an insoluble polymer on standing overnight. However this time the structure they proposed for the polymers suggested that N,N'-divinylurea (1.V) reacted via its tautomeric form (1.VI) leading to repeating units containing residual double bonds (1.VII) rather than structures (1.VIII) or (1.II, R=H).

(1.V)



(1.VII)

(1.VI)



(1.VIII)

Cairns[58], Schuster and Gassenmeier[59] reported polymerisations of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one as giving cross-linked polymers, but since these monomers were investigated before the discovery of the cyclopolymerisation mechanism, cyclic units were not expected nor were the polymers examined for such units. Crawshaw and Jones[55] re-investigated 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one with particular respect to the potential

of these monomers to give cyclopolymers. Using a variety of initiators and conditions favouring cyclopolymerisation they again found that only cross-linked polymers were produced.

In an attempt to offer some explanation for the non-cyclopolymerisation of N,N'-disubstituted-N,N'-divinylureas, Crawshaw and Jones[55] proposed for their structure a coplanar situation produced by conjugation of the lone pair electrons on the nitrogen atoms with the carbonyl and vinyl double bonds, (Figure 1.1).

Such a planar arrangement would tend to favour intermolecular propagation and the cross-linked polymers obtained experimentally, rather than the cyclopolymerisation mechanism.

This Chapter describes the synthesis of 1,3-divinylimidazolid-2-one, 1,3-divinylhexahydropyrimid-2-one, 1,3-diphenyl-1,3-divinylurea and 1,3-dimethyl-1,3-divinylurea, which has not been prepared previously, and further polymerisation studies of these monomers. These studies confirm the behaviour of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one to produce cross-linked polymers, as reported by Crawshaw and Jones[55]. However, 1,3-diphenyl-1,3-divinylurea and 1,3-dimethyl-1,3-divinylurea did not polymerise at all under the conditions studied and explanations are offered for this behaviour. The polymerisation of 1-ethyl-3-vinyl-imidazolid-2-one, which was synthesised to assist in the structural investigation of N,N'-divinylureas, is also described.

1.2 Synthesis and Polymerisation of 1,3-Divinylimidazolid-2-one.

1,3-Divinylimidazolid-2-one was prepared essentially by the method of Crawshaw and Jones[55]. The method chosen involved the Hofmann degradation route to the N,N'-divinylurea because of the substantially better yield over that obtained by the Cope reaction, (Chart A).

Imidazolid-2-one was converted into the di-sodium salt using sodium hydride in N,N -dimethylformamide, and N,N -dimethyl-2-chloroethylamine was added giving the di-tertiary amine 1,3-bis(N,N -dimethylaminoethyl) imidazolid-2-one (AI). The di-tertiary amine was converted without purification to the di-quaternary ammonium iodide (AII). Conversion of this iodide to the corresponding di-quaternary ammonium hydroxide (AIII) was effected using silver oxide in water. Concentration of the solution on a rotary evaporator under reduced pressure gave a brown oil which solidified on cooling and crystallisation from light petroleum gave a solid which had the correct analysis for 1,3-divinylimidazolid-2-one (AIV).

Confirmatory evidence for the structure was obtained from infrared, n.m.r. and mass spectrometry. The infrared and n.m.r. spectra were

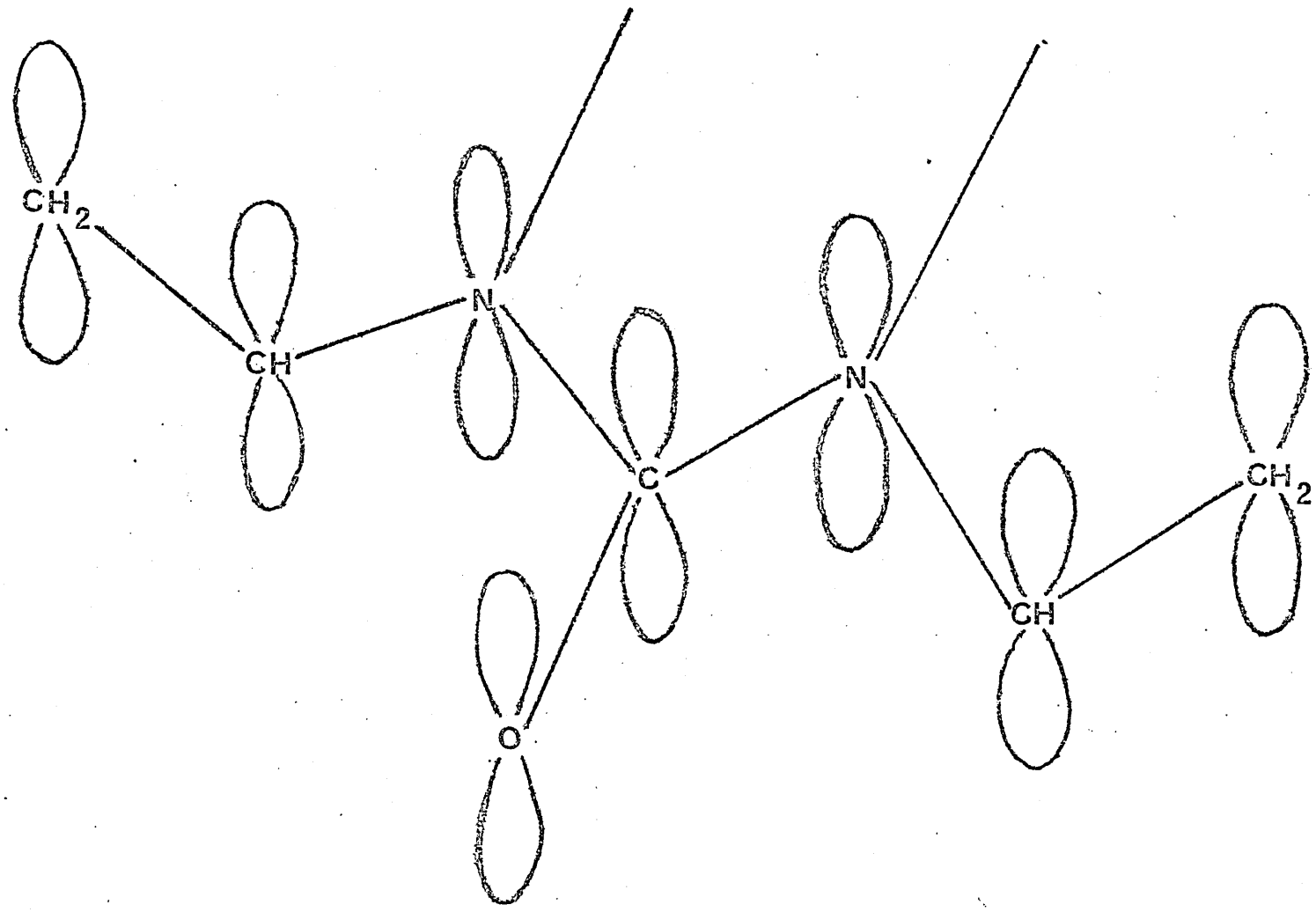


Figure 1.1

Proposed coplanar overlap of the CH_2=CH-N-CO-N-CH=CH_2 orbital system[55].

identical with the spectra obtained by Jones[60]. The mass spectrum showed a molecular ion at m/e 138 as the strongest (base) peak indicative of a stable cyclic structure. The fragmentation pattern is consistent with the structure: 112^+ being loss of C_2H_2 by a McLafferty re-arrangement; 111^+ the loss of CH_2=CH-; 110^+ loss of CO from the ring. The latter fragmentation can be used to verify the molecular ion by the observation of a metastable ion at m/e 87.7, using the relationship:

$$\frac{(\text{fragment ion})^2}{\text{parent ion}} = \text{metastable ion} \qquad \frac{110^2}{138} = 87.68$$

The polymerisation of 1,3-divinylimidazolid-2-one was achieved using various initiation techniques, the results and conditions being summarised in Table 1.1. The polymers were isolated either directly from the polymerisation reaction, if their insolubility caused spontaneous precipitation, or by dropwise addition into vigorously stirred ether or light petroleum.

Table 1.1.

Polymerisation of 1,3-divinylimidazolid-2-one.

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C	Conversion[a] %
0.5	toluene (5)	BF_3[b]	-	5	-80	31
0.5	-	DTBP[c]	1.41	3	130	90
0.5	toluene (10)	BF_3OEt_2	22.6	5	-50	62
0.5	benzene (20)	ABIN[d]	2.0	3	70	47
0.5	benzene (20)	DBP[e]	2.0	3	70	-

[a] estimated gravimetrically

[b] 10 ml of BF_3 gas injected into sample

[c] di-tert. butyl peroxide

[d] azobisisobutyronitrile

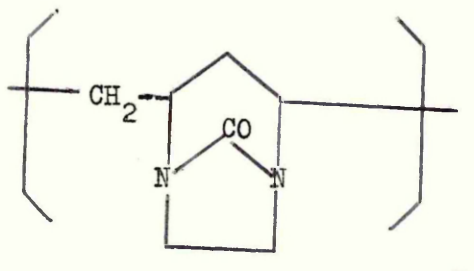
[e] dibenzoyl peroxide

The polymers isolated from all polymerisations were insoluble in a

wide variety of solvents, infusible and hence cross-linked. The infrared spectra of poly(1,3-divinylimidazolid-2-one) showed residual unsaturation, the spectra being almost identical to those of Jones[60]. These results are in agreement with those found by other workers[58,59] who reported insoluble cross-linked polymers.

Various attempts were made to polymerise 1,3-divinylimidazolid-2-one using acid-catalysed initiation, a similar procedure to that of Overberger, Montaudo and Ishida[57]. On addition of a catalytic amount of concentrated sulphuric acid to a solution of 1,3-divinylimidazolid-2-one in acetone an immediate precipitation occurred and a strong smell of acetaldehyde came from the mouth of the pyrex tube. The precipitate had an infrared spectrum different to 1,3-divinylimidazolid-2-one but almost identical to that of imidazolid-2-one. Controlled hydrolysis of 1,3-divinylimidazolid-2-one gave acetaldehyde (characterised as acetaldehyde 2,4-dinitrophenylhydrazone) and imidazolid-2-one. From these and later results (Chapter 4) it would seem unlikely that 1,3-divinylimidazolid-2-one could be polymerised using acid-catalysed initiation as hydrolysis to the corresponding urea and acetaldehyde would be a major competing reaction. In view of this, it is difficult to appreciate how Overberger *et.al*[57] can propose that acid-catalysis produces linear, soluble, polymers for several N-vinylureas. Hart[61], reported that moisture in the atmosphere was sufficient to hydrolyse N-isopropenylurea to acetone and urea!

These polymerisations represent a wider variety of attempts to obtain soluble polymers with a repeating unit containing a bicyclic ring (e.g. 1.IX). They also confirm the results of Crawshaw and Jones[55] indicating the failure of this monomer to cyclopolymerise.



(1.IX)

1.3 Synthesis and Polymerisation of 1,3-Divinylhexahydropyrimid-2-one.

1,3-Divinylhexahydropyrimid-2-one was prepared using an identical sequence of reactions to those used for 1,3-divinylimidazolid-2-one, again essentially by the synthetic route developed by Crawshaw and Jones[55] (Chart B).

2-Ketohexahydropyrimidine (BI) was prepared from 1,3-diaminopropane and urea,[62] and converted using sodium hydride into the di-anion which in turn was converted into 1,3-bis(N,N-dimethylaminoethyl) hexahydropyrimid-2-one (BII) by reaction with N,N-dimethyl-2-chloroethylamine. The di-tertiary amine was converted without purification into a solid dimethiodide (BIII). Reaction of this di-quaternary ammonium iodide with silver oxide in aqueous methanol gave the corresponding di-quaternary ammonium hydroxide (BIV) as a viscous syrup after removal of water and methanol under reduced pressure. Further concentration of the hydroxide under reduced pressure afforded a brown oil which crystallised from light petroleum as a solid with the correct analysis for 1,3-divinylhexahydropyrimid-2-one (BV).

The structure was confirmed using evidence obtained from infrared n.m.r. and mass spectrometry. The infrared and n.m.r. spectra were identical with the spectra obtained by Jones[60]. The mass spectrum showed a molecular ion m/e 152 as the base peak, indicative of a stable cyclic structure. The fragmentation pattern is consistent with the structure: 126^+ being loss of C_2H_2 by a McLafferty re-arrangement; 125^+ loss of $-CH=CH_2$; 83^+, the second most abundant peak in the spectrum, corresponds to loss of $CO-N-CH=CH_2$.

Polymerisation of 1,3-divinylhexahydropyrimid-2-one was accomplished using a variety of initiators both free radical and cationic, the results and conditions being summarised in Table 1.2. The polymers were isolated either directly from the polymerisation reaction or by dropwise addition into vigorously stirred ether or light petroleum.

Table 1.2.

Polymerisation of 1,3-divinylhexahydropyrimid-2-one.

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C	Conversion[a] %
0.5	toluene (5)	BF_3[b]	-	5	-80	26
0.5	-	DTBP[c]	1.54	3	130	72
0.5	toluene (10)	BF_3OEt_2	24.6	5	-50	53
0.5	benzene (20)	ABIN[d]	2.0	3	70	39
0.5	benzene (20)	DBP[e]	2.0	3	70	-

[a] estimated gravimetrically

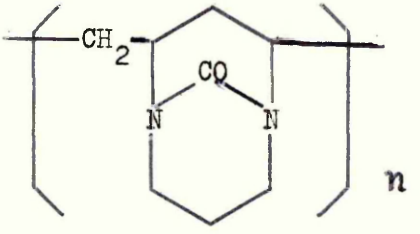
[b] 10 ml of BF_3 gas injected into sample

[c] di-tert. butyl peroxide

[d] azobisisobutyronitrile

[e] dibenzoyl peroxide

As with the polymers obtained from 1,3-divinylimidazolid-2-one, the products were insoluble in a variety of solvents, infusible up to 360° and contained residual unsaturation, evident from the infrared spectrum. These findings agree with those reported previously[55], i.e. radical polymerisation of 1,3-divinylhexahydropyrimid-2-one yields cross-linked polymers with no indication of a bicyclic repeating unit (e.g. 1.X).



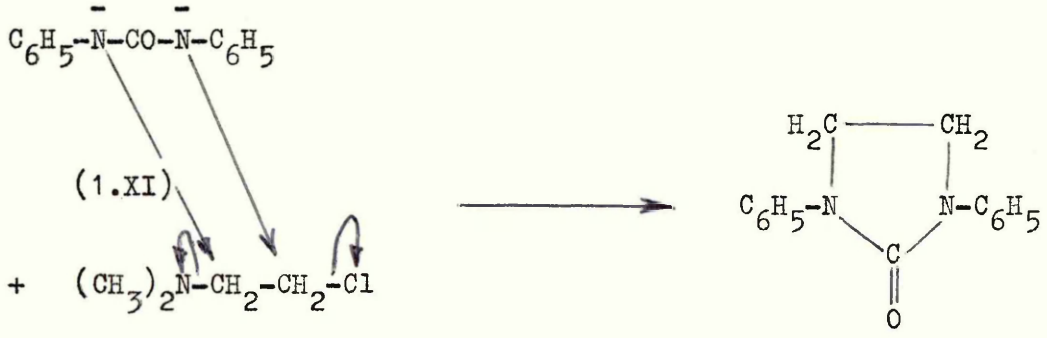
(1.X)

Again, addition of catalytic amounts of concentrated sulphuric acid caused hydrolysis to 2-ketohexahydropyrimidine and acetaldehyde, rather than polymerisation. The monomer is sufficiently sensitive to acidic conditions to be hydrolysed by N/100 hydrochloric acid.

1.4 Synthesis and Attempted Polymerisation of 1,3-Diphenyl-1,3-divinylurea

1,3-Diphenyl-1,3-divinylurea was synthesised using the sequence of reactions developed by Crawshaw and Jones[55] (Chart C).

The di-sodium salt of 1,3-diphenylurea was prepared from sodium hydride and 1,3-diphenylurea in anhydrous N,N-dimethylformamide and reacted with N,N-dimethyl-2-chloroethylamine to give 1,3-bis(N,N-dimethylaminoethyl)1,3-diphenylurea (CI). When the reaction mixture was poured into water prior to extraction with chloroform to remove the di-tertiary amine a precipitate was produced. Crystallisation of the precipitate gave 1,3-diphenylimidazolid-2-one (CIA). Jones[60] proposed that the di-anion of 1,3-diphenylurea (1.XI) attacked N,N-dimethyl-2-chloroethylamine (1.XII) with elimination of both Cl^- and $(CH_3)_2N^-$ (1.XIII).



(1.XI)

(1.XII)

(1.XIII)

After removal of 1,3-diphenylimidazolid-2-one by filtration, the aqueous solution was extracted with chloroform to remove the di-tertiary amine, which was converted into the di-methiodide (CII). The di-quaternary ammonium hydroxide (CIII) was obtained from the di-methiodide by reaction with silver oxide in aqueous methanol. Since the standard Hofmann procedure caused degradation, the di-quaternary ammonium hydroxide was decomposed by refluxing for 24h in cyclohexanol. During this time trimethylamine was continuously evolved. Removal of cyclohexanol under reduced pressure gave a solid which after crystallisation from light petroleum had the correct analysis for 1,3-diphenyl-1,3-divinylurea (CIV).

Confirmatory evidence for the structure was obtained from infrared, n.m.r. and mass spectrometry. The infrared and n.m.r. spectra were identical to those obtained by Jones[60]. The mass spectrum showed a molecular ion at m/e 264, with a base peak at m/e 104. The fragmentation pattern is consistent with the proposed structure for 1,3-diphenyl-1,3-

divinylurea: 237^+, loss of $CH{=}CH_2$; 236^+, loss of CH_2N; 146^+, loss of $CH_2{=}CH{-}N(C_6H_5){-}CO$; 118^+, loss of $CH_2{=}CH{-}N{-}C_6H_6$; and 77^+, due to $C_6H_5^+$. A metastable ion was observed at m/e 211 which confirms the parent ion and the ion at m/e 236.

Many attempts were made to polymerise 1,3-diphenyl-1,3-divinylurea, in every case no product was obtained on pouring the reaction mixture into vigorously stirred ether or light petroleum. These results are in agreement with Crawshaw and Jones [55] who attempted to polymerise the monomer using both free radical and anionic initiators. Table 1.3. shows the representative conditions employed in several polymerisation attempts. In each example shown in Table 1.3. the monomer was recovered almost quantitatively from the polymerisation attempts.

Table 1.3

Attempted polymerisation of 1,3-diphenyl-1,3-divinylurea.

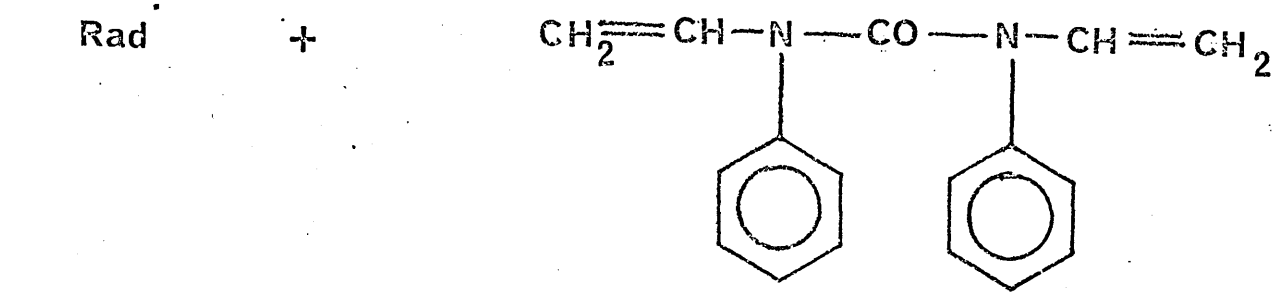
Wt. of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C
0.5	toluene (5)	BF_3 [a]	-	5	-80
0.5	-	DTBP [b]	3.0	3	130
0.5	toluene (5)	BF_3OEt_2	14.9	4	-50
0.5	-	ABIN [c]	2.0	24	70

[a] 10 ml of BF_3 gas injected into sample

[b] di-tert. -butyl peroxide

[c] azobisisobutyronitrile

The inability of 1,3-diphenyl-1,3-divinylurea to polymerise can be explained by considering the radical formed from the monomer. Addition of a radical to 1,3-diphenyl-1,3-divinylurea produces a highly resonance stabilised radical, (Figure 1.2). Kharash, Kane and Brown [63] proposed that the stability of free radicals could be equated to delocalisation, i.e. resonance stability of the radicals. Such an extensive delocalisation



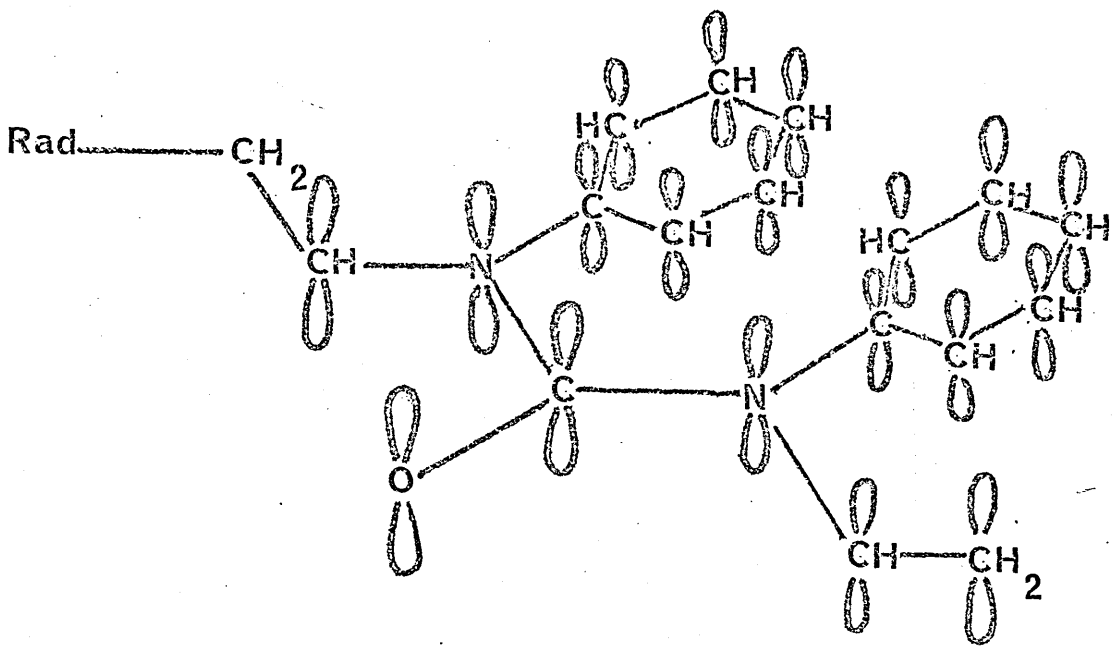


Figure 1.2

Representation of a 1,3-diphenyl-1,3-divinylurea radical indicating orbital overlap.

through the proposed conjugated system and the phenyl rings should be so stable as to prevent propagation with further molecules of 1,3-diphenyl-1,3-divinylurea. Some evidence to support this explanation is cited later (Chapter 2).

1.5. Synthesis and Attempted Polymerisation of 1,3-Dimethyl-1,3-divinylurea.

1,3-Dimethyl-1,3-divinylurea was prepared using a similar sequence of reactions to the other N,N'-divinylureas except that in the final steps the Cope elimination was used rather than the Hofmann degradation (Chart D).

1,3-Dimethylurea was converted into the corresponding di-sodium salt using sodium hydride in N,N-dimethylformamide. N,N-dimethyl-2-chloroethylamine was added to the solution of the salt to give the di-tertiary amine, 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (DI). The next step in the synthetic route could be conversion of the di-tertiary amine to the di-quaternary ammonium iodide using methyl iodide, followed by conversion to the di-quaternary ammonium hydroxide and then to the N,N'-divinylurea. Many attempts were made to convert the di-quaternary ammonium hydroxide of (DI) into 1,3-dimethyl-1,3-divinylurea, in every case with no success. The methods tried were the standard Hofmann degradation procedure, both with and without a nitrogen 'bleed', and decomposition of the amine hydroxide in refluxing cyclohexanol. The latter method had been successful for the synthesis of 1,3-diphenyl-1,3-divinylurea when direct degradation under reduced pressure had failed. The di-methiodide of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (DII) gave the correct analysis for the proposed structure thus proving that the di-tertiary amine (DI) was formed in the reaction of 1,3-dimethylurea and N,N-dimethyl-2-chloroethylamine.

In view of the repeated failure of the Hofmann degradation reaction to give 1,3-dimethyl-1,3-divinylurea a route involving the Cope elimination was used. 1,3-Bis(N,N-dimethylaminoethyl)-1,3-dimethylurea was converted into the amine oxide (DIII) using hydrogen peroxide under neutral conditions. The excess hydrogen peroxide was decomposed with manganese dioxide and the solution filtered and concentrated under reduced pressure. The amine oxide could not be crystallised and so was heated under reduced pressure, following the standard Cope elimination procedure. The fraction boiling 80-100° at 5.0mm Hg was collected and the distillation was stopped immediately since further heating invariably caused the residue to explode! The fraction collected was redistilled from solid sodium hydroxide giving a colourless liquid, b.p. 52-54° at 0.2mm Hg

n_D^{25} 1.5067, which had the correct analysis for 1,3-dimethyl-1,3-divinylurea (DIV). A gas-liquid chromatogram of a sample of 1,3-dimethyl-1,3-divinylurea showed only one peak. The structure of this hitherto unknown compound was confirmed using infrared, n.m.r. and mass spectrometry.

The infrared spectrum showed peaks at 1320, 978, and 845 cm^{-1} indicative of an N-vinyl grouping, together with peaks at 3100 and 1620 cm^{-1} characteristic of unsaturated groups. Peaks at 2910, 1675, and 1280 -1260 cm^{-1} were assigned to aliphatic C-H, C=O and Amide III bands, respectively. The n.m.r. spectrum showed three areas of absorption 3.2-3.7 τ(quartet), 5.7-6.1 τ(triplet) and 7.1 τ(singlet). These values were assigned to N-$\underline{CH}$=CH_2, N-CH=$\underline{CH_2}$ and N-CH_3 protons, respectively. A molecular ion appeared at m/e 140 in the mass spectrum which had a base peak at m/e 58. The fragmentation pattern showed peaks at 125^+, loss of CH_3; 114^+, loss of C_2H_2 by a McLafferty re-arrangement; 113^+, loss of -CH=CH_2; these peaks being consistent with the proposed structure.

Many attempts to polymerise 1,3-dimethyl-1,3-divinylurea were made using various initiators, both free radical and cationic with no success. Table 1.4 shows the representative conditions employed in several polymerisation attempts, in each case the monomer was recovered almost quantitatively from the reaction.

Table 1.4.

Attempted polymerisation of 1,3-dimethyl-1,3-divinylurea.

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C
0.5	-	DTBP[a]	1.0	4	140
0.5	-	ABIN[b]	1.0	4	70
0.5	-	DBP[c]	1.0	4	70
0.5	toluene (5)	BF_3OEt_2	22.4	5	-50
0.5	-	ABIN+hν	2.0	20	20

[a] di-tert. butyl peroxide

[b] azobisisobutyronitrile

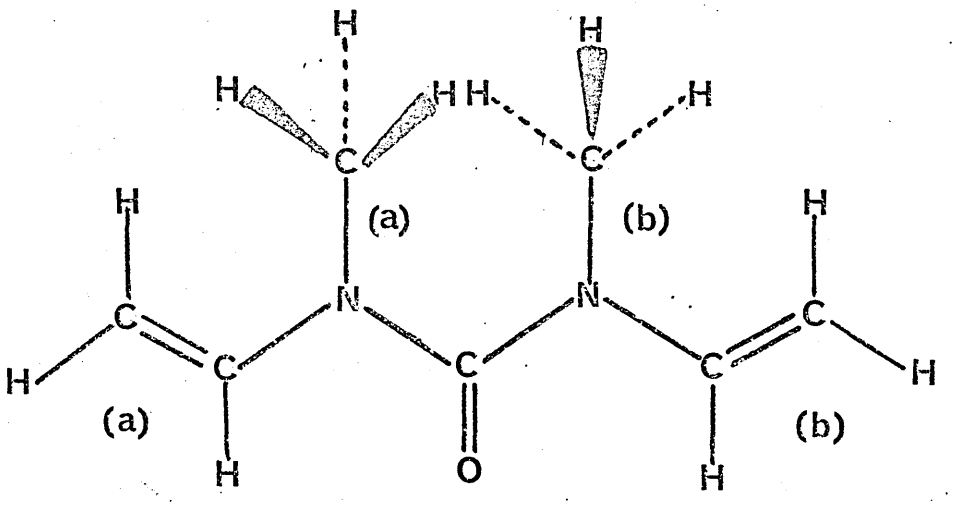
[c] dibenzoyl peroxide

It is difficult to explain the failure of 1,3-dimethyl-1,3-divinylurea to polymerise. Other workers have reported that certain N-vinylureas could not be polymerised; N-vinyl-N,N'-diethylurea[57]; N-vinyl-N',N'-methylphenylurea and N-isopropenyl-N'-phenylurea[61] failed to give polymers with a variety of initiators. Overberger et. al[57] suggests that this is due to di-substitution on the nonvinylic nitrogen atoms while not affecting vinyl polymerisation, inhibits the self addition process leading to polymer structure (1.VIII). Hart [61] offers no explanation for the inability of the unsaturated ureas to polymerise.

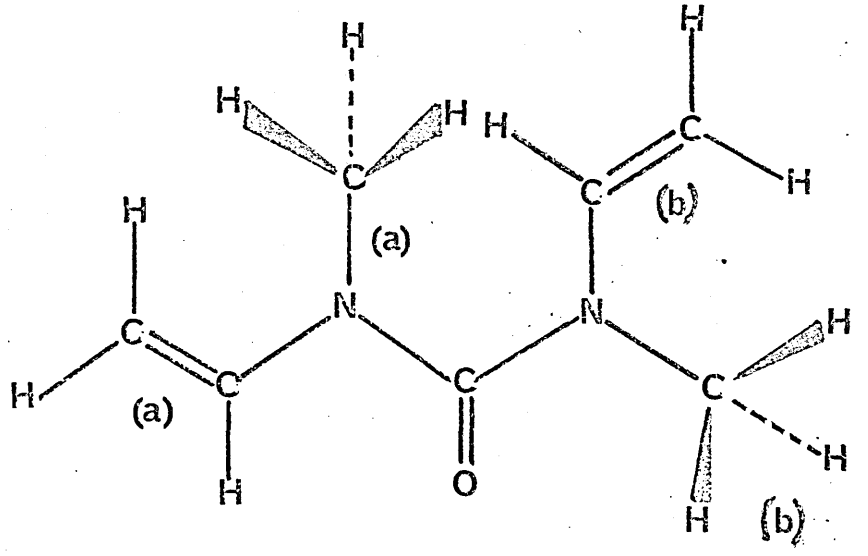
In the case of 1,3-dimethyl-1,3-divinylurea the rate of intermolecular reaction of the radical would be expected to be lower than that of a similar monomer with a non-interfering pendant group (less than four or five chain atoms in the pendant group). Interference by pendant groups lowers the rate of intermolecular reaction by sterically hindering the incoming monomer molecule[17]. The presence of five atoms between the radical and the end of the vinyl group in 1,3-dimethyl-1,3-divinylurea should thus favour the cyclopolymerisation mechanism at the expense of intermolecular reaction because the vinyl group will frequently be presented to the reactive centre in a conformation which is favourable for cyclisation. It was for this very reason that 1,3-dimethyl-1,3-divinylurea was synthesised originally.

Molecular models of 1,3-dimethyl-1,3-divinylurea indicate that if sp^3 hybridisation is proposed for the nitrogen atom together with sp^2 hybridisation for the carbonyl group, the radical on the α-carbon (to the nitrogen) can occupy a position favourable for intramolecular reaction. If, however, the nitrogen atoms are sp^2 hybridised (which would be necessary for the proposed overlap[55]) and conjugated with an sp^2 hybridised carbonyl group, it is more difficult for the second vinyl group to come within close proximity of the radical on the α-carbon atom.

If the vinyl groups are also conjugated with the sp^2 hybridised N-CO-N system there are two important conformations for 1,3-dimethyl-1,3-divinylurea (Figure 1.3). Conformation 1 has cis arrangements of the two methyl groups (a) and (b), and trans, trans positions of the vinyl groups (a) and (b) with respect to the carbonyl group. The other conformation (Conformation 2) has a trans arrangement of the methyl groups on the nitrogen atoms with vinyl group (a) trans to the carbonyl group and vinyl group (b) cis to methyl group (b). Such conformations are even less favourable for cyclopolymerisation. In Conformation 1 the



Conformation 1



Conformation 2

Figure 1.3

Conformations of 1,3-dimethyl-1,3-divinylurea assuming conjugation across CH_2=CH-N-CO-N-CH=CH_2 system.

methyl groups (a) and (b) interact if bonds to the nitrogen atom are in the same plane, a more stable conformation may be found by rotation about the N-CO-N bonds to reduce this interaction. This of course would reduce the degree of overlap of the orbitals which make up the conjugated system. In Conformation 2 the vinyl (b) and methyl (a) groups would similarly interact as above.

Either Conformation would be unfavourable for intramolecular reaction (cyclopolymerisation) and the motion of the pendant group would interfere with the intermolecular reaction. Further evidence will be discussed later concerning the structure of N,N'-divinylureas, but this explanation is offered for the inability of 1,3-dimethyl-1,3-divinylurea to polymerise.

1.6. Synthesis and Polymerisation of 1-Ethyl-3-vinylimidazolid-2-one.

1-Ethyl-3-vinylimidazolid-2-one was prepared using a similar sequence of reactions to those used for the N,N'-divinylureas. The synthetic route involved synthesis of 1-ethylimidazolid-2-one and then conversion into 1-ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one from which 1-ethyl-3-vinylimidazolid-2-one could be obtained using standard reactions (Chart E).

The first step in the synthesis was the preparation of N-ethylethylenediamine. The method chosen was that of O'Gee and Woodburn[64], rather than Aspinall's[65] method which involved protection of one of the nitrogen atoms in ethylene-diamine with an acetyl group, activation of the second nitrogen atom with a benzenesulphonyl group, alkylation and hydrolysis.

2-Bromoethylamine hydrogen bromide (EI) was synthesised from ethanolamine by refluxing with hydrobromic acid according to the method of Cortese[66]. 2-Bromoethylamine hydrobromide was then converted to N-ethylethylenediamine (EII) by refluxing with an excess of ethylamine[64]. Neutralisation of N-ethylethylenediamine with dilute hydrochloric acid followed by cyclisation with potassium cyanate[67,68] gave 1-ethylimidazolid-2-one (EIII) on distillation under reduced pressure. The infrared spectrum of 1-ethylimidazolid-2-one showed absorption bands at 1680 cm^{-1} (C=O), 3300-3350 cm^{-1} (N-H) and the n.m.r. spectrum showed a series of peaks at 6.7 τ(singlet), 6.8-7.0 τ (quartet) and 8.8-9.1 τ (triplet) assigned to ring protons, $N-C\underline{H}_2-CH_3$ and $N-CH_2-C\underline{H}_3$ protons, respectively. The infrared and n.m.r. spectra were in good agreement with details published by Scherer and Schmidt[69].

1-Ethylimidazolid-2-one was converted into the mono-sodium salt using sodium hydride in N,N-dimethylformamide which in turn was converted into 1-ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (EIV) by reaction with N,N-dimethyl-2-chloroethylamine. After dissolution in water the tertiary amine was extracted with chloroform and the chloroform removed under reduced pressure. Since the next step in the synthesis would provide a confirmatory derivative, the tertiary amine was converted without further purification to the quaternary ammonium iodide (EV) by addition of methyl iodide. This quaternary ammonium iodide was converted into the quaternary ammonium hydroxide (EVI) with silver oxide in aqueous ethanol. Water and ethanol were removed under reduced pressure and the viscous syrup obtained transferred to a distillation flask. The syrup was decomposed using the standard Hofmann technique with an oil bath temperature of 130-140° and a pressure of 1.5 mm Hg. Redistillation of the fraction collected gave a colourless liquid b.p. 116-118° at 1.5 mm Hg n_D^{25} 1.4991 which had the correct analysis for 1-ethyl-3-vinylimidazolid-2-one (EVII). A gas-liquid chromatogram of a sample of 1-ethyl-3-vinylimidazolid-2-one showed only one peak. The structure was confirmed using evidence supplied by infrared, n.m.r. and mass spectrometry.

An infrared spectrum indicated the presence of an N-vinyl group with absorption bands at 990 and 838 cm^{-1}, the unsaturation also giving rise to peaks at 3120 and 1635 cm^{-1}, and a carbonyl absorption at 1705 cm^{-1}.

The n.m.r. spectrum of 1-ethyl-3-vinylimidazolid-2-one showed five sets of peaks, the low field signal 2.8-3.3 τ is due to the N-C<u>H</u>=CH_2 proton and appears as a quartet, the signal between 5.8-6.2 τ appears as two overlapping quartets and is due to the N-CH=C<u>H</u>$_2$ protons. The signal at 6.6 τ, a singlet, has been assigned to the ring protons of the imidazolid-2-one ring, the peaks at 6.6-6.9 and 8.7-9.0 τ which appear as a quartet and a triplet were assigned to C<u>H</u>$_2$-CH_3 and CH_2-C<u>H</u>$_3$ protons, respectively. The relative areas of the five signals from low to high field were 1:2:4:2:3, which agrees with the theoretical integration.

The mass spectrum showed a molecular ion at m/e 140 with a base peak of 56^+. The fragmentation pattern was consistent with the structure; 125^+ loss of CH_3; 114^+ loss of C_2H_2 by a McLafferty rearrangement; 113^+ loss of CH_2=CH-. Three possibilities occur for the peak found at 112^+. Either, loss of C=O from the ring, loss of C_2H_4 from the ring or loss of CH_2=CH_2 by a McLafferty rearrangement, the carbonyl group attacking the ethyl group and removing a proton.

The polymerisation of 1-ethyl-3-vinylimidazolid-2-one was achieved using various initiators, the results and conditions being summarised in Table 1.5. The polymers were isolated from the polymerisation reaction by dropwise addition into vigorously stirred ether or light petroleum. All the polymers below had softening points between 165 and 185°.

Table 1.5.

Polymerisation of 1-ethyl-3-vinylimidazolid-2-one.

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C	Conversion[a] %	Reduced[b] specific viscosity $\eta_{sp/c}$
0.75	-	DTBP[c]	1.6	2	140	86	-
0.5	-	ABIN[f]	2.0	4	70	50	0.145
0.5	benzene (20)	ABIN	2.0	4	70	38	0.09
0.9	benzene (20)	ABIN	1.5	24	70	83	0.16
1.0	benzene (25)	ABIN	1.75	4	70	46	0.19[c]
2.0	-	ABIN + hν	0.8	2	25	90	0.208[d]
0.75	toluene (10)	BF_3OEt_2	10.3	5	-50	86	0.114[d]

[a] estimated gravimetrically by precipitation in ether

[b] for toluene solutions

[c] intrinsic viscosity

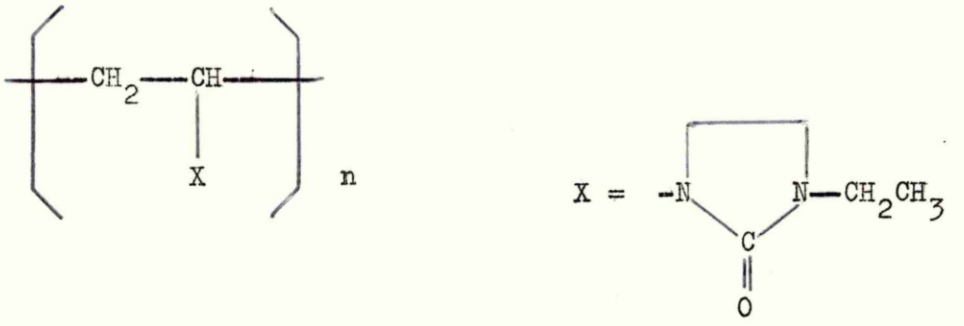
[d] for aqueous solutions

[e] di-tert.butyl peroxide

[f] azobisisobutyronitrile

No acid-catalysed polymerisations were attempted in view of the ease of hydrolysis of the N-vinyl group in the N,N'-divinylureas.

The infrared and n.m.r. spectra of poly(1-ethyl-3-vinylimidazolid-2-one) showed no residual unsaturation. The polymers were soluble in a variety of solvents; benzene, toluene, water and N,N-dimethylformamide, for example. These facts, supported by the fusibility of the polymer, suggest a linear structure with repeating groups as expected for a vinyl monomer (1.XIV).



(1.XIV)

Poly(1-ethyl-3-vinylimidazolid-2-one) would be expected to show some similarities with other N-vinylamide polymers, in particular N-vinylpyrrolid-2-one. Poly(N-vinylpyrrolid-2-one) is water soluble but does not precipitate from aqueous solution on raising the temperature to 100°, in contrast to poly(N-vinylcaprolactam) and poly(N-vinylpiperid-2-one)[70,71]. Poly(N-vinylcaprolactam) precipitates at 35° [71] whereas poly(vinylpiperid-2-one) precipitates at 64-65° [71]. Poly(1-ethyl-3-vinylimidazolid-2-one), however, precipitates from aqueous solution at 45°. Poly(1-ethyl-3-vinylimidazolid-2-one) forms complexes with polybasic acids such as tannic acid, these complexes are water insoluble but the reaction can be reversed by neutralising the polyacid with base. This property of complex formation is extensively found for poly(N-vinylpyrrolid-2-one) which forms complexes with iodine, polybasic acids, toxins and drugs. Poly(N-vinylpyrrolid-2-one) has been extensively studied as a plasma volume expander for use in the control of shock due to excessive blood loss, extensive burns or dehydration[71]. Due to the similarity with poly(N-vinylpyrrolid-2-one), poly(1-ethyl-3-vinylimidazolid-2-one) could be a possible substitute plasma expander.

CHAPTER 2

Copolymerisation Studies

2.1 Introduction

As a means of gaining further information on the nature and reactivity of N-vinyl- and N,N'-divinylureas and the radicals produced from them, a number of copolymerisation studies were carried out. This chapter describes the use of the copolymer composition equation to determine the reactivity ratios and Q and e parameters for the copolymerisation of N-vinyl monomers with ethyl acrylate.

A radical produced from one monomer, A, in a binary copolymerisation reaction can either add to a like monomer, A, or add to an unlike monomer, B. If the radical from monomer A reacts preferentially with monomer A in the copolymer mixture then the resultant copolymer produced will contain, on analysis, substantially more A than B. Only when most of A is exhausted will the growing polymer chain, which is essentially A, react with monomer B. If however the radical from monomer A had equal preference for A or B, then, on analysis of the copolymer, equal amounts of A and B would be expected. These two extremes represent idealised systems. The degree of preference of two monomer pairs can be calculated from the copolymerisation composition equation. The copolymerisation equation was derived almost simultaneously by three sets of workers[72-74] in 1944. The derivation of this equation is based on the assumption that the concentration of each type of radical quickly achieves a value which remains constant throughout the major part of the copolymerisation reaction.

The relationship for the composition of copolymers from pairs of vinyl monomers is usually written:

$$\frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{\left[M_1\right]}{\left[M_2\right]} \cdot \frac{r_1\left[M_1\right] + \left[M_2\right]}{r_2\left[M_2\right] + \left[M_1\right]} \qquad (2\text{-}1)$$

Where the reactivity ratios $r_1 = \frac{k_{11}}{k_{12}}$ and $r_2 = \frac{k_{22}}{k_{21}}$

At low conversion $$\frac{d\left[M_1\right]}{d\left[M_2\right]} \simeq \frac{\left[m_1\right]}{\left[m_2\right]} \qquad (2\text{-}2)$$

where m_1 and m_2 refer to monomer residues in the copolymer.

The reactivity ratios represent the ratios of rate constants for homopropagation over the rate constants for heteropropagation. Mayo and Lewis[72] determined reactivity ratios by a graphical method using the integrated form of equation (2-1). Another method is to measure the initial and final slopes of the copolymerisation curve in which copolymer composition is plotted against monomer composition [75]. A method of increasing application in determining reactivity ratios is that of Fineman and Ross[76] using a rearranged form of equations (2-1) and (2-2).

If $f = (m_1/m_2)$ and $F = (M_1/M_2)$ then equations (2-1) and (2-2) can be written as:

$$f = F \cdot \frac{r_1 F + 1}{r_2 + F} \qquad (2\text{-}3)$$

By rearranging terms:

$$\frac{F}{f}(f-1) = r_1 \cdot \frac{F^2}{f} - r_2 \qquad (2\text{-}4)$$

A plot of $(F/f)(f-1)$ as ordinate and (F^2/f) as abscissa should give a straight line whose slope is r_1 and intercept minus r_2.

Equation (2-3) can also be rearranged to:

$$\frac{f-1}{F} = -r_2 \frac{f}{F^2} + r_1 \qquad (2\text{-}5)$$

In this case the slope is minus r_2 and the intercept r_1. The use of equations (2-4) and (2-5) permits the use of the method of least squares to get the best fit to the experimental data. Having the two equations is also an advantage since sometimes one of the two plots gives a better straight line through the points[76]. McCaffery [77] gives a computer program (FORTRAN II) for the least squares calculation and determination of reactivity ratios. For our purposes this has been rewritten in FORTRAN IV programming language (Appendix 1).

Since the relative reactivity ratios depend on the system used for their determination they would have to be determined experimentally for each monomer pair of interest. The need for more general and constant factors by which a given monomer can be characterised has led to the

development of the copolymerisation parameters, Q and e, by Alfrey and Price[78]. Alfrey and Price defined an equation for each cross-propagation term, k_{12} or k_{21}, in terms of three constants characteristic of the structure of the monomer: P, Q and e, equation (2-6).

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \qquad (2\text{-}6)$$

When reactivity ratios are calculated for the reactivity of two monomers with one radical the P term is eliminated, equation (2-7).

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_1 Q_1 \exp(-e_1 e_2)}{P_1 Q_2 \exp(-e_1 e_2)} = \frac{Q_1}{Q_2} \exp\left[e_1 (e_2 - e_1)\right] \qquad (2\text{-}7)$$

Q is assumed to denote the general reactivity of the monomer, and e is assumed to indicate its polar properties.

Since the equation is empirical a standard monomer was chosen and given arbitary values for Q and e. Styrene was chosen for the reference monomer and given the values Q = 1.0, e = -1.0[78], but later the value of e was revised to -0.8[79]. The values of Q and e quoted in this chapter were calculated from equations (2-8) and (2-9)[80].

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{\frac{1}{2}} \qquad (2\text{-}8)$$

$$Q_2 = Q_1 / r_1 \exp\left\{e_1 (e_1 - e_2)\right\} \qquad (2\text{-}9)$$

2.2 Copolymerisation of 1,3-Divinylimidazolid-2-one with Ethyl Acrylate

Mixtures of 1,3-divinylimidazolid-2-one and ethyl acrylate in benzene were copolymerised to low conversions using azobisisobutyronitrile as initiator. After precipitation and purification, the copolymers were analysed for nitrogen content from which the percentage and mole percentage of 1,3-divinylimidazolid-2-one residues in the copolymer were calculated. Table 2.1 gives monomer feeds, conversions and analyses for the copolymerisation reactions, and Table 2.2 the mole percentage data from which Figure 2.1 is plotted.

Beynon[81,82] investigated the copolymerisation of difunctional monomers (diallyl phosphonates and diallylureas) with monofunctional comonomers using the normal form of the copolymerisation equation, (equation 2-1). He decided that this equation could be used if the two

groups in the difunctional monomer were equivalent, whether or not both functional groups are involved in the polymerisation. Thus, for the copolymerisation of 1,3-divinylimidazolid-2-one with ethyl acrylate equation 2-1(and its derivatives)has been used for the determination of reactivity ratios.

Table 2.1

Copolymerisation of 1,3-divinylimidazolid-2-one (DVI) with ethyl acrylate (EtA)[a]

Feed			Copolymer							
Wt of DVI g	Wt of EtA g	Conversion[b] %	Analysis 1 %			Analysis 2 %			% DVI by wt	% EtA by wt
			C	H	N	C	H	N		
0.265	1.735	2.1	56.75	7.44	5.98	57.07	7.49	6.09	30.04	69.96
0.512	1.488	5.9	57.41	7.54	6.68	59.54	7.83	7.09	34.97	65.03
0.743	1.257	6.9	59.75	7.92	8.15	59.56	7.71	8.16	40.25	59.75
0.958	1.042	6.6	59.33	7.88	8.78	60.13	7.79	8.92	44.00	56.00
1.160	0.840	3.2	58.08	7.55	8.57	59.52	7.80	8.86	43.71	56.29
1.348	0.652	3.6	58.72	7.97	9.39	58.52	7.77	9.43	46.52	53.48
1.520	0.480	4.3	58.93	7.91	9.79	59.26	7.75	9.81	48.39	51.61
1.693	0.307	4.1	58.95	7.54	9.73	58.86	7.64	9.89	48.79	51.21
1.850	0.150	3.5	58.54	7.45	10.48	58.59	7.44	10.50	51.80	48.20

[a] polymerised at 10% $^{w}/_{w}$ monomer concentration in benzene with 0.1 mole % azobisisobutyronitrile as initiator at 60 $\pm$ 0.1°C.

[b] estimated gravimetrically by precipitation in light petroleum (b.p. 40 -60°).

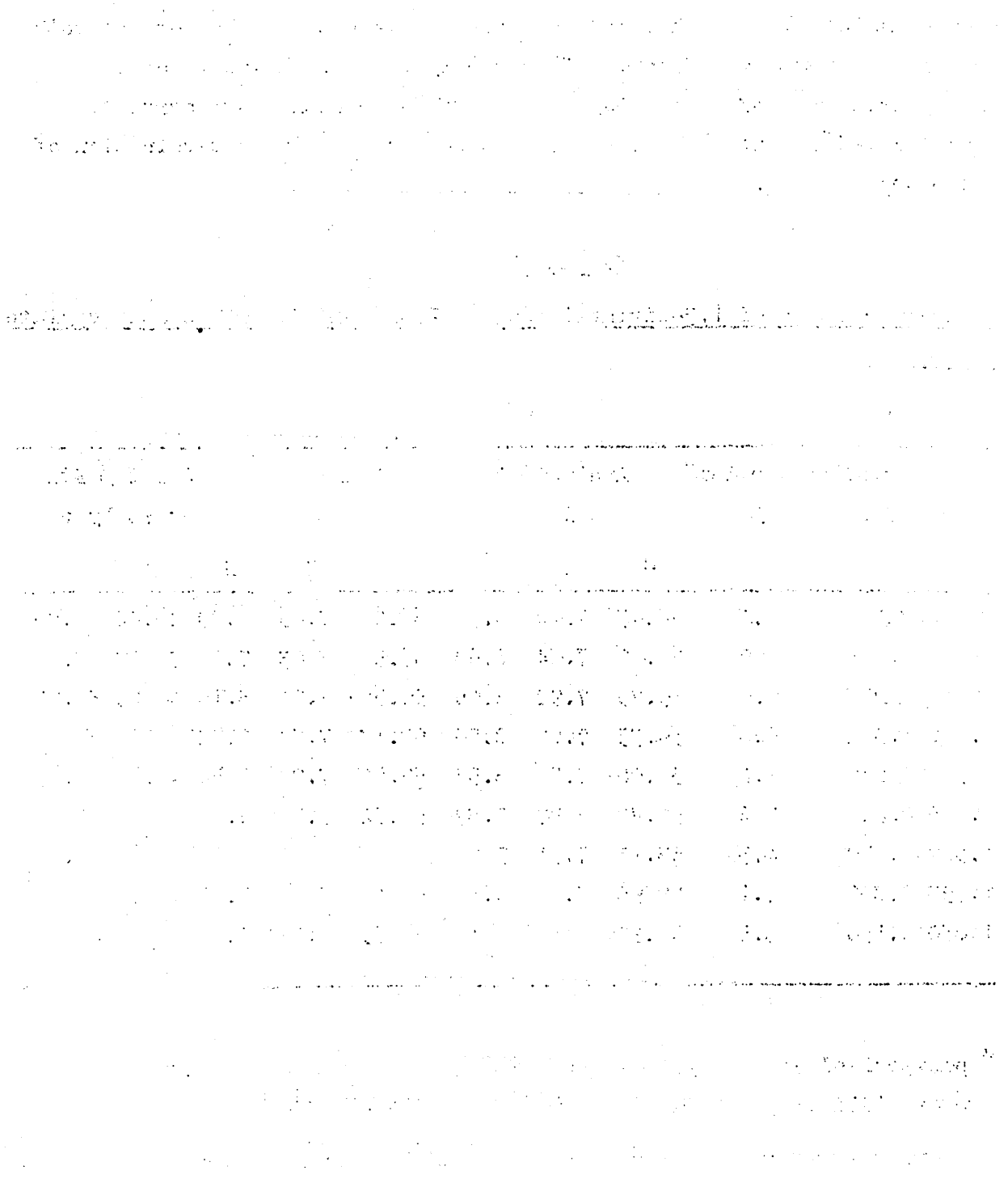


Table 2.2

Copolymerisation of 1,3-divinylimidazolid-2-one (DVI) with ethyl acrylate (EtA)

Feed		Copolymer	
mole % DVI M_1	mole % EtA M_2	mole % DVI m_1	mole % EtA m_2
10.00	90.00	23.73	76.27
20.00	80.00	28.04	71.96
30.00	70.00	32.81	69.19
40.00	60.00	36.28	63.72
50.00	50.00	36.01	63.99
60.00	40.00	38.67	61.33
70.00	30.00	40.46	59.54
80.00	20.00	40.84	59.16
90.00	10.00	43.78	56.21

Inspection of the shape of the monomer-copolymer composition curve, Figure 2.1, gives an indication of the values of the reactivity ratios of the two monomers. The shape of Figure 2.1 suggests that both r_1 and r_2 are less than one[83]. The curve also contains a point which crosses the diagonal line. This is the azeotropic copolymerisation composition (34.2 mole % 1,3-divinylimidazolid-2-one) where the copolymer would have the same composition as the monomer feed mixture. Table 2.3 gives the data calculated for the Fineman--Ross plots for 1,3-divinylimidazolid-2-one and ethyl acrylate.

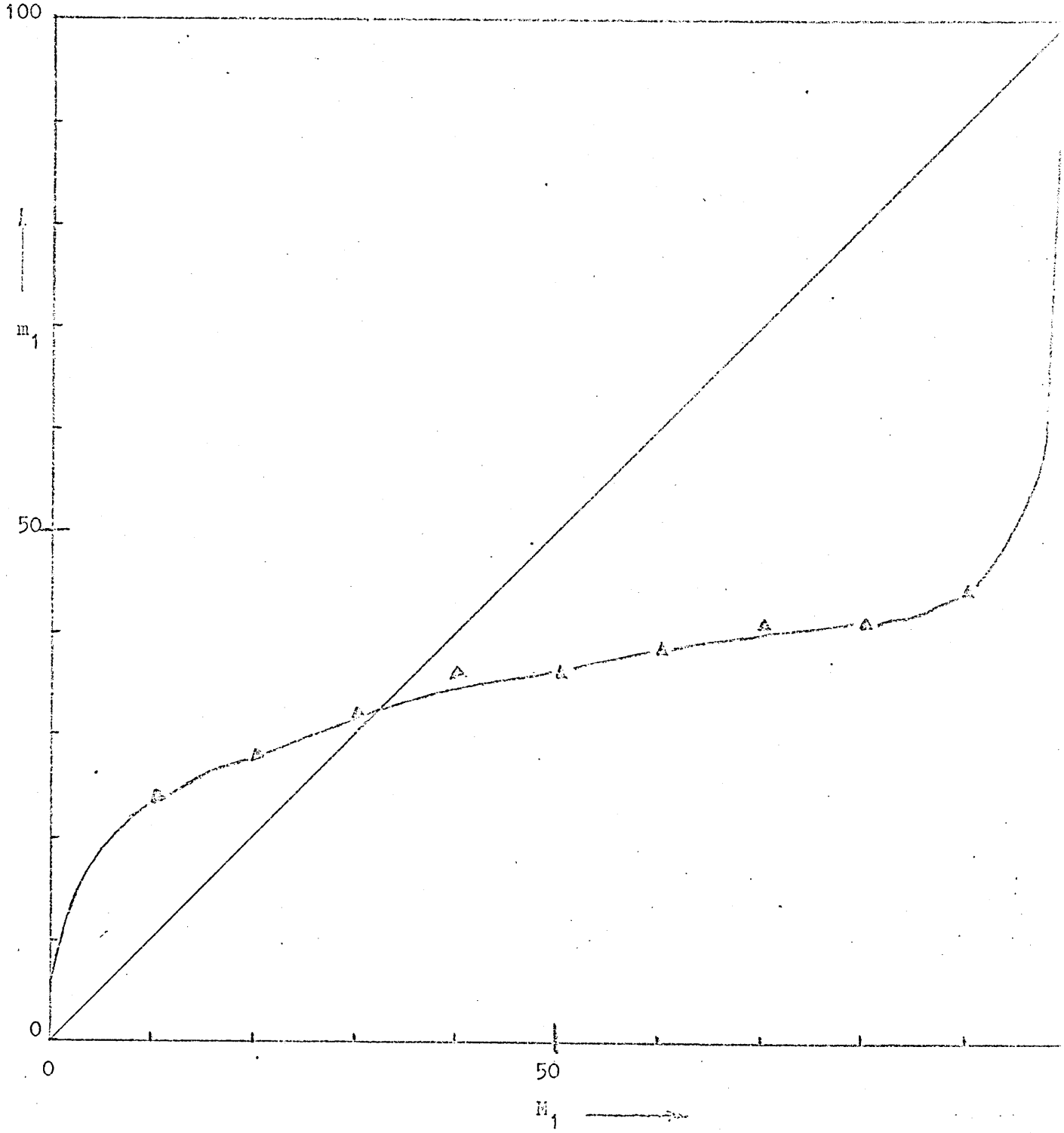


Figure 2.1

Monomer - polymer composition curve for the copolymerisation of 1,3-divinylimidazolid-2-one with ethyl acrylate at 60°.

Table 2.3

Data for Fineman--Ross plots for the copolymerisation of 1,3-divinylimidazolid-2-one with ethyl acrylate.

$F = \frac{M_1}{M_2}$	$f = \frac{m_1}{m_2}$	f-1	F/f	F^2	(F/f)(f-1)	F^2/f	$\frac{f-1}{F}$	$\frac{f}{F^2}$
0.111	0.311	-0.689	0.357	0.012	-0.246	0.039	-6.206	25.251
0.250	0.389	-0.611	0.641	0.062	-0.391	0.160	-2.441	6.233
0.428	0.489	-0.511	0.874	0.183	-0.446	0.374	-1.193	2.672
0.666	0.569	-0.431	1.169	0.443	-0.504	0.779	-0.646	1.283
1.000	0.562	-0.438	1.777	1.000	-0.777	1.777	-0.437	0.563
1.500	0.630	-0.370	2.379	2.250	-0.879	3.568	-0.246	0.280
2.333	0.679	-0.321	3.433	5.444	-1.100	8.011	-0.137	0.125
4.000	0.690	-0.310	5.794	16.000	-1.794	23.178	-0.077	0.043
9.000	0.778	-0.222	11.556	81.000	-2.556	104.000	-0.024	0.009

Figures 2.2 and 2.3 show the plots of (F/f)(f-1) vs. F^2/f and f-1/F vs. f/F^2 from the data in Table 2.3. The reactivity ratios obtained from the intercepts and slopes of Figures 2.2 and 2.3 which are plots of equations (2-4) and (2-5) are shown in Table 2.4.

Table 2.4

Reactivity ratios of 1,3-divinylimidazolid-2-one with ethyl acrylate.

System	From plot of equation (2-4) (Figure 2.2)		From plot of equation (2-5) (Figure 2.3)	
	r_1	r_2	r_1	r_2
1,3-divinylimidazolid-2-one (M_1), ethyl acrylate (M_2)	0.099	0.39	0.08	0.386
	$r_1 = 0.0897$		$r_2 = 0.388$[a]	

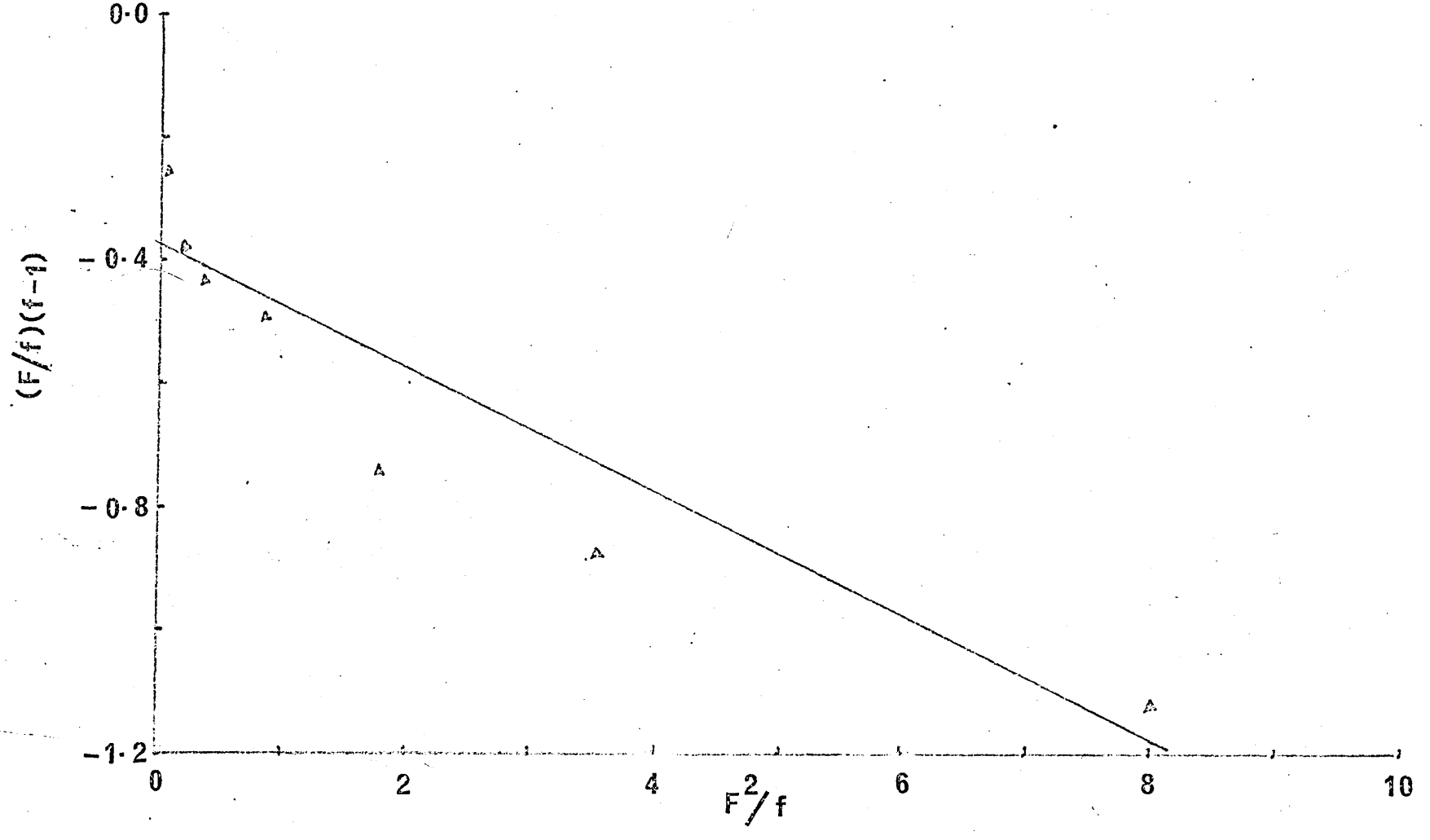


Figure 2.2

Fineman-Ross plot for the copolymerisation of 1,3-divinylimidazolid-2-one with ethyl acrylate.

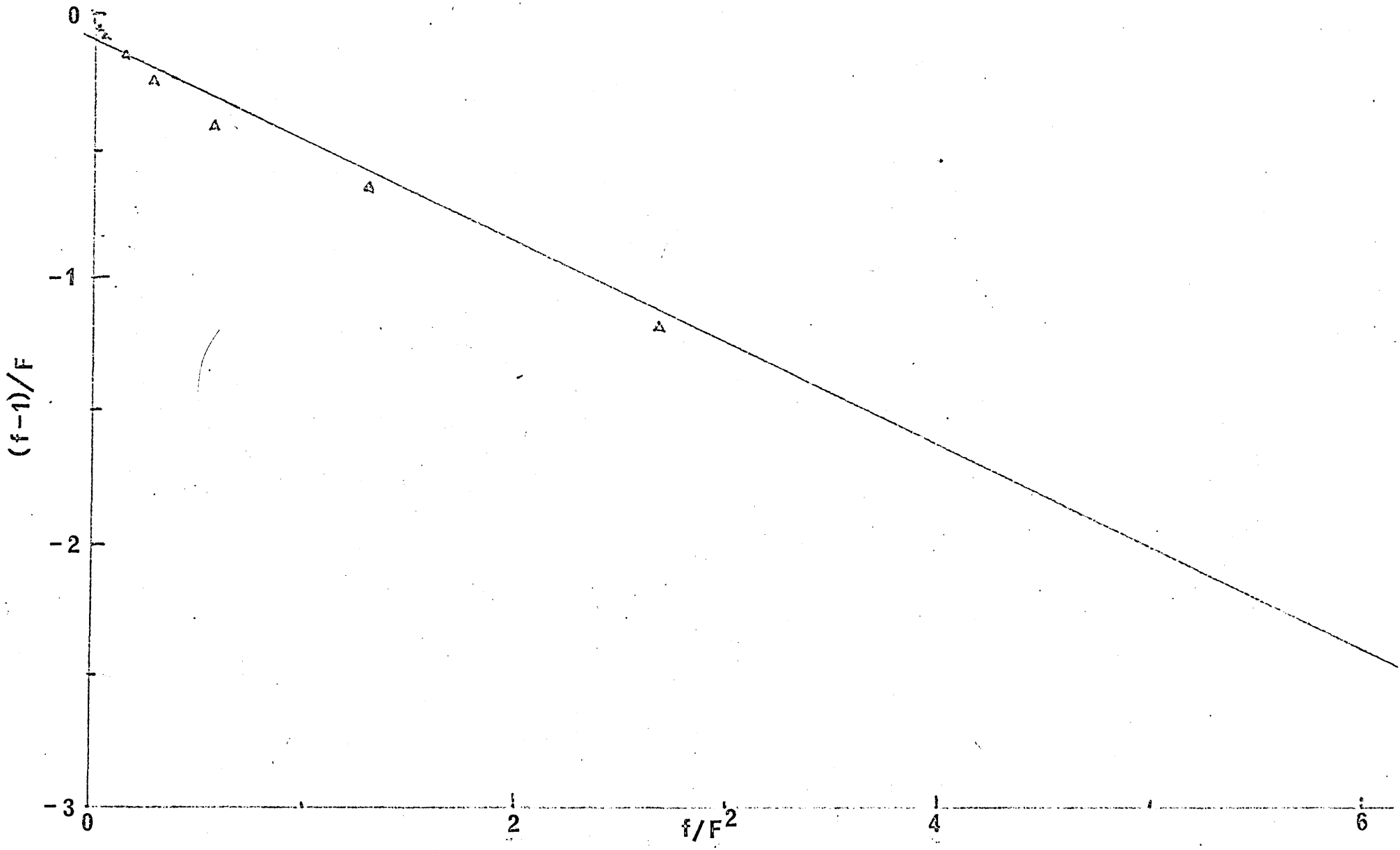


Figure 2.3

Fineman-Ross plot for the copolymerisation of 1,3-divinylimidazolid-2-one with ethyl acrylate.

[a] results from computer program (Appendix 1)

The Q and e values obtained for 1,3-divinylimidazolid-2-one, using equations (2-8) and (2-9), and values of Q = 0.52, e = 0.22 for ethyl acrylate, were Q = 0.84, e =-1.58. The Q and e values obtained for 1,3-divinylimidazolid-2-one are compared with those for other N-vinyl compounds in Chapter 2.5.

At the azeotropic copolymerisation composition the polymer has the same composition as the monomer feed mixture, and a polymeric product of constant composition is formed throughout the copolymerisation reaction. A relationship can be derived to calculate this critical monomer feed by solving a form of equation (2-1) for the case where $M_1 = m_1$. The equation then reduces to equation (2-10)[84].

$$(m_1)_c = \frac{1-r_2}{2-(r_1 + r_2)} \qquad (2\text{-}10)$$

Substitution of the r_1 and r_2 values into equation (2-10) gives the critical monomer feed as 39.9 mole % compared to 34.2 mole % obtained from Figure 2.1. However,only the best values of r_1 and r_2 have been calculated and the corresponding standard deviations have not been determined.

2.3 Copolymerisation of 1,3-Divinylhexahydropyrimid-2-one with Ethyl Acrylate.

Mixtures of 1,3-divinylhexahydropyrimid-2-one and ethyl acrylate in benzene were copolymerised using azobisisobutyronitrile as initiator to the low conversion necessary to use the copolymerisation equation. After precipitation and purification, the copolymers were analysed for nitrogen content from which the percentage and mole percentage of 1,3-divinylhexahydropyrimid-2-one residues in the copolymer were calculated. The monomer feeds, conversions and analyses are given in Table 2.5 and Table 2.6 gives the calculated mole percentages for the monomer feeds and the copolymers. The monomer-copolymer composition curve is shown in Figure 2.4.

Table 2.5

Copolymerisation of 1,3-divinylhexahydropyrimid-2-one (DVHHP) with ethyl acrylate (EtA)[a]

Feed			Copolymer				
Wt of DVHHP g	Wt of EtA g	Conversion[b] %	Analysis % C	H	N	% DVHHP by wt	% EtA by wt
0.289	1.711	2.8	59.02	7.95	4.08	22.17	77.83
0.550	1.450	3.2	60.38	8.04	6.04	32.82	67.17
0.790	1.210	6.9	60.83	8.16	6.97	37.88	62.12
0.984	1.016	6.2	60.69	8.04	7.56	41.08	58.92
1.007	0.993	4.9	60.96	8.07	7.53	40.92	59.08
1.108	0.892	3.9	59.48	7.99	8.17	44.40	56.60
1.208	0.792	6.5	60.93	8.02	8.49	46.14	53.86
1.390	0.610	3.3	60.85	8.19	8.64	46.96	53.04
1.560	0.440	5.3	60.90	8.15	9.31	50.60	49.40
1.718	0.282	3.7	60.16	8.16	9.49	51.57	48.43
1.862	0.138	4.9	61.08	8.15	11.85	64.40	35.60

[a] polymerised at 10% $^{w}/_{w}$ monomer concentration in benzene with 0.2 mole % azobisisobutyronitrile as initiator at 60 $\pm$ 0.1°C.

[b] estimated gravimetrically by precipitation in light petroleum (b.p. 40-60°)

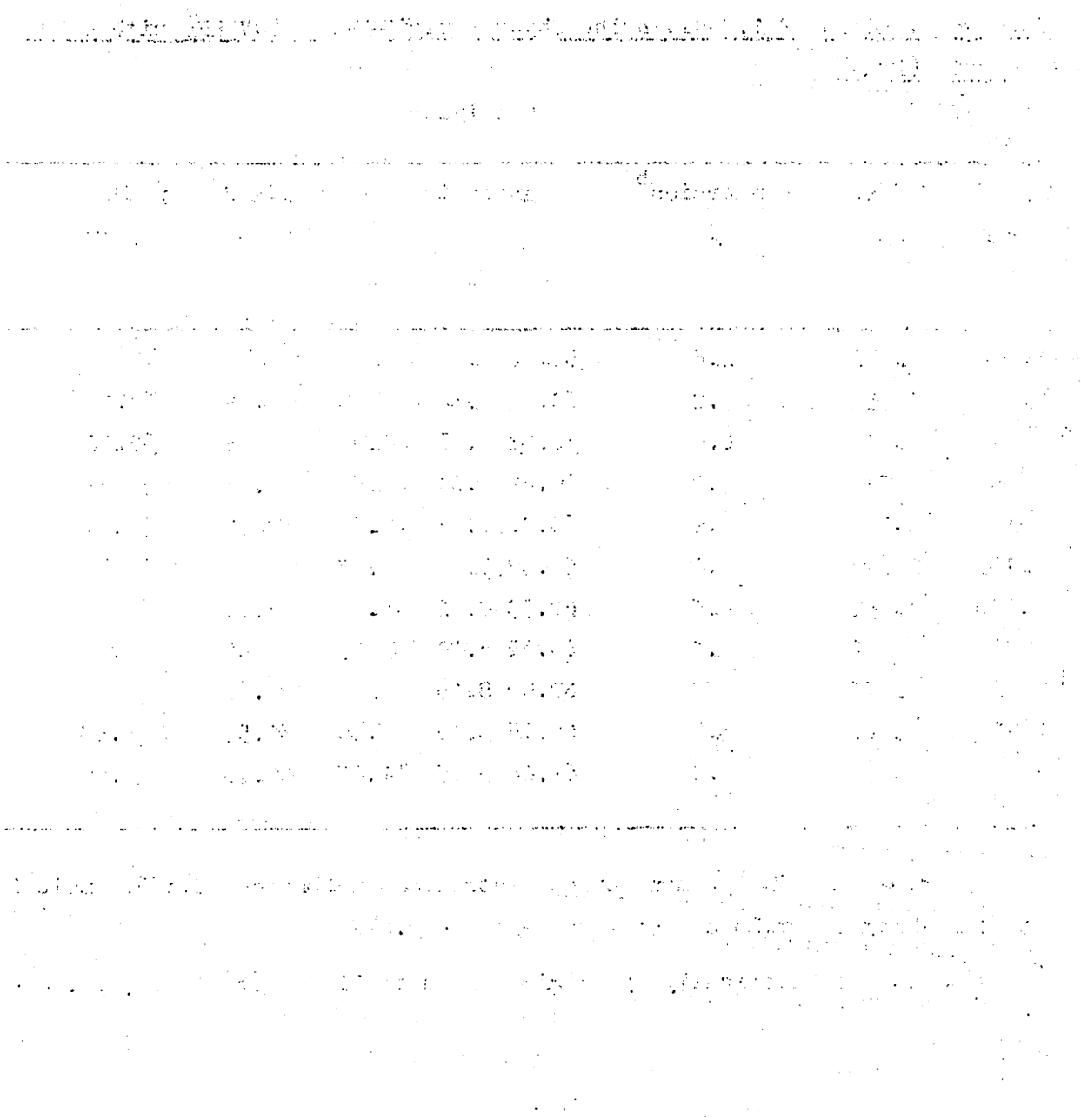


Table 2.6

Copolymerisation of 1,3-divinylhexahydropyrimid-2-one (DVHHP) with ethyl acrylate (EtA).

Feed		Copolymer	
mole % DVHHP M_1	mole % EtA M_2	mole % DVHHP m_1	mole % EtA m_2
10.00	90.00	15.79	84.21
20.00	80.00	24.34	75.66
30.00	70.00	28.65	71.35
35.00	65.00	31.46	68.54
40.00	60.00	31.22	68.68
45.00	55.00	34.47	65.53
50.00	50.00	36.07	63.93
60.00	40.00	36.82	63.18
70.00	30.00	40.28	59.72
80.00	20.00	41.22	58.78
90.00	10.00	54.37	45.63

From the shape of Figure 2.4 the reactivity ratios, r_1 and r_2, were predicted to be both less than one[83]. The point where the monomer and copolymer curves intersect, the azeotropic copolymerisation composition, occurs at 27.5 mols %. The data calculated for plotting graphs according to the Fineman-Ross equations is given in Table 2.7.

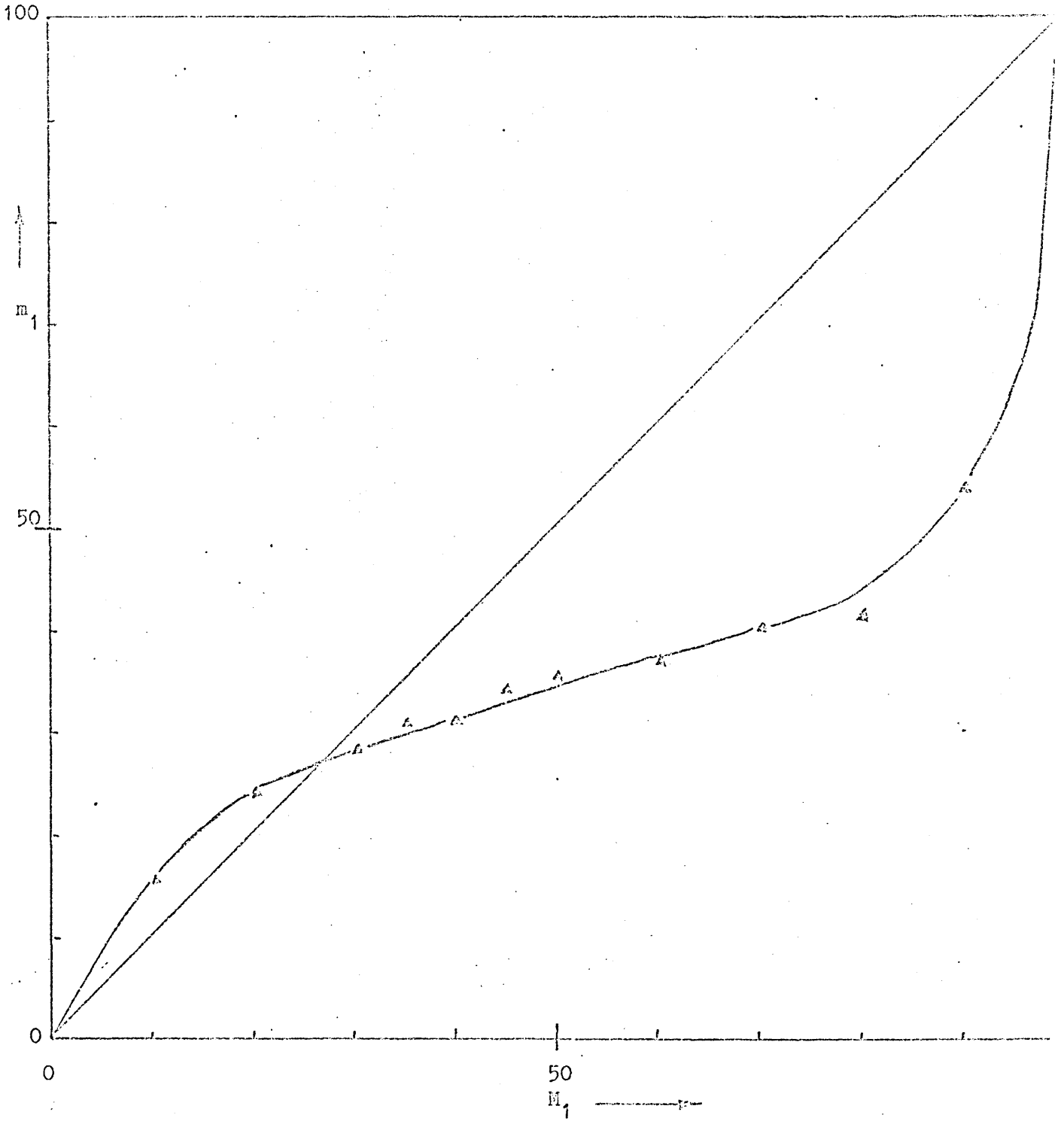


Figure 2.4.

Monomer - polymer composition curve for the copolymerisation of

1,3-divinylhexahydropyrimid-2-one with ethyl acrylate at 60°.

Table 2.7

Data for Fineman--Ross plots for the copolymerisation of 1,3-divinylhexahydropyrimid-2-one with ethyl acrylate.

$F = \frac{M_1}{M_2}$	$f = \frac{m_1}{m_2}$	f-1	F/f	F^2	(F/f)(f-1)	F^2/f	$\frac{f-1}{F}$	$\frac{f}{F^2}$
0.111	0.187	-0.813	0.593	0.012	-0.482	0.065	-7.324	15.203
0.250	0.322	-0.678	0.776	0.062	-0.526	0.194	-2.712	5.152
0.428	0.401	-0.599	1.067	0.183	-0.639	0.456	-1.399	2.191
0.538	0.459	-0.541	1.172	0.285	-0.634	0.621	-1.006	1.610
0.666	0.456	-0.544	1.462	0.443	-0.795	0.971	-0.817	1.029
0.818	0.526	-0.474	1.555	0.669	-0.737	1.272	-0.579	0.786
1.000	0.564	-0.436	1.773	1.000	-0.773	1.773	-0.436	0.564
1.500	0.583	-0.417	2.573	2.250	-1.073	3.859	-0.278	0.259
2.333	0.674	-0.326	3.461	5.444	-1.128	8.076	-0.140	0.124
4.000	0.701	-0.299	5.706	16.000	-1.706	22.824	-0.075	0.044
9.000	1.191	+0.191	7.557	81.000	+1.443	68.010	+0.002	0.015

Figures 2.5 and 2.6 show plots of $(F/f)(f-1)$ vs. F^2/f and $f-1/F$ vs. f/F^2, respectively from the data in Table 2.7. The reactivity ratios obtained from the intercepts and slopes of Figures 2.5 and 2.6 are shown in Table 2.8.

Table 2.8

Reactivity ratios of 1,3-divinylhexahydropyrimid-2-one and ethyl acrylate

System	From plot of equation (2-4) (Figure 2.5)		From plot of equation (2-5) (Figure 2.6)	
	r_1	r_2	r_1	r_2
1,3-divinylhexahydropyrimid-2-one (M_1) ethyl acrylate (M_2)	0.13	0.56	0.14	0.538
	$r_1 = 0.137$, $r_2 = 0.549$ [a]			

[a] results from computer program (Appendix 1)

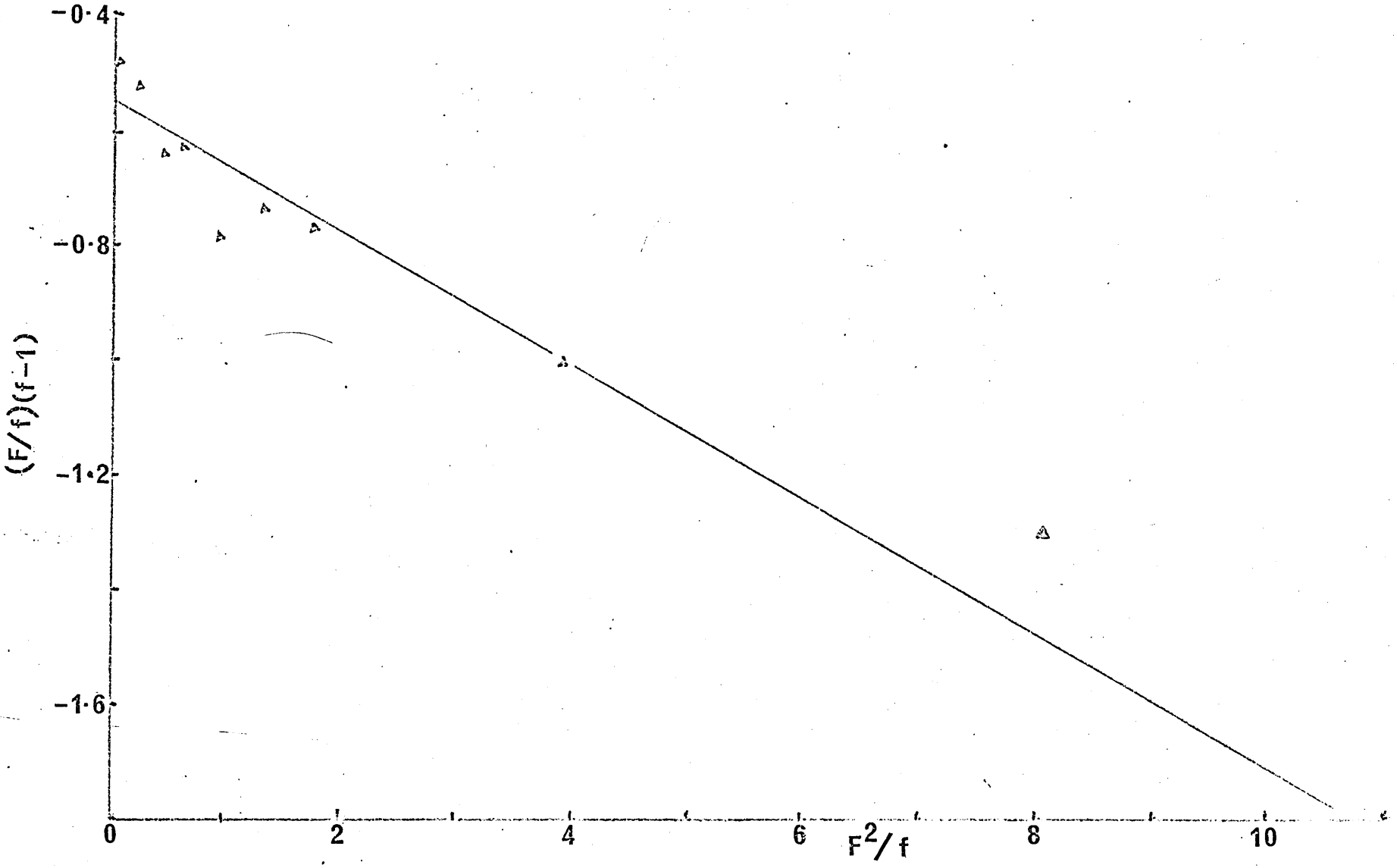


Figure 2.5

Fineman-Ross plot for the copolymerisation of 1,3-divinylhexahydropyrimid-2-one with ethyl acrylate.

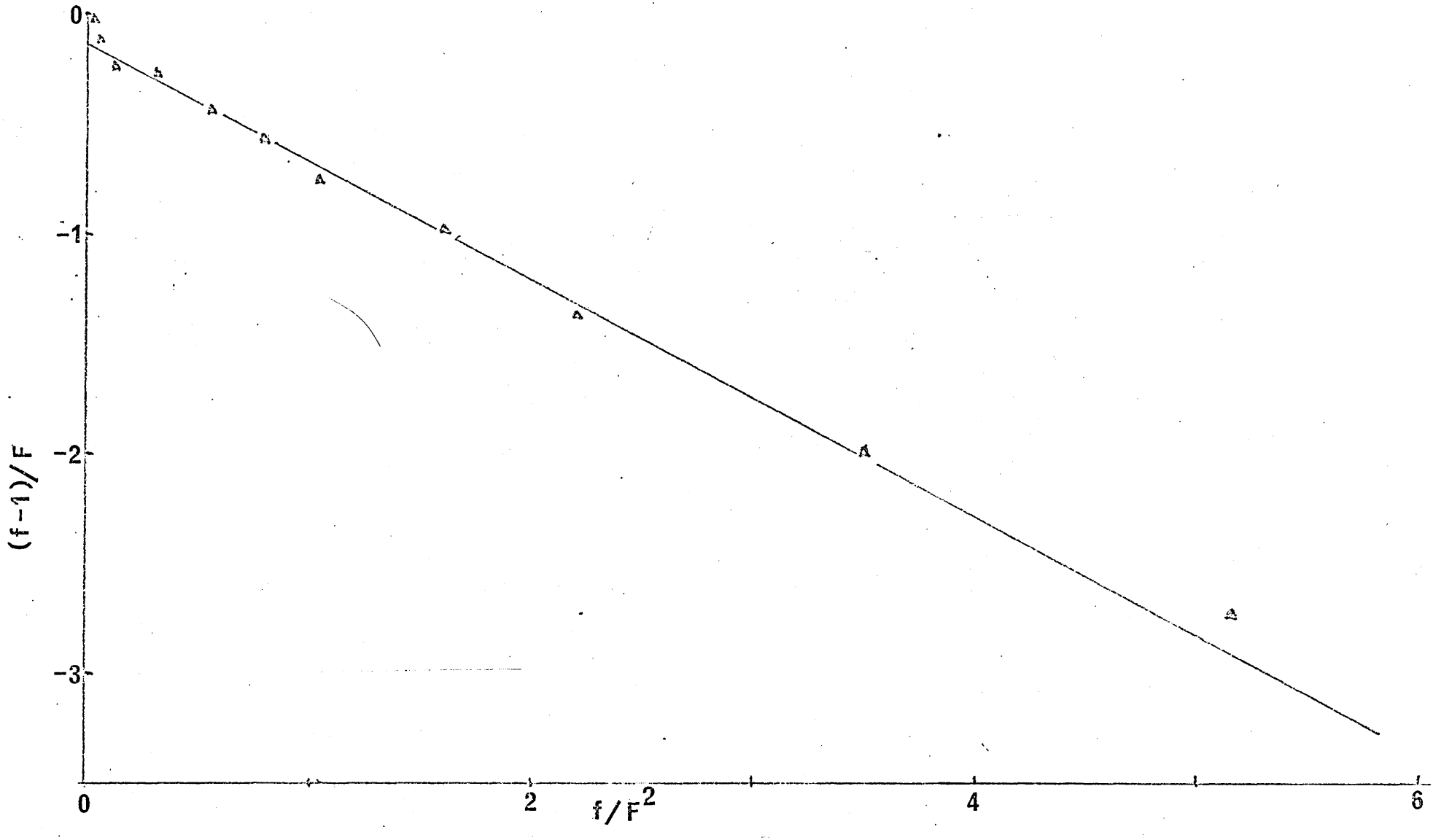


Figure 2.6

Fineman-Ross plot for the copolymerisation of 1,3-divinylhexahydropyrimid-2-one with ethyl acrylate.

Using equations (2-8) and (2-9) and Q = 0.52 and e = 0.22 for ethyl acrylate, the calculated Q and e values for 1,3-divinylhexahydropyrimid-2-one were Q = 0.68 and e =-1.40. The Q and e values obtained for 1,3-divinylhexahydropyrimid-2-one are compared with those for other N-vinyl compounds in Chapter 2.5. Substitution of the r_1 and r_2 values obtained into equation (2-10) gives the critical monomer feed as 33.6 mole % 1,3-divinylhexahydropyrimid-2-one compared to 28.0 mole % obtained from Figure 2.4. Again, only the best values of r_1 and r_2 were calculated and the corresponding standard deviations were not determined.

2.4 Copolymerisation of 1-Ethyl-3-vinylimidazolid-2-one with Ethyl Acrylate

Mixtures of 1-ethyl-3-vinylimidazolid-2-one and ethyl acrylate total weight 2.000g, were copolymerised in benzene to low conversions using azobisisobutyronitrile as initiator. Nitrogen analysis of the purified copolymers enabled calculation of the percentage and mole percentage of 1-ethyl-3-vinylimidazolid-2-one residues in the copolymers. The monomer feeds, conversions and analyses are given in Table 2.9. The monomer - copolymer composition diagram Figure 2.7 is plotted from the mole percentage data in Table 2.10.

Table 2.9

Copolymerisation of 1-ethyl-3-vinylimidazolid-2-one (EVI) with ethyl acrylate (EtA)[a]

Feed			Copolymer				
Wt of EVI g	Wt of EtA g	Conversion[b] %	Analysis %			% EVI by wt	% EtA by wt
			C	H	N		
0.269	1.731	3.1	59.38	8.08	1.97	9.82	90.18
0.518	1.482	2.6	58.67	8.30	6.40	31.90	68.10
0.750	1.250	4.3	58.93	8.48	8.36	41.67	58.33
0.965	1.035	5.8	59.80	8.40	9.03	45.01	54.99
1.167	0.833	5.3	58.79	8.38	9.52	47.46	52.54
1.355	0.645	4.1	59.11	8.49	10.34	51.55	48.45
1.531	0.469	2.4	58.68	8.41	11.08	55.23	44.77
1.697	0.303	6.5	58.79	8.47	11.46	57.13	42.87
1.853	0.147	2.1	58.83	8.52	11.33	56.48	43.52

[a] polymerised at 10% $^{w}/_{w}$ monomer concentration in benzene with 0.2 mole % azobisisobutyronitrile as initiator at 60 $\pm$ 0.1°C

[b] estimated gravimetrically by precipitation in light petroleum (b.p. 40-60°)

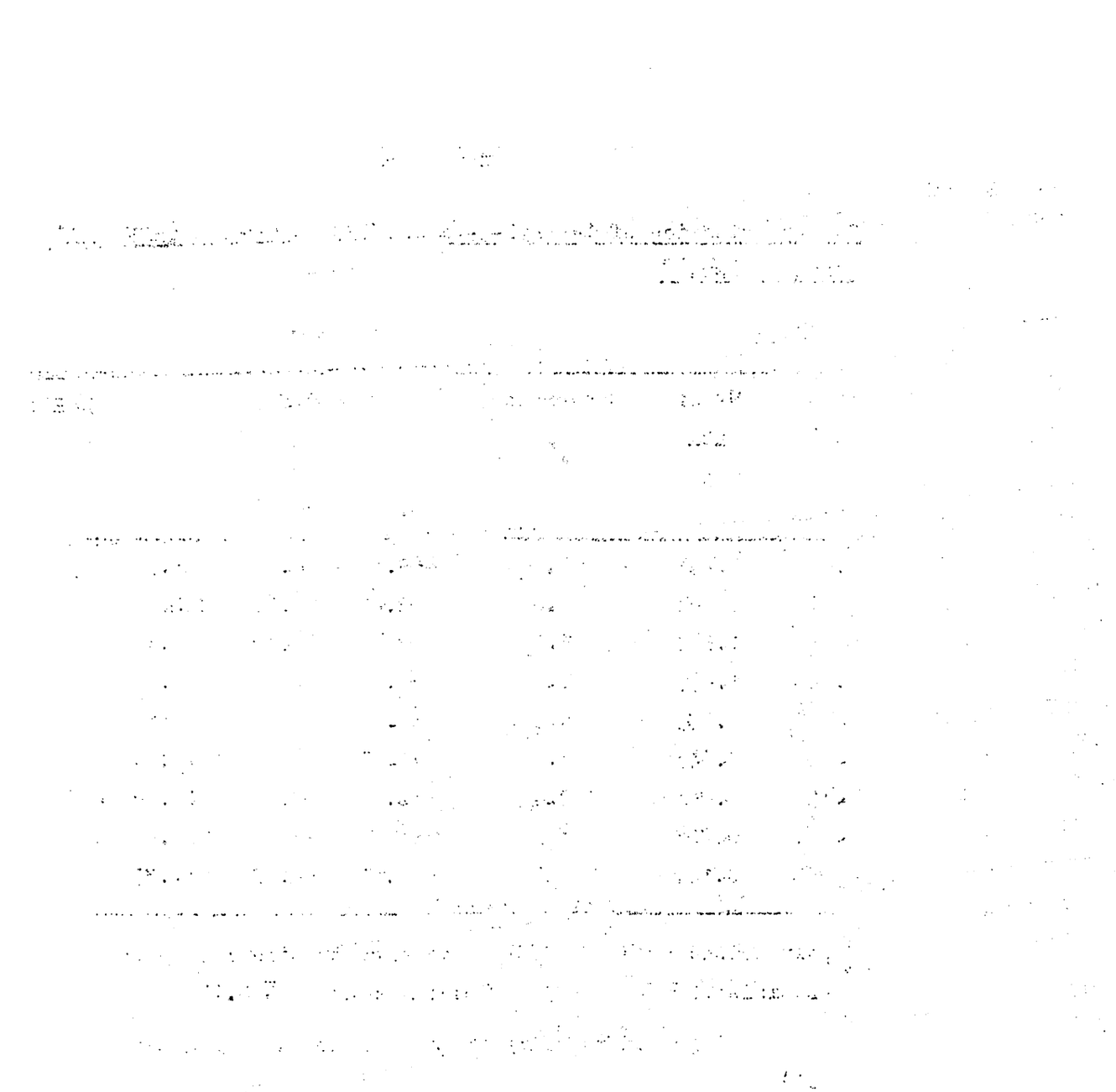


Table 2.10

Copolymerisation of 1-ethyl-3-vinylimidazolid-2-one (EVI) with ethyl acrylate (EtA)

Feed		Copolymer	
mole % EVI M_1	mole % EtA M_2	mole % EVI m_1	mole % EtA m_2
10.00	90.00	7.22	92.78
20.00	80.00	25.24	74.76
30.00	70.00	33.80	66.20
40.00	60.00	36.92	63.08
50.00	50.00	39.24	60.76
60.00	40.00	43.21	56.79
70.00	30.00	46.87	53.13
80.00	20.00	48.80	51.20
90.00	10.00	48.13	51.87

The shape of Figure 2.7 enables a prediction to be made of the reactivity ratios[83]. In this case, both r_1 and r_2 are predicted to be less than one. The azeotropic copolymerisation composition occurs at 36.5 mole % 1-ethyl-3-vinylimidazolid-2-one. Table 2.11 gives the calculated data for the Fineman--Ross plots which are shown in Figures 2.8 and 2.9.

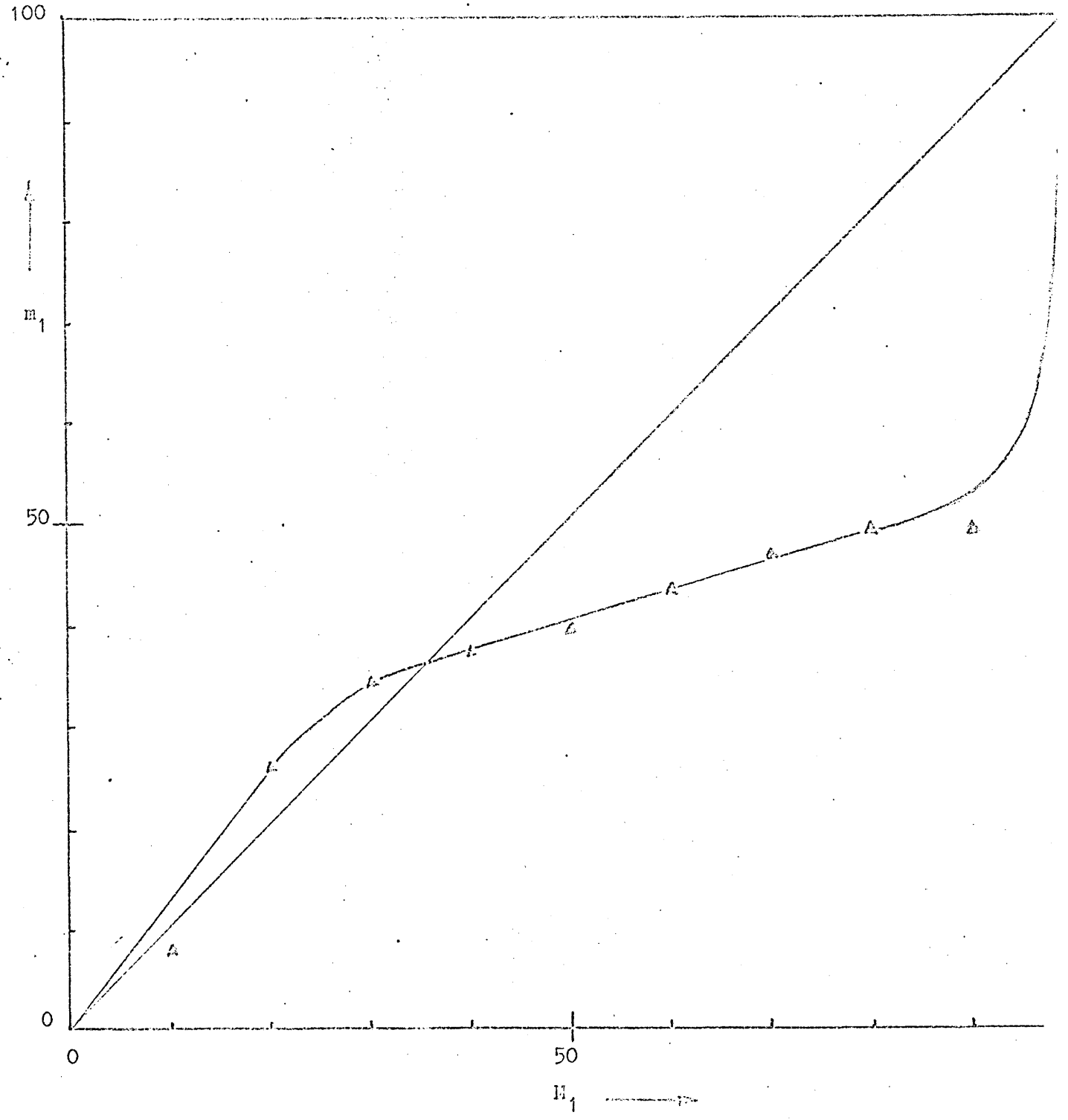


Figure 2.7

Monomer - polymer composition curve for the copolymerisation of 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate at 60°.

Table 2.11

Data for Fineman--Ross plots for the copolymerisation of 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate.

$F = \frac{M_1}{M_2}$	$f = \frac{m_1}{m_2}$	f-1	F/f	F^2	(F/f)(f-1)	F^2/f	$\frac{f-1}{F}$	$\frac{f}{F^2}$
0.111	0.073	-0.922	1.423	0.012	-1.312	0.154	-8.306	6.500
0.250	0.337	-0.663	0.742	0.062	-0.492	0.184	-2.652	5.435
0.428	0.510	-0.490	0.839	0.183	-0.411	0.359	-1.145	2.787
0.666	0.583	-0.415	1.139	0.443	-0.473	0.757	-0.622	1.320
1.000	0.646	-0.354	1.548	1.000	-0.548	1.548	-0.354	0.646
1.500	0.761	-0.239	1.971	2.250	-0.471	2.956	-0.159	0.338
2.333	0.882	-0.118	2.645	5.444	-0.312	6.172	-0.050	0.162
4.000	0.953	-0.047	4.197	16.000	-0.197	16.789	-0.012	0.059
9.000	0.928	-0.072	9.670	81.000	-0.696	87.284	-0.008	0.011

The slopes and intercepts calculated from Figures 2.8 and 2.9 give the reactivity ratios for the two monomers; Table 2.12 shows the values obtained.

Table 2.12

Reactivity ratios of 1-ethyl-3-vinylimidazolid-2-one and ethyl acrylate.

System	From plot of equation(2-4) (Figure 2.8)		From plot of equation(2-5) Figure (2.9)	
	r_1	r_2	r_1	r_2
1-ethyl-3-vinylimidazolid-2-one (M_1), ethyl acrylate (M_2)	0.09	0.48	0.07	0.50
	$r_1 = 0.094$, $r_2 = 0.53$[a]			

[a] results from computer program (Appendix 1)

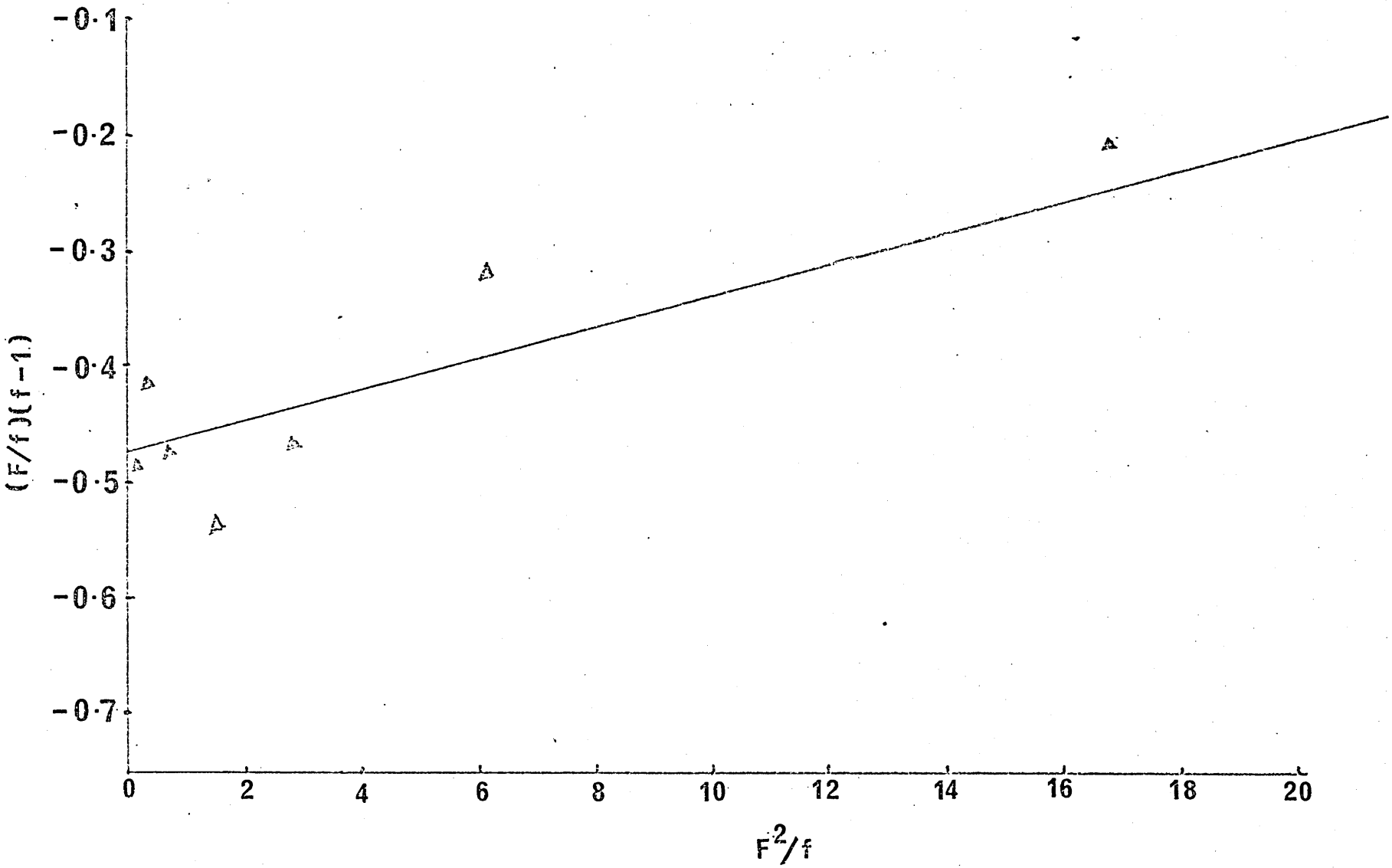


Figure 2.8

Fineman-Ross plot for the copolymerisation of 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate.

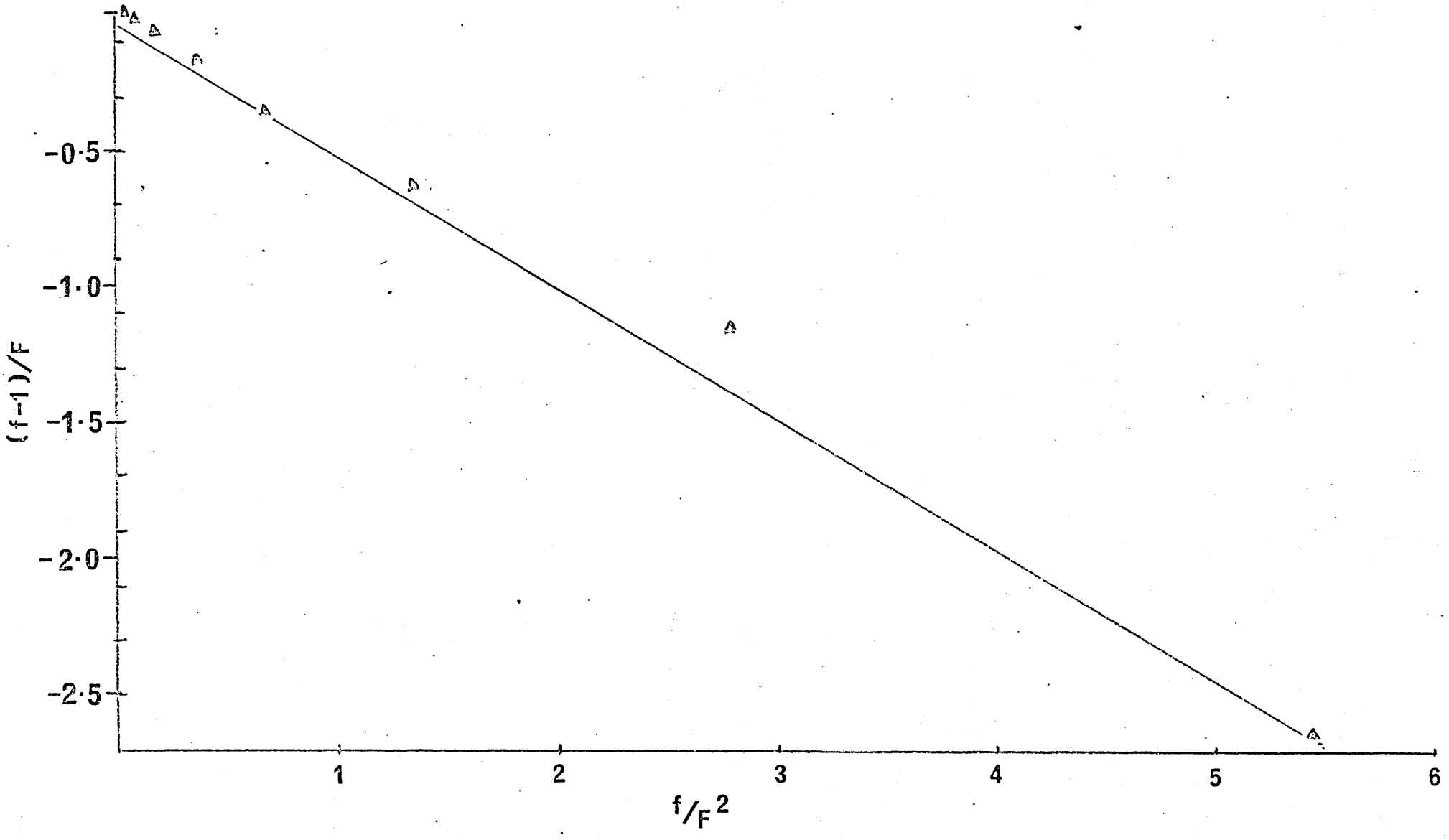


Figure 2.9

Fineman-Ross plot for the copolymerisation of 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate.

The Q and e values obtained for 1-ethyl-3-vinylimidazolid-2-one using equations (2-8) and (2-9) and Q = 0.52 and e = 0.22 for ethyl acrylate, are Q = 0.67 and e = -1.53. The Q and e values obtained for 1-ethyl-3-vinylimidazolid-2-one are compared with those for other N-vinyl compounds in Chapter 2.5. Substitution of the r_1 and r_2 values obtained into equation (2-10) gives a value of 35.7 mole % for the critical monomer feed compared with a value of 36.5 mole % obtained from Figure 2.7. This agreement seems to be satisfactory.

2.5 Comparison of the Copolymerisation Behaviour of N-Vinyl Monomers.

The reactivity ratios r_1 and r_2 for the copolymerisation of all the N-vinyl monomers studied and ethyl acrylate were both less than one. In such cases $k_{11} < k_{12}$ and $k_{22} < k_{21}$, so that there is a strong tendancy to form alternating copolymers. This was evident from the times required for the polymerisation of the various compositions of the N-vinyl monomers and ethyl acrylate to reach 5% conversion. When the concentration of ethyl acrylate was low the polymerisation took several hours to yield approximately 5% conversion, but as the concentration of ethyl acrylate increased so the time to reach approximately 5% conversion decreased. Finally, when the concentration of ethyl acrylate was high the time to give approximately 5% conversion increased. This behaviour is consistent with r_1 and r_2 being less than one, since the greatest rate of formation of an alternating copolymer would be when the concentrations of both comonomers were approximately equal. When one comonomer is present in a high concentration the growing polymer chain has statistically less chance to react with another monomer molecule in correct sequence and the rate of polymerisation is diminished.

The values of r_2 under discussion are the reactivity ratios for ethyl acrylate relative to the N-vinylurea molecules. If the reactivity ratios (R_2) of ethyl acrylate relative to the N-vinyl groups in the N-vinylureas are calculated, we obtain:

ethyl acrylate - 1,3-divinylimidazolid-2-one ($R_2=2r_2$), $R_2=0.776$

ethyl acrylate - 1,3-divinylhexahydropyrimid-2-one ($R_2=2r_2$), $R_2=1.098$

ethyl acrylate - 1-ethyl-3-vinylimidazolid-2-one ($R_2=r_2$), $R_2=0.53$

Thus, the N-vinyl groups in 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one are less reactive than the N-vinyl group in 1-ethyl-3-vinylimidazolid-2-one. This seems to support the proposal of Crawshaw and Jones[55], that a conjugated (resonance stabilised) structure would explain their inability to cyclopolymerise.

Table 2.13 gives the Q and e values for some N-vinyl monomers with the values obtained for 1,3-divinylimidazolid-2-one, 1,3-divinylhexahydropyrimid-2-one and 1-ethyl-3-vinylimidazolid-2-one included for comparison.

Table 2.13

Q and e parameters for some N-vinyl monomers[a]

Monomer	e	Q
N-Vinylurethane	-1.62	0.19
1,3-Divinylimidazolid-2-one	-1.58	0.84
N,N-Divinylaniline	-1.54	0.19
N-Ethyl-N-vinylurea	-1.53	0.13
1-Ethyl-3-vinylimidazolid-2-one	-1.53	0.67
N-Vinylphthalimide	-1.53	0.36
N-Vinylcarbazole[b]	-1.49	0.28
1,3-Divinylhexahydropyrimid-2-one	-1.40	0.68
S-Ethyl-N-methyl-N-vinylmonothiocarbamate	-1.29	0.11
N-N-Ethylene-N'-vinylurea	-1.19	0.18
N-Vinyl glycidylurethane	-1.15	0.18
N-Vinylpyrrolid-2-one	-1.14	0.14
N-Methyl-N-vinyl-p-toluenesulphonamide	-1.10	0.082
N-Vinyl-2-oxazolidone	-0.80	0.057
N-Vinylsuccinimide	-0.34	0.13

[a] values taken from reference 85 unless otherwise stated

[b] reference 86

The values in Table 2.13 show that the e values for the new N-vinyl compounds are consistent with other N-vinyl monomers. Since the N-vinyl group will dominate the copolymerisation behaviour, and the influence of the various N-substituents will be very similar, it is understandable that the parameter, e, which denotes the polar properties of the monomers and their radicals, will be similar for this series of compounds.

The Q values for the new monomers are much higher than those for the other monomers. However, since the Q-e scheme is an empirical method of analysis, the parameters of which are susceptible only to a quasi-theoretical interpretation, it would be extending the significance of the scheme

beyond the authors' intention to attach fundamental importance to these high results.

2.6 Attempted Copolymerisation of 1,3-Diphenyl-1,3-divinylurea with Various Comonomers.

Previously it has been reported that 1,3-diphenyl-1,3-divinylurea does not homopolymerise[55], and this behaviour attributed to the formation of a resonance stabilised free radical (Chapter 1.4). Such a radical may influence the polymerisation of other monomers in copolymerisation reactions.

Mixtures of 1,3-diphenyl-1,3-divinylurea and 1,3-divinylimidazolid-2-one or 1,3-divinylhexahydropyrimid-2-one were prepared, initiator (1 mole %) added, and the mixture heated at 150° for 5h. On cooling no polymerisation could be detected, the infrared spectrum showing essentially a mixture of the two monomers. The polymer tube was purged with nitrogen, resealed, 2 mole % initiator added and the mixture heated for a further 5h at 150°. Again no polymerisation could be detected. The process was repeated with 5 mole % of initiator, which again resulted in no polymerisation. The failure of mixtures of 1,3-diphenyl-1,3-divinylurea and other N,N'-divinylureas to polymerise is attributed to the ability of 1,3-diphenyl-1,3-divinylurea to quench radicals formed by the decomposition of the initiator. Finally, an excess of initiator, corresponding to a total concentration of 101 mole % (based on 1,3-diphenyl-1,3-divinylurea), was added. After 4.5h at 150° hard glassy polymers were obtained which after grinding to a powder and extracting with ethanol had infrared spectra almost identical to the spectra of poly(1,3-divinylimidazolid-2-one) or poly(1,3-divinylhexahydropyrimid-2-one), respectively. The spectra, after extraction, showed infrared bands at 700 and 760 cm^{-1} which were attributed to either residual 1,3-diphenyl-1,3-divinylurea as an end group, or, to some copolymerisation of 1,3-diphenyl-1,3-divinylurea with the N,N'-divinylurea co-monomer. Table 2.14 summarises the results obtained.

Table 2.14

Attempted copolymerisation of 1,3-diphenyl-1,3-divinylurea (DPDVU) with other N,N'-divinylureas[a]

Feed							
wt of DPDVU g	wt of DVI g	wt of DVHHP g	Initiator[b] mole %[c] Increment	Total	Time h Increment	Total	Result
0.50	0.50	-	1	1	5	5	no polymer
"	"	-	2	3	5	10	"
"	"	-	5	8	4.5	14.5	"
"	"	-	93	101	4.5	19.0	poly (DVI)
0.50	-	0.50	1	1	5	5	no polymer
"	-	"	2	3	5	10	"
"	-	"	5	8	4.5	14.5	"
"	-	"	93	101	4.5	19.0	poly (DVHHP)

[a] bulk polymerisation at 150°C

[b] di-tert.-butyl peroxide

[c] with respect to DPDVU only

Some monomers do not homopolymerise but are very reactive in copolymerisation, e.g. maleic anhydride does not readily homopolymerise but forms a highly regular alternating copolymer when copolymerised with styrene. When 1,3-diphenyl-1,3-divinylurea was investigated as a comonomer with vinyl acetate ethyl acrylate, methyl methacrylate and acrylic anhydride, no polymerisation occurred for 50% $^{w}/_{w}$ bulk polymerisations with 2-3 mole % of initiator. In each case a sample of the pure monomer gave high yields of homopolymer using identical conditions to those which failed to give a polymer when 50% of the monomer was replaced by 1,3-diphenyl-1,3-divinylurea. These results seemed to suggest that 1,3-diphenyl-1,3-divinylurea was acting as an inhibitor for these comonomers. This suggestion would support the proposal that the radical from 1,3-diphenyl-1,3-divinylurea is highly resonance stabilised, unable to homopropagate

or to propagate in copolymerisation reactions.However, when copolymerisation of 1,3-diphenyl-1,3-divinylurea was attempted with styrene as comonomer, some polymer precipitated when the reaction mixture was poured into methanol. The results obtained are given in Table 2.15.

Table 2.15

Attempted copolymerisation of 1,3-diphenyl-1,3-divinylurea with styrene[a]

Feed			Copolymer	
% DPDVU by wt	% styrene by wt	Conversion[b] %	% DPDVU[c] in polymer by wt	Reduced[d] Specific Viscosity
0.0	100.00	22	0.0	0.256
5.0	95.0	20	1.5	0.228
10.0	90.0	18	2.3	0.166
20.0	80.0	16	2.7	0.124
30.0	70.0	14	3.5	0.109

[a] polymerised at 50% $^{w}/_{w}$ monomer concentration in benzene with 0.5% $^{w}/_{w}$ azobisisobutyronitrile as initiator for 5h at 70°C

[b] estimated gravimetrically by precipitation in methanol

[c] calculated from nitrogen analysis

[d] determined in toluene

The results appear to indicate that 1,3-diphenyl-1,3-divinylurea does not copolymerise with styrene but in fact adds on to the propagating polymer chain as an end group. This is suggested by the small amount of 1,3-diphenyl-1,3-divinylurea incorporated in the polymer and the decrease in percentage conversion with increasing urea content for a fixed polymerisation time. These results would be expected, since a larger percentage of 1,3-diphenyl-1,3-divinyurea would terminate more growing polymer chains by forming end groups resistant to further propagation. The viscosity of the

polymers reflects the molecular weight, which, if end groups are terminating the propagation, would be expected to be lower for a higher percentage of terminating species. The results indicate that this is the case, the viscosity decreases as the concentration of 1,3-diphenyl-1,3-divinylurea increases.

Obviously, 1,3-diphenyl-1,3-divinylurea is not acting as an inhibitor in styrene polymerisations but the results suggest that some retardation in the rate of polymerisation is occurring. For identical polymerisation times the conversion drops from 22 to 14% as the concentration of 1,3-diphenyl-1,3-divinylurea is raised from 0 to 30%. It is useful at this stage to define the terms inhibitor and retarder. The generally accepted classification[87,88] is that inhibitors and retarders are substances which react with free radicals to form products which are incapable of further addition. Inhibitors react with radicals as soon as the radicals are formed and polymerisation cannot occur until all the inhibitor has been used up. In the presence of an inhibitor polymerisation will be preceeded by an induction period, the length of which depends on the amount of inhibitor used. Retarders are less reactive and compete with monomer for free radicals, reducing the rate and degree of polymerisation.

Thus, 1,3-diphenyl-1,3-divinylurea appears to act as a retarder for styrene polymerisations. To investigate this proposal a simple dilatometric study of the rate of polymerisation of styrene and styrene plus 1,3-diphenyl-1,3-divinylurea was undertaken. Table 2.16 gives the results obtained for the rate of polymerisation of styrene and styrene plus 5% $^{w}/_{w}$ of 1,3-diphenyl-1,3-divinylurea and Figure 2.10 shows a plot of the data in Table 2.16.

Table 2.16

Thermal polymerisation of styrene and styrene plus 5% 1.3-diphenyl-1,3-divinylurea (DPDVU)[a]

Time m (t)	Styrene		Styrene + 5% DPDVU	
	Dilatometer reading at time (t) - reading at t (0) cm[b]	Polymerisation %	Dilatometer reading at time (t) - reading at t(0) cm[b]	Polymerisation %
0	-	-	-	-
1	2.4	1.0	1.5	0.6
2	4.2	1.7	3.1	1.2
3	5.8	2.3	4.4	1.8
4	7.5	3.0	5.7	2.3
5	9.0	3.7	7.1	2.9
7	11.9	4.9	8.4	3.4
10	15.9	6.5	12.5	5.1
15	21.5	8.8	16.2	6.6
20	26.5	10.8	19.7	8.0
25	30.6	12.5	22.4	9.1
30	33.9	13.9	25.6	10.4
40	39.0	16.0	29.7	12.1

[a] at 70 ± 0.1°C

[b] mean of three readings

The results indicate that replacing part of the styrene with 5% $^{w}/_{w}$ of 1,3-diphenyl-1,3-divinylurea causes the rate of polymerisation to decrease. The plot shows no induction period, as would be typical of an inhibitor, but shows a rate decrease, typical of a retarder. 1,3-Diphenyl-1,3-divinylurea is not such an efficient retarder/inhibitor as tert. butyl catechol , for example, which causes inhibition of styrene at concentrations of 50 p.p.m. or less[89], but the results suggest that 1,3-diphenyl-1,3-divinylurea does form a stable radical which supports the proposal of a highly conjugated resonance stabilised structure made in Chapter 1, (Figure 1.2).

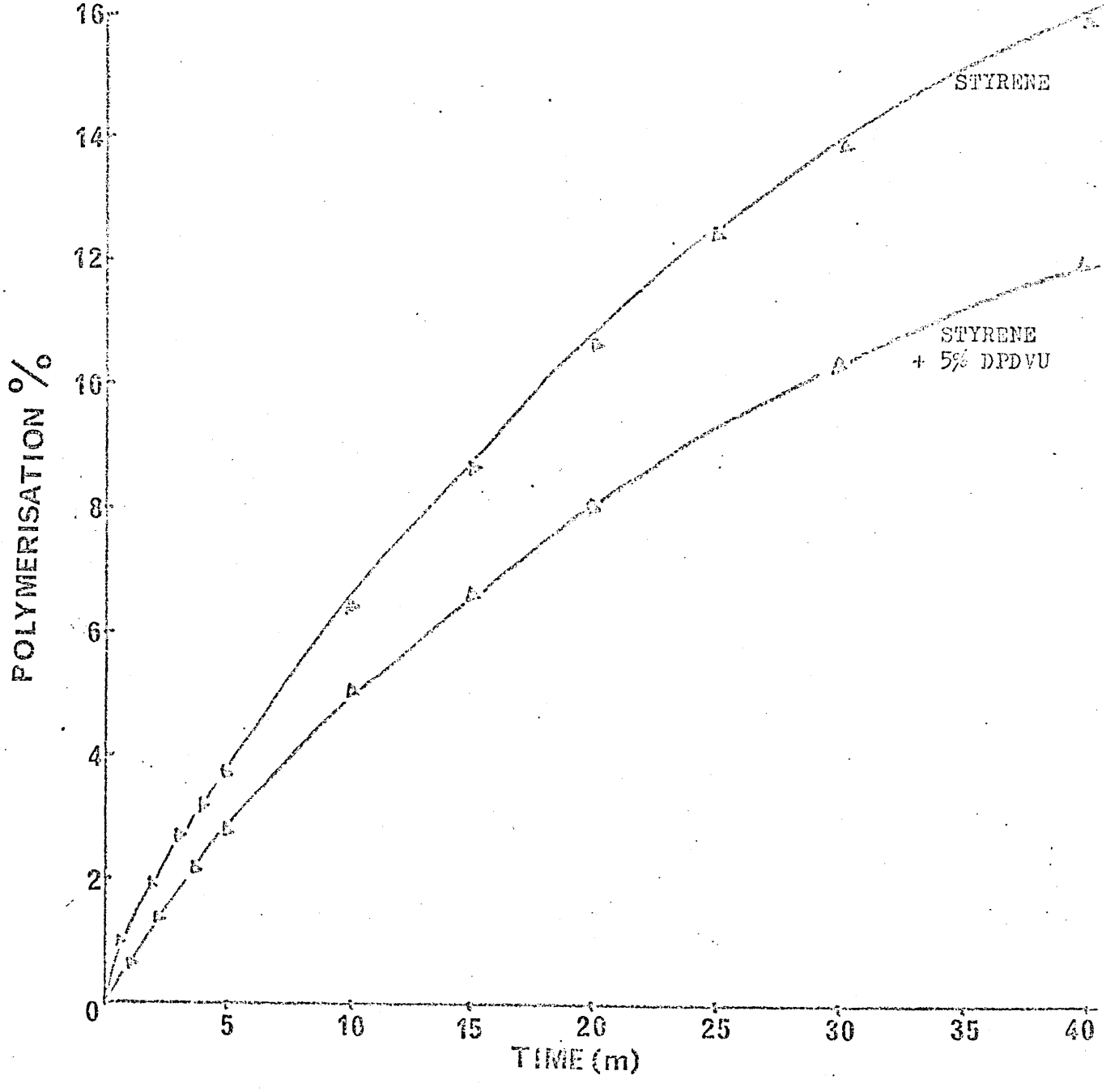


Figure 2.10

Thermal polymerisation of styrene and styrene plus 5% 1,3-diphenyl-1,3-divinylurea (DPDVU) at 70°C.

CHAPTER 3

Ultraviolet Absorption Spectroscopy applied to N,N'-Disubstituted Ureas

3.1 Introduction

To explain the inability of the various N,N'-disubstituted-N,N'-divinylureas to produce cyclopolymers, it has been proposed[55] that conjugation of the lone pair electrons on the nitrogen atoms with the vinyl and carbonyl double bonds produces a coplanar arrangement of these groups (Figure 1.1). Naturally, therefore, electronic absorption spectroscopy should make an important contribution to an investigation of the structure of these compounds.

In N,N'-divinylureas there are several chromophores, the carbonyl group, the vinyl groups and, in the case of 1,3-diphenyl-1,3-divinylurea, the phenyl groups. When two or more isolated chromophores occur in the same molecule, in relative positions such that there is no interaction between the chromophores, the resulting absorption curve is a summation of the absorption of individual chromophores. Any departure from such linear summation indicates the operation of some other effect causing interaction between the chromophores.

Interaction of two or more multiple bonds produces a conjugated system, which normally results in a bathochromic shift (to longer wavelength) of the position of the absorption band from that of the isolated multiple bond. Also, because the cross-sectional area of the absorbing electron system is increased on conjugation an increase in intensity (hyperchromic effect) arises on conjugation. These two effects are of prime importance in the use and interpretation of electronic spectra of organic molecules, because conjugation shifts the absorption of chromophores from a region of the spectrum that is not readily accessible to a region that is easily studied.

Table 3.1 shows a series of results for some polyenes, showing that increasing conjugation produces a smooth change in both position and intensity of absorption.

Table 3.1

Ultraviolet absorption of some conjugated polyenes[a]

$H \cdot (CH = CH)_n \cdot H$

n	ν_{max} cm^{-1}	λ_{max} nm	ε_{max}	Solvent
1	61500	163	15000	hexane
2	47000	217	21000	hexane
3	36300	268	34600	iso-octane
4	32900	304		cyclohexane
5	30000	334	121000	iso-octane
6	27500	364	138000	"
7	25600	390		"
8	24400	410		"
10	22400	447		"

[a] Reference 90

Over the range of n equal to 2,3 and 4 the trend may be approximated to:

$$\nu_{max} = 59000 - (n \times 7000)$$

$$\varepsilon_{max} = n \times 10000$$

Substitution by auxochromic groups usually produces a bathochromic shift with a hyperchromic effect on the extinction coefficient. These empirical correlations can be extended to other conjugated systems, including those containing multiple bonds between a carbon atom and a hetero atom. Such correlations are less accurate in these systems (Table 3.2) but they do indicate the approximate extent of conjugation from the main electronic absorption band.

Table 3.2

Ultraviolet absorption due to two conjugated chromophores[a]

System	Example	λ_{max} nm	ε_{max}
C=C-C=N	N-Butylcrotonaldimine	220	23000
N=C-C=N	Diacetyl-n-butylimine	209	18500
C=N-N=C	Butyraldazine	205	13000
C=C-C=O	Crotonaldehyde	217	16000

[a] Reference 91

Thus, assuming coplanarity of the conjugated system which results in the maximum overlap of the π-orbitals, the main electronic absorption band in N,N'-disubstituted-N,N'-divinylureas should be found above 200nm (λ_{max}) with an extinction coefficient (ε_{max}) of at least 10000. Comparisons within a series of N,N'-disubstituted ureas should serve to indicate the extent of the conjugated system and the relative degrees of coplanarity of similar systems.

3.2 Ultraviolet Absorption Spectra of N,N'-Disubstituted Ureas.

The ultraviolet absorption spectra of a number of substituted ureas have been recorded; λ_{max} and ε_{max} values are given in Table 3.3.

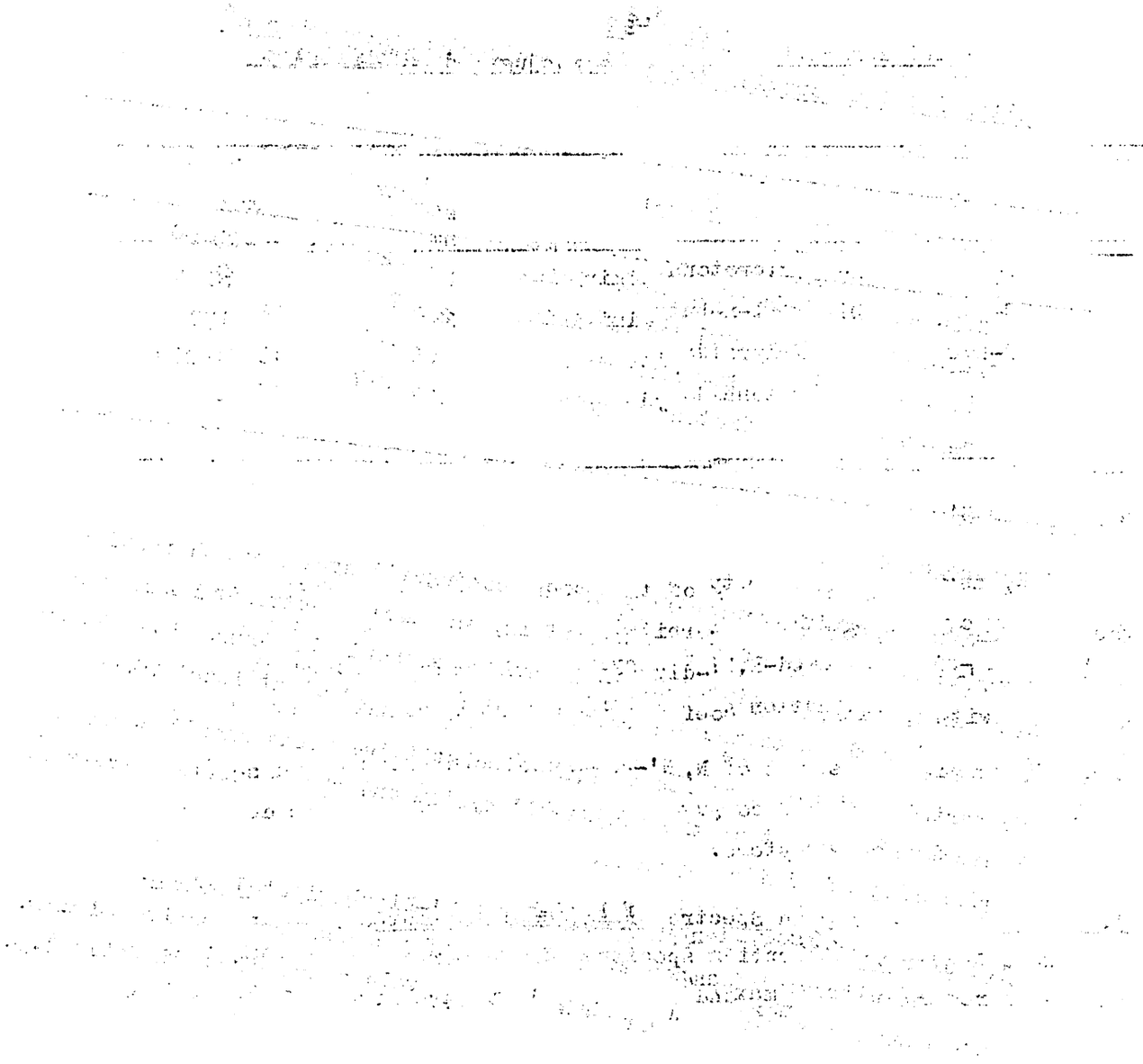


Table 3.3

Ultraviolet data of some substituted ureas[a]

No	Compound	Chart Reference	λ_{max}	ε_{max}	Reference
I	1,3-Divinylimidazolid-2-one	AIV	251	37600	
II	1-Ethyl-3-vinylimidazolid-2-one	EVII	230	20800	
III	1,3-Diacetylimidazolid-2-one	FII	227[b]	25500[b]	
IV	1-Acetylimidazolid-2-one	FI	215[b]	13000[b]	
V	1-Formylimidazolid-2-one	FIII	214[b]	14250[b]	
VI	1,3-Diphenylimidazolid-2-one	CIA	266	37000	
VII	1,3-Dibenzylimidazolid-2-one	FVII	260	400	
VIII	1,3-Divinylhexhydropyrimid-2-one	BV	248	40800	
IX	1,3-Dimethyl-1,3-divinylurea	DIV	245	15700	
X	1,3-Diphenyl-1,3-divinylurea	CIV	253	18200	
XI	1,3-Diethyl-1,3-diphenylurea	-	247[c]	8700[c]	92
XII	1-Phenyl-3-vinylurea	-	250	38000	93
XIII	1-Ethyl-3-phenylurea	-	240[c]	19800[c]	92
XIV	1,3-Diphenylurea	-	256[c]	37200[c]	92

[a] recorded in methanol unless otherwise stated

[b] recorded in water

[c] recorded in ethanol

All of the N,N'-divinylureas which have been studied have a strong absorption band in the ultraviolet region of the spectrum (compounds I, VIII, IX and X in Table 3.3). The position and intensity of the bands are unlike those of isolated chromophores of the type contained in these compounds, which is good evidence that conjugation of the electron pairs on the nitrogen atoms with the π electrons of the vinyl and carbonyl double bonds is responsible for the ultraviolet absorption of N,N'-divinylureas. Such an overlap needs some degree of coplanarity to be successful, which would explain the inability of these compounds to cyclopolymerise. The conjugation prevents the second vinyl group in an initiated molecule from adopting a conformation suitable for the

Table 5.1

intramolecular cyclisation reaction.

That the vinyl groups are involved in this conjugation, is shown by the fact that when a vinyl group on an imidazolid-2-one ring is replaced by an ethyl group, there is a hypsochromic shift and a hypochromic effect on the extinction coefficient (compare compounds I and II, Table 3.3). Although the data were recorded in different solvents, a similar effect is found in the N,N'-diphenylurea system, compounds X and XI, and the derivatives of phenylurea, compounds XII and XIII.

Other unsaturated groups (acetyl, formyl or phenyl) attached to the nitrogen atoms in ureas are also found to be conjugated with the carbonyl of the urea group 1,3-diacetylimidazolid-2-one has a strong absorption band which is modified by removal of one of the acetyl groups (compounds III and IV). 1-Formylimidazolid-2-one, (compoundV) has a similar absorption spectrum to 1-acetylimidazolid-2-one. 1,3-Diphenylimidazolid-2-one (compound VI) has a strong absorption band which is again attributed to conjugation of the aromatic rings with the urea carbonyl group via the nitrogen atoms. In 1,3-dibenzylimidazolid-2-one (VII) the aromatic rings cannot be conjugated with the urea carbonyl group because of the presence of the methylene groups. Here, the data are typical of two isolated aromatic rings[94]. A comparison of compounds XIII and XIV is further evidence that a decrease in the number of unsaturated groups attached to the nitrogen atoms results in a hypsochromic shift and has a hypochromic effect on the extinction coefficient.

If the hydrogen atoms attached to the nitrogens of 1,3-diphenylurea (XIV) are replaced by ethyl groups (XI) there is a considerable change in the spectrum which indicates that there is a diminished interaction between the π - orbitals of the aromatic rings and the urea group. This seems to be a steric effect due to the presence of the relatively bulky ethyl groups. The aromatic rings are unable to take up a planar conformation because of overcrowding in the molecule. Presumably the steric strain is relieved by twisting the essentially single bond between the aromatic ring and the nitrogen atom and/ or the essentially single bond in the urea group. Since there is a considerable hypsochromic shift and a large decrease in absorption intensity, the departure from coplanarity must be significant.

In 1,3-diphenyl-1,3-divinylurea (X) the introduction of vinyl groups to replace ethyl groups produces, as expected, a bathochromic shift and has a hyperchromic effect on the extinction coefficient. There is certainly an increase in conjugation in the system. However, the position

[illegible]

[illegible] in [illegible] required [illegible]

[illegible]

[illegible]

cap [illegible]

only [illegible]

[illegible]

[illegible] the [illegible] effect [illegible] coefficient.

If the hydrogen atom [illegible]

(IV) are replaced [illegible]

in the same [illegible]

between [illegible]

seems [illegible]

only [illegible]

[illegible]

are [illegible]

[illegible]

and intensity of the absorption band indicates the overlap of orbitals is not as successful as in 1,3-diphenylurea (XIV). The spectrum of 1,3-diphenyl-1,3-divinylurea (X) suggests that the molecule does not adopt a conformation with either the two phenyl groups or the two vinyl groups, or one phenyl and one vinyl group coplanar with the urea group (carbonyl). The intensity of the absorption band is far less than those of compounds XIV, VI, I, VIII or XII. However, it does show that there is considerable conjugation in this molecule which would support the proposal that a resonance stabilised radical is responsible for its inability to polymerise, (Figure 1.2).

1,3-Diphenylimidazolid-2-one (XV) has a similar absorption spectrum to 1,3-diphenylurea (XIV), which suggests that the phenyl groups can assume a conformation coplanar with the cyclic urea group. Thus, the steric effect of substituents on the nitrogen atoms is removed if they are part of a five-membered ring system. Since compounds I and VIII have similar absorption bands the same effect is found if the substituents are part of a six-membered ring.

In 1,3-dimethyl-1,3-divinylurea (IX), the absorption spectrum indicates that there is a conjugated system but that it is unable to take up a completely planar conformation because of overcrowding of the groups attached to the nitrogen atoms. This departure from coplanarity effects the position and intensity of the absorption band of the conjugated system compared to 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one. Two possible conformations for 1,3-dimethyl-1,3-divinylurea molecules have been proposed in Chapter 1. In either conformation, steric interactions involving the methyl groups would explain the lack of coplanarity in the conjugated system. Since both 1,3-divinylimidazolid-2-one and 1,3-divinyl-hexahydropyrimid-2-one form polymers via an intermolecular propagation reaction, it would seem that the methyl group attached to the same nitrogen atom as an initiated vinyl group is sterically hindering approach of another molecule. In the cyclic ureas these groups are held back by the ring of which they are a part, thus allowing polymerisation to proceed.

Chapter 5 describes some other techniques which were investigated in an attempt to elucidate the structures of cyclic and acyclic N,N'-divinyl-ureas.

3.3 Synthesis of N,N'-Disubstituted Ureas.

Chapter 1 describes the synthesis of the N,N'-divinylureas mentioned in this Chapter. N,N'-Dibenzylimidazolid-2-one and the N,N'-dialkylureas referred to in Chapter 5 were synthesised from the di-sodium salt of the appropriate urea and an alkyl halide. The di-sodium salt of each urea was

prepared using sodium hydride in anhydrous N,N-dimethylformamide. Charts F and G show the N,N'-disubstituted ureas prepared by this method, which proved to be a facile and versatile synthetic route. Previous routes to N,N'-disubstituted imidazolid-2-ones and hexahydropyrimid-2-ones used phosgene and N,N'-disubstituted ethylenediamines[95,96].

1-Acetylimidazolid-2-one (FI) was synthesised by refluxing imidazolid-2-one with acetic anhydride in glacial acetic acid[97], and 1,3-diacetyl-imidazolid-2-one (FII) by refluxing imidazolid-2-one with acetyl chloride in glacial acetic acid[98]. 1-Formylimidazolid-2-one (FIII) was prepared from imidazolid-2-one using a mixture of acetic anhydride and formic acid.

CHAPTER 4

Hydrolysis of N,N'-Divinylureas

4.1 Introduction.

This section of the work on N,N'-divinylureas was a result of attempted polymerisations under weakly acidic conditions. Since the ultraviolet absorption spectra of N,N'-divinylureas (Chapter 3) had provided proof of conjugation across the $CH_2=CH-N-CO-N-CH=CH_2$ system, it was considered that protonation of the nitrogen atoms would remove this conjugation and allow the vinyl groups to undergo cyclopolymerisation. If the conjugation were removed in this way, then polymerisation using redox initiators in aqueous solution might be possible. These conditions would be less severe than addition of concentrated acid, the technique used by Overberger[57], which, in my attempts resulted in the hydrolysis of N,N'-divinylureas (Chapter 1).

N-vinylamides are known to hydrolyse to acetaldehyde and the corresponding amide[99], and I have already commented on the hydrolysis of N,N'-divinylureas. However, the rate of hydrolysis is the important factor. If the rate of hydrolysis is comparable with the rate of polymerisation, the formation of cyclopolymers will be impossible. A study of the hydrolysis of N-vinylpyrrolid-2-one in aqueous acid at room temperature showed that at pH 5 only 1% of the monomer hydrolysed in 6h[99]. This monomer can be polymerised to a high molecular weight polymer in aqueous solution.

4.2 Effect of Acidic Solutions on the Ultraviolet Absorption Spectra of N,N'-Divinylureas.

The absorption spectra of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one were recorded in solutions of varying pH values. The spectra were found to be pH dependent; lowering the pH caused the absorption bands to diminish and finally disappear. This was considered to reflect the equilibrium between the free N,N'-divinylurea and the nitrogen-protonated species:

$$CH_2=CH-N-CO-N-CH=CH_2 \rightleftharpoons CH_2=CH-N-CO-\overset{+}{N}(H)-CH=CH_2 \rightleftharpoons CH_2=CH-\overset{+}{N}(H)-CO-\overset{+}{N}(H)-CH=CH_2$$

However, it was soon apparent that the spectra were also time dependent. The absorption bands diminished and disappeared on leaving acidic solutions of the ureas standing. The rate of disappearance of the band was dependent upon the pH of the solution; in solutions of low pH

the peak diminished at a greater rate than in solutions of higher pH. Even aqueous (neutral) solutions of these N,N'-divinylureas after standing for several days were found to have no ultraviolet absorption band at the position where they previously had an intense absorption. This led to the suggestion that hydrolysis of the N-vinyl group was occuring:

$$CH_2{=}CH{-}\underset{|}{N}{-}CO{-}\underset{|}{N}{-}CH{=}CH_2 \quad + \quad 2H_2O \longrightarrow 2CH_3CHO \quad + \quad \underset{|}{H.N}{-}CO{-}\underset{|}{NH}$$

Controlled hydrolysis of these ureas did yield acetaldehyde and the corresponding urea (Chapter 1).

The ultraviolet absorption maxima of acidic solutions of both 1,3-dimethyl-1,3-divinylurea and 1-ethyl-3-vinylimidazolid-2-one were also found to decrease with time due to hydrolysis of the N-vinyl groups.

A dilute acid solution (pH 3.5), which caused rapid hydrolysis of the other N-vinylureas, had no immediate effect on the absorption spectrum of 1,3-diphenyl-1,3-divinylurea. However, increasing the strength of the acid solution to 2· molar caused the absorption at 253nm to increase. The equilibrium absorbance value corresponded to a molar extinction coefficient, ε = 28000, based on 1,3-diphenyl-1,3-divinylurea. The increase in absorbance is consistent with the proposal that hydrolysis would produce 1,3-diphenylurea, which has an ε value of 37000 compared with 18200 for 1,3-diphenyl-1,3-divinylurea (Table 3.3). The value, ε = 28000, is based on 1,3-diphenyl-1,3-divinylurea; if this value is modified by using the molecular weight for 1,3-diphenylurea in the calculation, then the ε value becomes 35000, which compares very well with the value 37000 for 1,3-diphenylurea in ethanol[92]. Apart from steric effects, the difference in reactivity between 1,3-diphenyl-1,3-divinylurea and the other N-vinylureas may be interpreted in terms of resonance stabilisation by the phenyl groups on the N-vinylurea structure, thus lowering the nucleophilic reactivity of the β-carbon atoms and the basicity of the nitrogen atoms.

4.3 Rates of Hydrolysis of 1,3-Divinylimidazolid-2-one and 1,3-Divinylhexahydropyrimid-2-one in Acidic Solutions.

As both 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one have intense ultraviolet absorption bands, the rate of disappearance of the absorption band can be used as a measure of the rate of hydrolysis. The absorbance of various concentrations of these N,N'-divinylureas in water was measured at the respective absorption maximum for each compound to produce a calibration curve. The results are given in Table 4.1 and Figures 4.1 and 4.2 show the calibration curves.

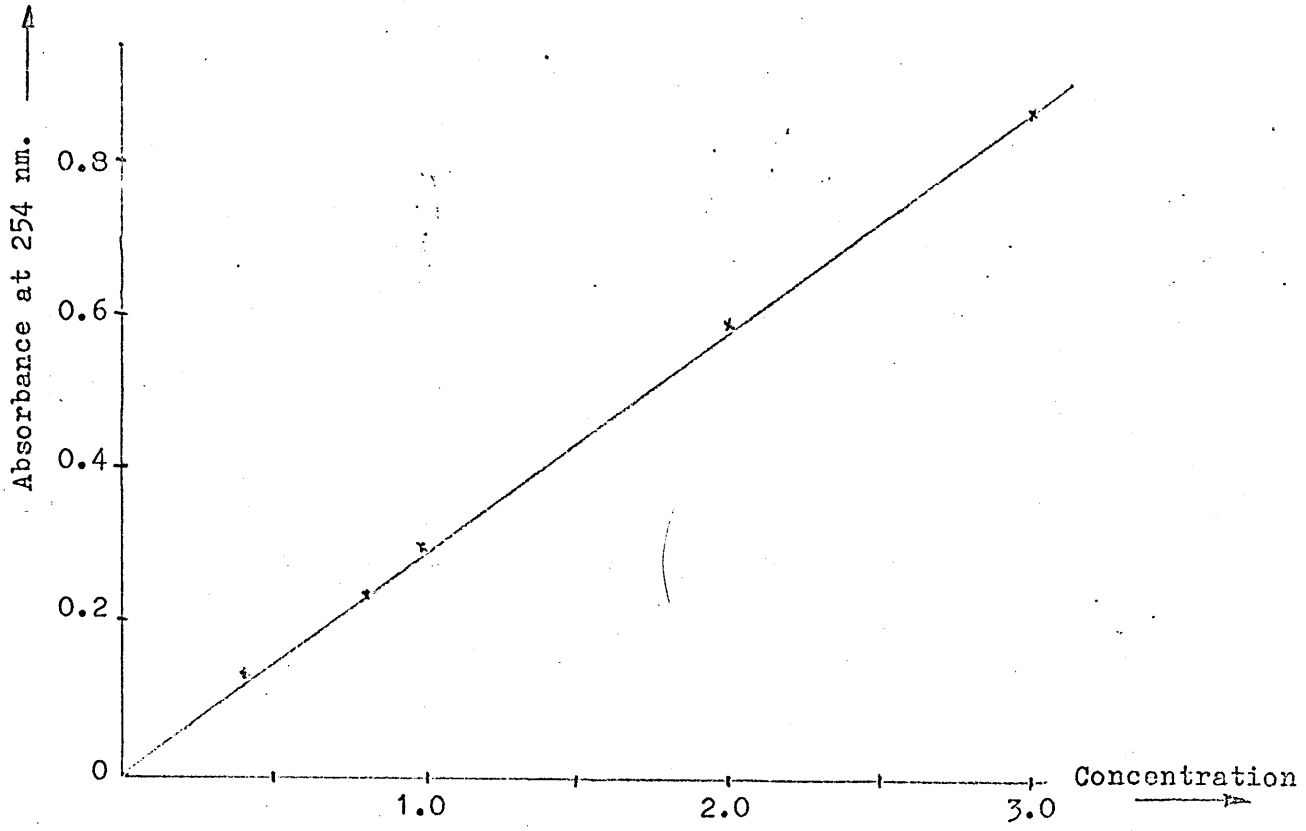


Figure 4.1

Beer-Lambert plot for 1,3-divinylhexahydropyrimid-2-one

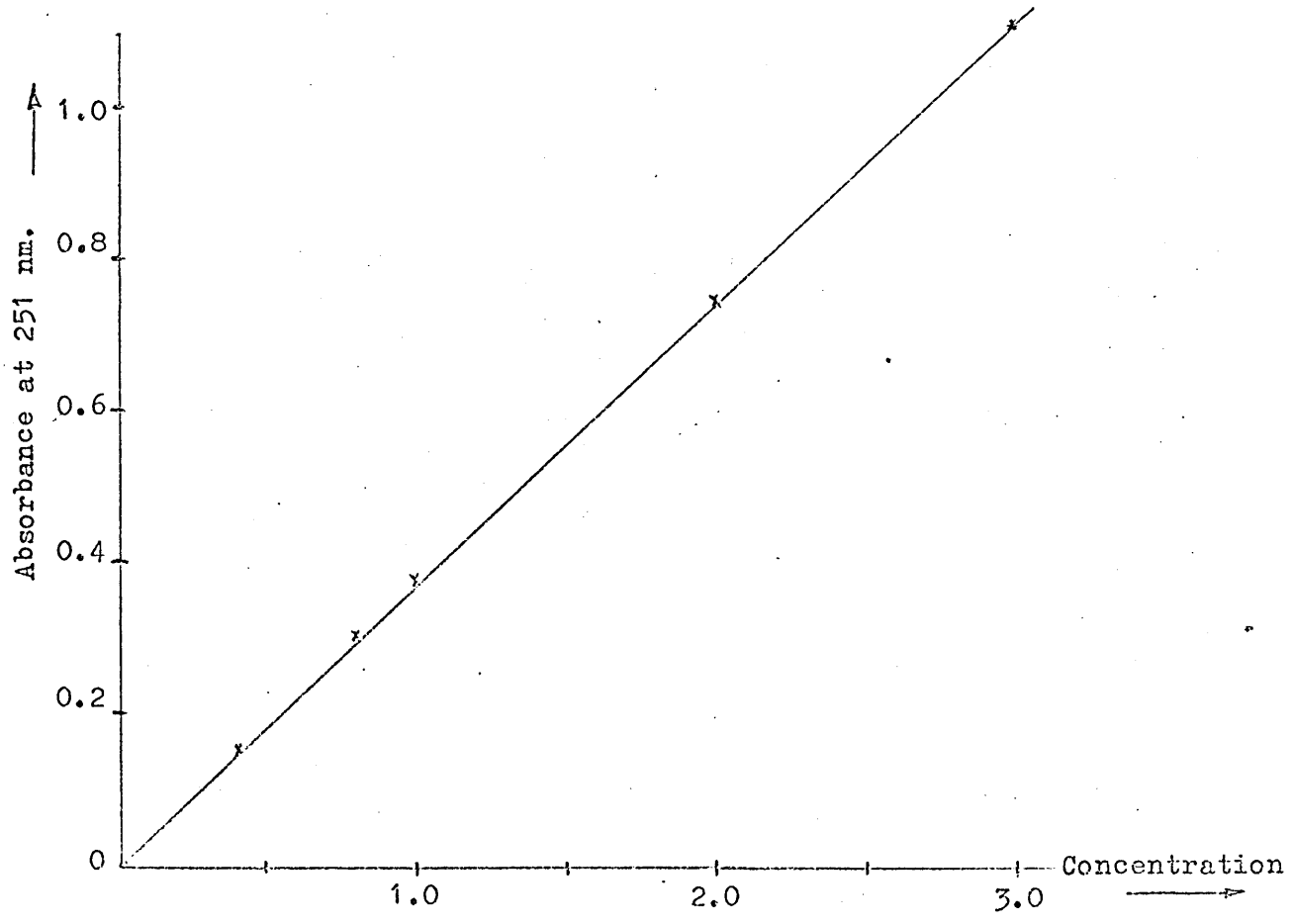


Figure 4.2

Beer-Lambert plot for 1,3-divinylimidazolid-2-one.

Table 4.1

Data for calibration curves of absorbance against concentration for 1,3-divinylimidazolid-2-one and 1,3-divinylhexhydropyrimid-2-one

Concentration[a] ($X10^{-5}$) mol	Absorbance[b] at 254 nm for 1,3-divinylhexahydro-pyrimid-2-one	Absorbance[b] at 251 nm for 1,3-divinylimida-zolid-2-one
0.4	0.128	0.154
0.8	0.237	0.301
1.0	0.298	0.381
2.0	0.588	0.745
3.0	0.872	1.103

[a] in water

[b] mean values of 3 readings whose difference did not exceed $\pm$ 0.002 absorbance units on Unicam SP 500 instrument

The calibration curves obtained were straight lines showing that absorbance and concentration are directly related. Thus the concentration of N,N'-divinylurea can be measured from the absorbance of the solution (Beer-Lambert Law).

The rates of hydrolysis of 1,3-divinylimidazolid-2-one and 1,3-divinylhexhydropyrimid-2-one were measured by transferring aliquots from a standard solution of each urea to graduated flasks containing constant ionic strength buffer solutions[100]. All solutions were maintained at a constant temperature (25°C). Zero time was measured from the moment when half the aliquot had been pipetted into the flask, which was then made up to the graduation mark with buffer solution. A sample of the mixture was then transferred to a 1 cm. silica cell and the absorbance of the solution was determined against a blank of the buffer solution at 2 minute intervals. The temperature was maintained throughout at 25°C.

The hydrolysis data exhibited firstorder kinetics; that is, a plot of the logarithm of the concentration of N,N'-divinylurea against time produced a straight line (Figure 4.3). Since the concentration of the buffer solution is very much greater than that of the N,N'-divinylurea, the

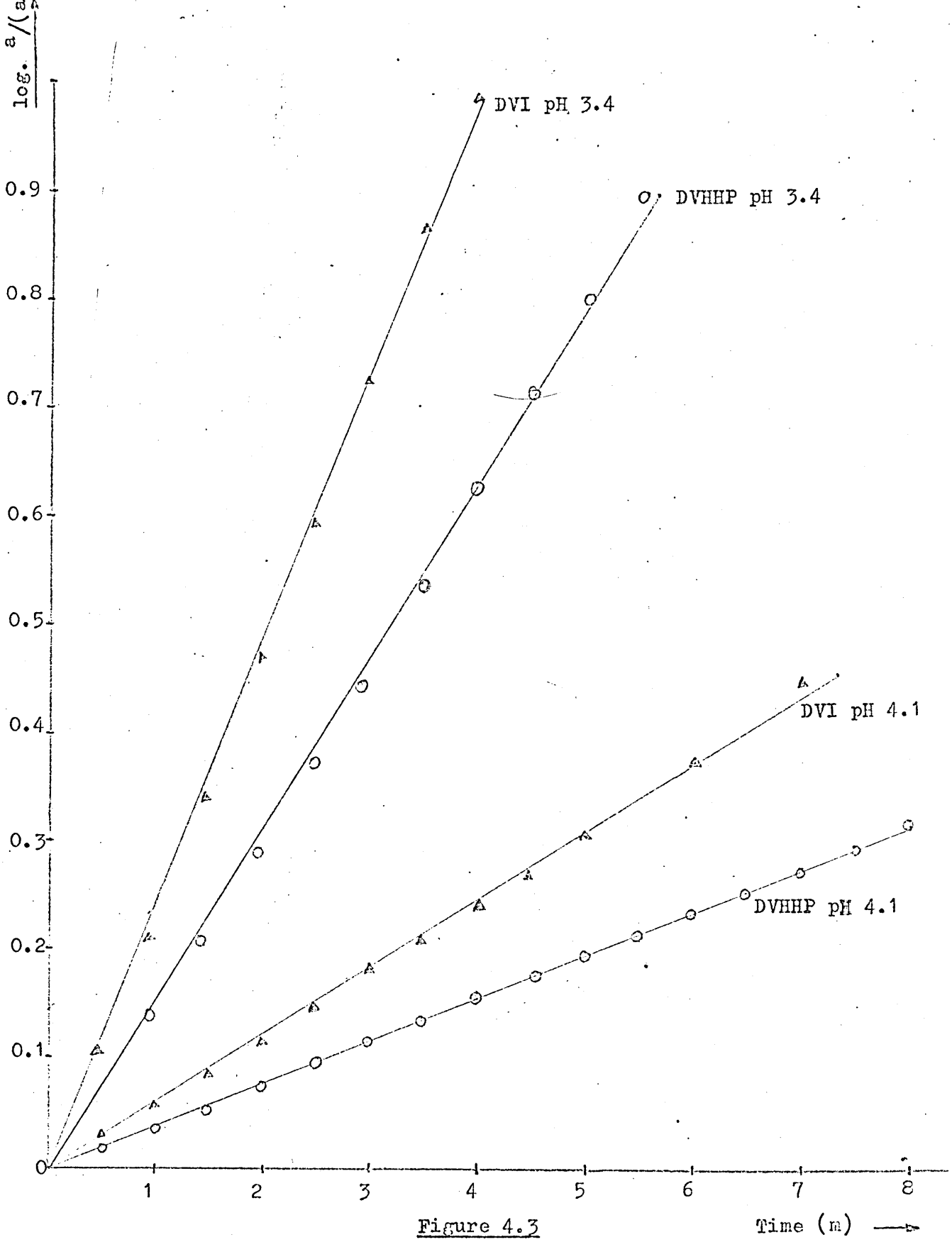


Figure 4.3

First order plots for the hydrolysis of 1,3-divinylimidazolid-2-one (DVI) and 1,3-divinylhexahydropyrimid-2-one (DVHHP) at different pH values.

change in the buffer concentration is negligible compared with the change in urea concentration and the reaction order is termed pseudo first order. Most hydrolysis reactions in aqueous solution exhibit pseudo first-order kinetics since water is usually present in great excess.

Table 4.2 gives the pseudo first order rate constants for the hydrolysis of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one.

Table 4.2

Pseudo first order rate constants in constant ionic strength buffers (Z=0.10) of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one at $25^{o} \pm 0.1^{o}$

pH (Z=0.10)	Rate constants of 1,3-divinylimidazolid-2-one (DVI) $k \times 10^{3}\ s^{-1}$	Rate constants of 1,3-divinylhexahydropyrimid-2-one (DVHHP) $k \times 10^{3}\ s^{-1}$	ratio DVI / DVHHP
4.10	1.07	0.70	1.53
3.80	2.06	1.24	1.66
3.40	4.36	2.60	1.67

The data in Table 4.2 show that the N,N'-divinylureas are rapidly hydrolysed by dilute acidic solutions. At pH 4.10, 1,3-divinylimidazolid-2-one has a half-life of approximately 320 seconds, which means that 50% of the urea will be hydrolysed in about 5 minutes. This is much faster than the rate of hydrolysis of N-vinylpyrrolid-2-one; 1% hydrolysis over 6h at pH 5. These results indicate that it is not practicable to cyclopolymerise the N,N'-divinylureas studied in aqueous solutions because of the rate at which hydrolysis takes place.

4.4 Mechanism of the Hydrolysis Reaction.

By analogy with the reaction schemes proposed for the hydrolysis of enamines[101], the hydrolysis of N-vinylureas to acetaldehyde and the corresponding urea can be written as shown in Figure 4.4.

The acid-base equilibrium (a) is set up very rapidly and causes a decrease in concentration of the conjugated N-vinylurea molecules immediately the compound is dissolved in the buffer solution. Only the fraction $k/(k + A_{H_3O^+})$ of the total amount is present as conjugated molecules which explains the pH dependence of the ultraviolet absorption

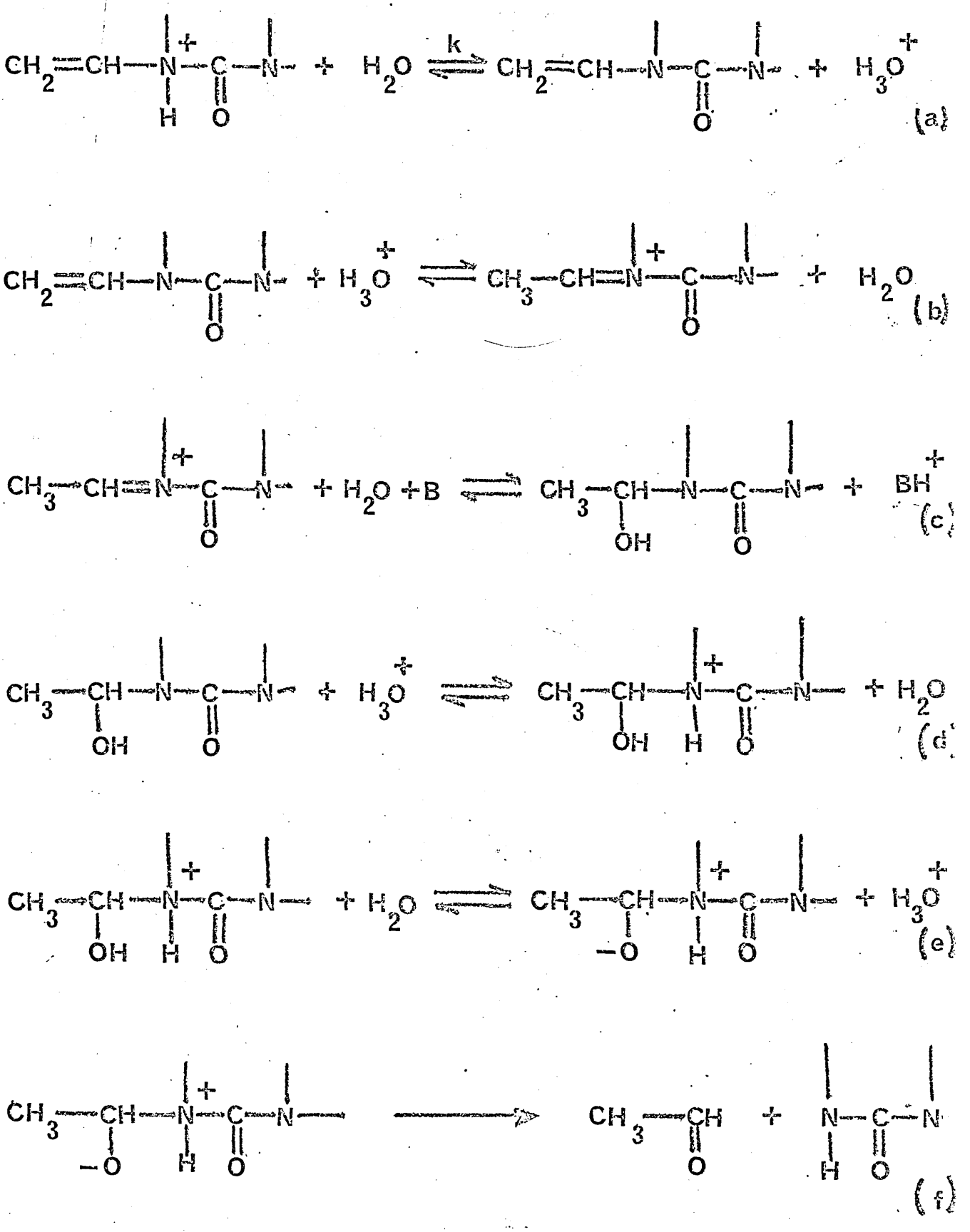


Figure 4.4

Proposed mechanism for the hydrolysis of N-vinylureas.

spectra of N-vinylureas.

The double bond of the nitrogen-protonated species would presumably be stable with respect to electrophilic attack under the reaction circumstances, since the electron pair on nitrogen is no longer available for interaction with π electrons of the double bond.

Proton transfer to the β-carbon atom (b) has been proposed as the rate determining step in the hydrolysis of certain enamines in alkaline and neutral solution[101]. The observation of immonium ions in strongly acidic solutions by ultraviolet and n.m.r. spectroscopy also indicates that these equilibria do exist.

Base-catalysed hydration of these ions to the amino alcohol (c) is assumed as the rate determining step of the hydrolysis of enamines in weakly acidic media. The catalysing action involves the removal of a proton from a water molecule in its attack on the immonium ion. The rate of hydrolysis of certain Schiff bases in acidic solution is also determined by attack of base (hydroxide ion or water) on the protonated Schiff bases[102].

In strongly acidic media the amino alcohol will be nitrogen-protonated (d) and in equilibrium with the dipolar structure (e). The zwitterion is assumed to be the active intermediate in the decomposition of certain enamines and Schiff bases[101,102] to the carbonyl compound, an irreversible reaction (f).

The hydrolysis of N-vinylureas may be considered to proceed via these separate equilibrium reactions. Which reaction in the sequence becomes rate-determining will depend on the pH of the solution as well as on the structure of the intermediates. However, kinetic protonation in the hydrolysis of these compounds occurs at the nitrogen atom, whereas the reaction to the thermodynamic product takes place via protonation at the β-carbon atom.

4.5 Rates of Hydrolysis of 1,3-Divinylimidazolid-2-one and 1,3-Divinylhexahydropyrimid-2-one at Different Temperatures.

Using the procedure outlined in 4.3, the rates of hydrolysis of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one were measured at two temperatures in solutions with a constant pH value. The results obtained are shown in Table 4.3.

Table 4.3

Pseudo first order rate constants in constant ionic strength buffers (Z=0.10) of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one at various temperatures.

Temperature °C	pH (Z=0.10)	Rate constants of 1,3-divinylimidazolid-2-one (DVI) $k \times 10^3$ s^{-1}	Rate constants of 1,3-divinylhexahydropyrimid-2-one (DVHHP) $k \times 10^3$ s^{-1}	Ratio DVI / DVHHP
40	4.80	0.80	-	
41	4.80	-	0.73	
50	4.80	1.59	1.13	1.41

Table 4.4 shows the entropies and enthalpies of activation, calculated from the data in Table 4.3.

Table 4.4

Entropies and enthalpies of activation for the hydrolysis of 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one.

	$Ea^{\neq}$ KJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} deg^{-1}
1,3-divinylimidazolid-2-one	57.3	83
1,3-divinylhexahydropyrimid-2-one	40.6	142

The data show that the $\Delta S^{\neq}$ value is important in the hydrolysis of these N,N'-divinylureas. Although the activation energy for the hydrolysis of the five-membered ring urea is higher than that for the six-membered ring urea, 1,3-divinylimidazolid-2-one hydrolyses approximately one and a half times faster than 1,3-divinylhexahydropyrimid-2-one.

It seems that the change in structure from the five-membered ring to the six-membered ring changes the shape of the energy surface at the transition state, which produces this difference in the entropy of activation. Models of these two N,N'-divinylureas, using sp^2 hybridisation

for the nitrogen atoms, indicate that 1,3-divinylimidazolid-2-one forms a rigid, planar ring whereas 1,3-divinylhexahydropyrimid-2-one forms a puckered ring with carbon atom C_5 able to move above and below the plane of the rest of the ring.

Stamhuis[103] found that the rates of hydrolysis of pyrrolidino enamines were much greater than the corresponding piperidino compounds, despite the fact that the basicities were very similar. Stamhuis suggests that the five-membered ring enamine forms an exocyclic double bond more easily than the corresponding six-membered ring enamine. This is found in other reactions of these enamines with electrophilic reagents[104,105]. Similarly, the results in this Chapter show that 1,3-divinylimidazolid-2-one, a five-membered ring N,N'-divinylurea, is more reactive in hydrolysis reactions than 1,3-divinylhexahydropyrimid-2-one, a six-membered ring N,N'-divinylurea.

CHAPTER 5

Investigation of the Structure of N,N'-Divinylureas using other Physical Methods.

5.1 Introduction

Nuclear magnetic resonance spectroscopic data has been used to indicate the degree of overlap between the electron pair on the nitrogen atom and the vinylic double bond in certain enamines. It is suggested that the higher the field at which the vinylic proton absorbs,[106,107] the greater is the degree of p-π overlap. Also, the high intensity of the C=C stretching vibration in the infrared spectra of enamines has been attributed to the overlap of electrons on the nitrogen atom and the π electrons of the double bond. Further, hypsochromic shifts of 20-50 cm^{-1} and enhancement of intensities in the double bond stretching region of protonated enamines have been used to determine the position of the double bond. In enamines where protonation at the β-carbon atom is not allowed due to lack of coplanarity (electronic overlap) these effects are not exhibited[106]. This Chapter describes the results obtained from nuclear magnetic resonance and infrared spectroscopic investigations of N,N'-divinylureas.

For a complete elucidation of the absolute structure of one of the N,N'-divinylureas X-ray diffraction information from a single crystal would be required. This Chapter includes preliminary results of such an investigation.

5.2 Nuclear Magnetic Resonance Spectroscopy.

As mentioned previously, the position at which the vinylic proton occurs in the n.m.r. spectrum of certain enamines seems to be dependent on the degree of p-π electron overlap. The greater the overlap the smaller is the chemical shift from tetramethylsilane. A similar effect is observed for the chemical shift values of the N-C<u>H</u>=CH_2 protons in N-vinylureas, which are given in Table 5.1. together with their ultraviolet absorption intensity.

Table 5.1

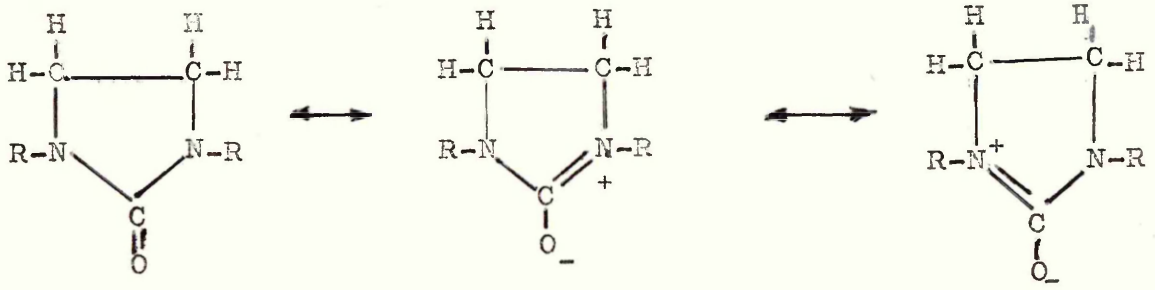
Chemical shift values of the N-C<u>H</u>=CH_2 protons in some N-vinylureas

	Compound	Chemical shift of C<u>H</u>=CH_2 protons τ	Ultraviolet[a] absorption ε max
I	1,3-Divinylhexahydropyrimid-2-one	2.3-2.7	40800
II	1,3-Divinylimidazolid-2-one	2.8-3.3	37600
III	1-Ethyl-3-vinylimidazolid-2-one	2.8-3.3	20800
IV	1,3-Diphenyl-1,3-divinylurea	3.3-3.5	18200
V	1,3-Dimethyl-1,3-divinylurea	3.2-3.7	15700

[a] values taken from Table 3.3

These results also seem to indicate that the greater the p-π overlap the lower the chemical shift for the N-C<u>H</u>=CH_2 protons. On the basis of their ultraviolet absorption spectra compounds I,II and III exhibit a greater degree of p-π overlap than compounds IV and V. In the coplanar situation proposed[55] for the CH_2=CH-N-CO-N-CH=CH_2 system, the nitrogen atoms are assumed to be sp^2 hybridised rather than sp^3 hybridised. N.m.r. spectroscopy cannot distinguish between these two extremes at ambient temperature but useful information may be obtained at lower temperatures.

Consider 1,3-dimethylimidazolid-2-one (5.I, R=CH_3, FVI)



(5.I) (5.Ia) (5.Ib)

If the nitrogen atoms are sp^2 hybridised due to a large contribution from polar resonance structures (5.Ia,b)protons on carbon atoms 4 and 5 will be equivalent and a singlet will be expected for the signal due to these

protons. On lowering the temperature no change will be expected in this signal. If, however, the nitrogen atoms are sp^3 hybridised then significant changes might be observed on lowering the temperature. A singlet will still be expected at room temperature because nitrogen inversion is very rapid on the n.m.r. time scale at such temperature. On lowering the temperature the nitrogen inversion will be slowed and broadening of the singlet and eventual splitting into a doublet may be observed. The n.m.r. spectrum in dichlorodifluoromethane showed no change attributable to broadening of the ring methylene protons on cooling to $-135^{\circ}C$. Either, the nitrogen inversion rate is still very rapid at the temperature quoted and the two conformations of the methyl group about each nitrogen atom cannot be detected, or the methyl carbon atoms are in the same plane as the ring nitrogen atoms.

The n.m.r. spectra of 1,3-diethylimidazolid-2-one (FV) and 1,3-diethylhexahydropyrimid-2-one (GII) showed that the protons on ring carbon atoms adjacent to the nitrogen atoms and the methylene protons of the ethyl groups had overlapping signals. This complication meant that these compounds could not be studied at low temperatures.

The corresponding signals in 1,3-dibenzylimidazolid-2-one (5.1, R= $C_6H_5CH_2$, FVII) were well separated and the n.m.r. spectrum was recorded at temperatures from $+24^{\circ}$ to $-111^{\circ}C$ in carbon disulphide (Table 5.2). Considerable broadening of the signals occured below $-80^{\circ}C$ which may indicate inversion about nitrogen occuring rather slowly and/or slow rotation about the C-N bond joining the benzyl group to the ring depending on whether the nitrogen is assumed to be sp^3 or sp^2 hybridised. If the nitrogen atoms are assumed to be sp^2 hybridised the most stable conformations for the benzyl group would be with the aromatic ring above or below the plane of the imidazolid-2-one ring.

Table 5.2

N.m.r. spectrum of 1,3-dibenzylimidazolid-2-one[a]

Temperature °C	Band width at ½ height Hz (ring methylene protons)[b]	Band width at ½ height Hz ($N-C\underline{H}_2-C_6H_5$ protons)[b]
24	3	3
-80	6	5
-90	16	11
-111	24	20

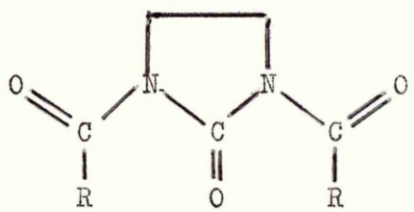
[a] recorded at 60 MHz in carbon disulphide

[b] band width of T.M.S. protons signal remained at 3-5 Hz throughout

The temperature limit of this system was -120°C, any further cooling causing crystallisation of the solvent. Dichlorodifluoromethane (m.p.-158°C) was tried as an alternative solvent, but unfortunately 1,3-dibenzylimidazolid-2-one was insoluble in this solvent.

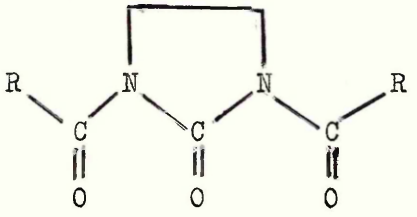
No change occured in the spectra of 1,3-divinylimidazolid-2-one (-90°C) 1,3-divinylhexahydropyrimid-2-one (-85°C) and 1,3-diphenyl-1,3-divinylurea (-52°C) on lowering the temperature (for carbon disulphide solutions). Either the nitrogen inversion is still very rapid at the temperature quoted or nitrogen inversion is not possible at all.

N.m.r. spectroscopy has been used to determine structures for 1,3-diacyl derivations of imidazolid-2-one[108]. When the acyl groups are acetyl, benzoyl or trifluoroacetyl, it is suggested that the molecules adopt a planar configuration with the acyl carbonyl groups trans, trans to the ring carbonyl group (5.II)



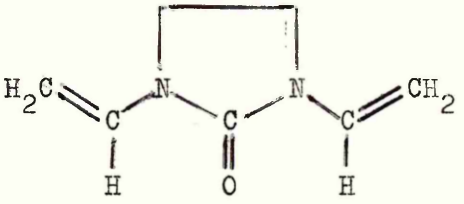
(5.II)

The alternative planar cis, cis configuration (5.III) was discounted since calculated τ values for the ring methylene protons did not compare with values obtained experimentally, whereas calculated τ values for the same protons in (5.II) were in agreement with experiment...



(5.III)

By analogy with 1,3-diacetylimidazolid-2-one, I propose for 1,3-divinylimidazolid-2-one a planar configuration with the vinyl groups trans, trans to the ring carbonyl group (5.IV).



(5.IV)

5.3 Infrared Spectroscopy.

The infrared absorption band attributed to the ring carbonyl and the ultraviolet absorption intensity for some N,N'-disubstituted imidazolid-2-ones are given in Table 5.3

Table 5.3

Carbonyl infrared absorption frequencies and ultraviolet extinction coefficients of some substituted imidazolid-2-ones

	Compound	ε_{max} [a]	$\nu_{C=O}$ [b] cm^{-1}	$\nu_{C=O}$ ref. lit. values cm^{-1}
I	Imidazolid-2-one	-	1660	1661[109]; 1660[110]
II	1,3-Diethylimidazolid-2-one	-	1685[c]	-
III	1,3-Dibenzylimidazolid-2-one	400	1685	-
IV	1,3-Diphenylimidazolid-2-one	37,000	1690	1690[60]
V	1-Ethyl-3-vinylimidazolid-2-one	20,800	1705[c]	-
VI	1,3-Divinylimidazolid-2-one	37,600	1725	1715-1725[55]
VII	1-Formylimidazolid-2-one	14,250	1725	-
VIII	1-Acetylimidazolid-2-one	13,000	1750	1750[109]; 1740[108]; 1749[111]
IX	1,3-Diacetylimidazolid-2-one	25,500	1755	1750, 1760[109]; 1759[108] (doub)

[a] taken from Table 3.3

[b] potassium bromide disc unless otherwise stated

[c] liquid film

The data in Table 5.3 indicate that the carbonyl absorption frequency of imidazolid-2-one is shifted to a higher frequency on substitution with a group which can be conjugated with the carbonyl group via the nitrogen atom. Compare $\nu_{C=O}$ for compound I with compounds VII and VIII and compare compound II with compound V. The effect also appears to be additive; two substituents causing a greater frequency shift than does one substituent. Compare compounds I, VIII and IX and compounds II, V and VI. This effect

correlates with the extinction coefficients of the ultraviolet absorption bands (and hence degree of conjugation).

Greenhaigh and Weinberger[108] have related the frequencies assigned to the ring carbonyl in mono- and di-acylimidazolid-2-ones to the degree of acylation of the molecule and with the electron-withdrawing power of the acyl group. They state that acylation reduces the availability of the electrons on the nitrogen atom, decreasing the mesomeric effect of the ring carbonyl, which results in a higher carbonyl frequency. Richards and Thompson[112] observed a similar increase in the carbonyl frequency in a series of anilides. In this case the aromatic ring on the nitrogen atom reduces the availability of the lone pair of electrons on this atom thus reducing the ionic form of the carbonyl group.

For 1,3-diethylimidazolid-2-one (II), 1-ethyl-3-vinylimidazolid-2-one (V) and 1,3-divinylimidazolid-2-one (VI), the increase in conjugation is in the order, II $<$ V $<$ VI. This increase in conjugation reduces the availability of electrons at the nitrogen atoms and hence the ring carbonyl frequencies increase with increasing conjugation. Similar effects have been observed for other N,N'-divinylureas and the results are shown in Table 5.4 along with the data for some analogous saturated ureas. Again a system with conjugation shows an increase in carbonyl absorption frequency over a non-conjugated system. The changes in carbonyl frequencies are less marked in these examples than the five-membered ring imidazolid-2-one series (Table 5.3).

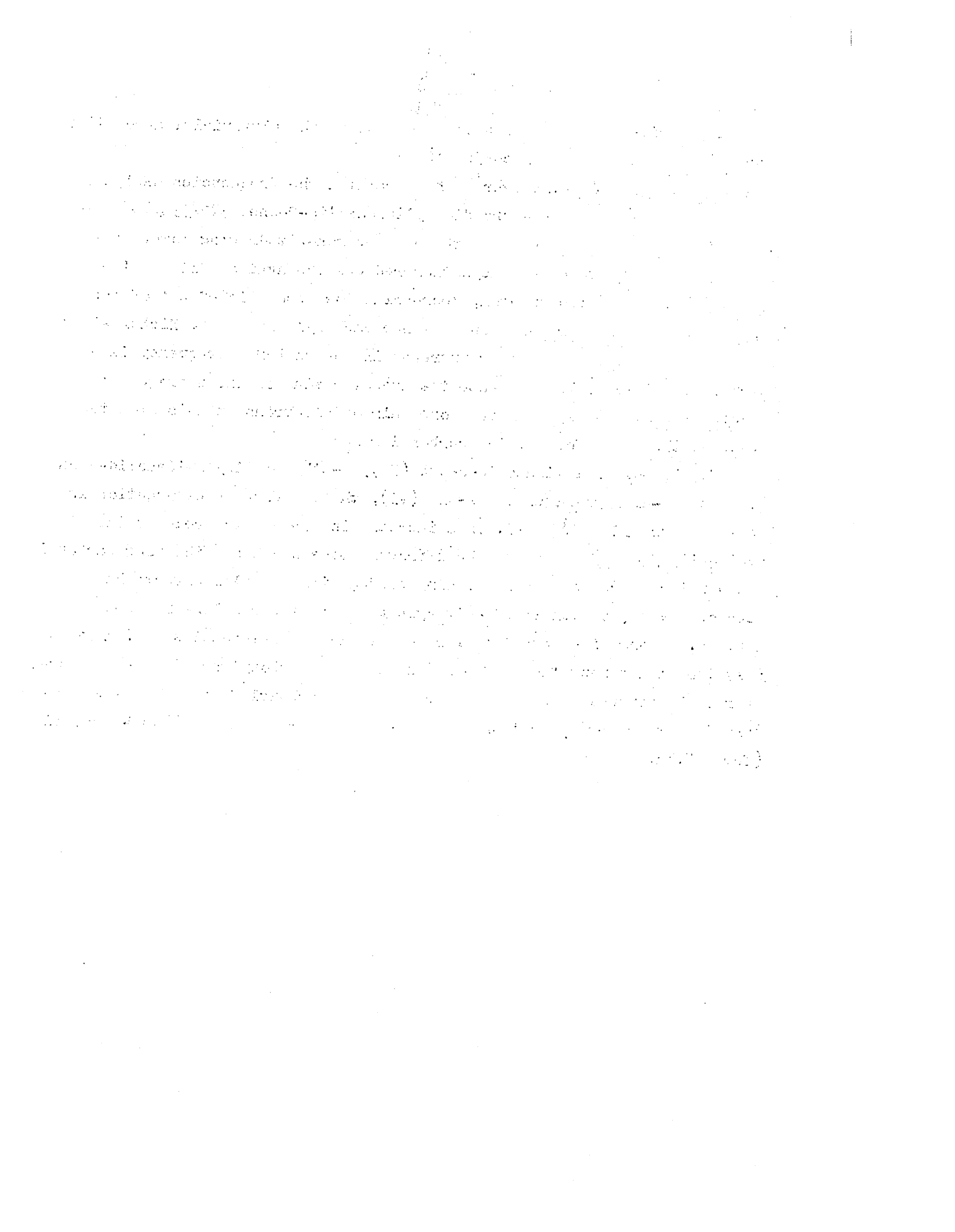


Table 5.4

Carbonyl infrared absorption frequencies of some substituted ureas

Compound	$\nu_{C=O}$ [a] cm^{-1}	Reference
1,3-Dimethyl-1,3-divinylurea	1665 [b]	-
1,1,3,3-Tetramethylurea	1640 [b]	-
1,3-Diphenyl-1,3-divinylurea	1675	-
1,3-Diphenylurea	1660	-
1,3-Dimethyl-1,3-diphenylurea	1635	113
1,3-Divinylhexahydropyrimid-2-one	1665	-
1,3-Diethylhexahydropyrimid-2-one	1645 [b]	-
1,3-Divinylurea	1660	60
1,3-Dimethylurea	1640	-

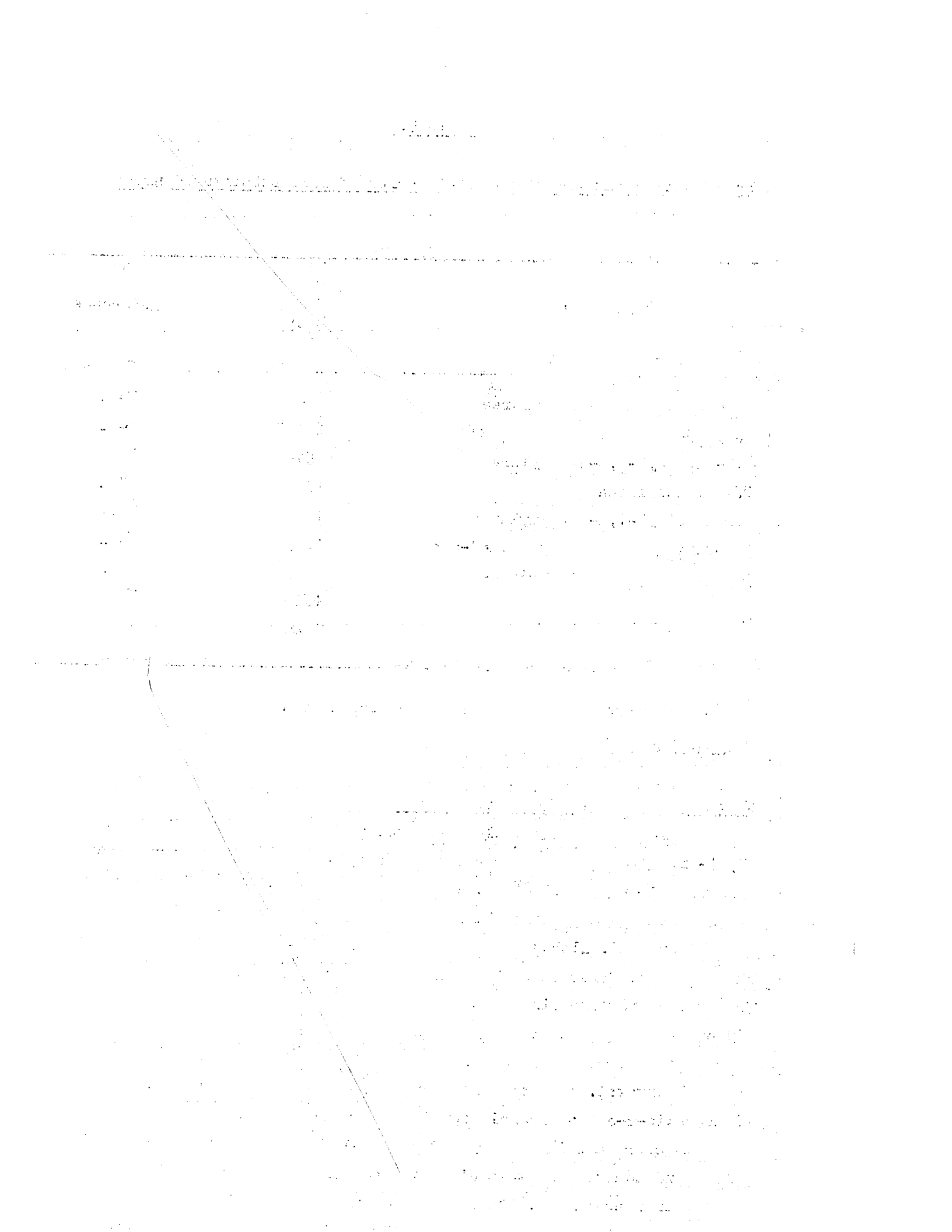
[a] potassium bromide disc unless otherwise stated

[b] liquid film

5.4 Single Crystal X-ray Diffraction

In order to try and elucidate the precise structure of one of the N,N'-divinylureas suitable crystals of 1,3-divinylimidazolid-2-one were grown for X-ray examination. The crystals were fragile and showed a prominent cleavage plane which suggests a layer structure for the molecules in the crystal. Although a satisfactory rotation photograph was obtained the zero and first layer Weissenberg photographs indicated that the crystal was decomposing quite rapidly on irradiation. This would mean that in order to complete the crystal structure determination the crystal would have to be replaced many times. In view of the complexity of alignment of each crystal, the determination of the crystal structure of 1,3-divinyl-imidazolid-2-one was considered to be impracticable.

However, a suitable crystal of 1,3-diphenyl-1,3-divinylurea was grown and mounted and this did not decompose when irradiated with X-rays in the diffractometer. The determination of the absolute structure of 1,3-diphenyl-1,3-divinylurea will be undertaken by Dr. G.H.W.Milburn in



this department. The size of the unit cell for a crystal of 1,3-diphenyl-1,3-divinylurea has been obtained from rotational, zero and first layer Weissenberg photographs. The cell dimensions are:
a = 16.40 A^{o}; b = 8.96 A^{o}; c = 10.93 A^{o}; with angles of: $\alpha = \gamma = 90^{o}$; $\beta = 114.6^{o}$. These values suggest that the unit cell will be of the monoclinic type (Figure 5.1)

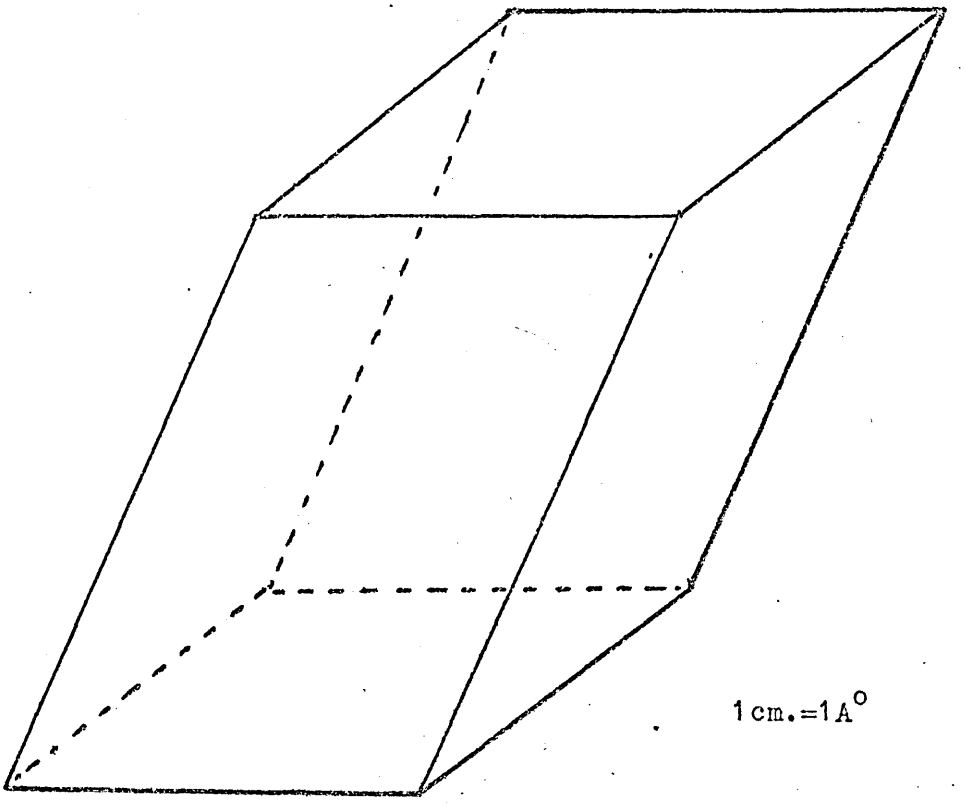


Figure 5.1

Space lattice of a 1,3-diphenyl-1,3-divinylurea molecule
(monoclinic unit cell)

CONCLUSIONS - PART 1

The synthesis of 1,3-divinylimidazolid-2-one (DVI), 1,3-divinylhexahydropyrimid-2-one (DVHHP), 1,3-diphenyl-1,3-divinylurea (DPDVU) and 1,3-dimethyl-1,3-divinylurea (DMDVU) is described. Homopolymerisation of DVI and DVHHP produced insoluble, infusible and hence cross-linked polymers confirming the results of Crawshaw and Jones[55] and indicating the failure of those monomers to cyclopolymerise. DPDVU and DMDVU could not be polymerised under a variety of conditions and initiators.

Crawshaw and Jones proposed for the structure of DVI and DVHHP a coplanar arrangement of the $CH_2=CH-\dot{N}-CO-\dot{N}-CH=CH_2$ system produced by conjugation of the lone pair electrons on the nitrogen atoms with the carbonyl and vinyl double bonds. Such a planar arrangement would tend to favour intermolecular propagation rather than the cyclopolymerisation mechanism. Copolymerisation studies using ethyl acrylate as comonomer suggest that the N-vinyl group in these N,N-divinylureas are less reactive than the N-vinyl group in 1-ethyl-3-vinylimidazolid-2-one. This seems to support the proposal of Crawshaw and Jones.

The inability of DPDVU to polymerise can be explained by the fact that addition of a radical to this monomer produces a resonance stabilised free radical. This compound acts as an inhibitor of the polymerisation of DVI and DVHHP and a retarder of the polymerisation of styrene.

It is suggested that DMDVU is also a conjugated molecule a situation which would not favour the intramolecular reaction (cyclopolymerisation). The failure of the intermolecular propagation reaction also is attributed to steric hinderance towards other molecules by the methyl group attached to the same nitrogen atom as an initiated vinyl group. This would not occur in the cyclic ureas DVI and DVHHP.

All of the N,N'-divinylureas have a strong absorption band in the ultraviolet region of the spectrum, which is good evidence for the conjugation of the electron pairs on the nitrogen atom with the π electrons of the vinyl and carbonyl double bond. Further support for such conjugation is obtained from nuclear magnetic resonance and infrared spectroscopy.

Rapid hydrolysis of the N-vinyl group in aqueous solution, yielding acetaldehyde and the corresponding urea, does not allow the possibility of polymerisation of these monomers under conditions where the conjugation has been removed by protonation of the nitrogen atom. Although kinetic protonation of these compounds takes place at the nitrogen atom, reaction

to the thermodynamic product takes place via protonation at the β-carbon atom.

This work has made a contribution to a better understanding of the structure and polymerisation behaviour of N,N'-divinylureas.

RESULTS AND DISCUSSION

PART 2

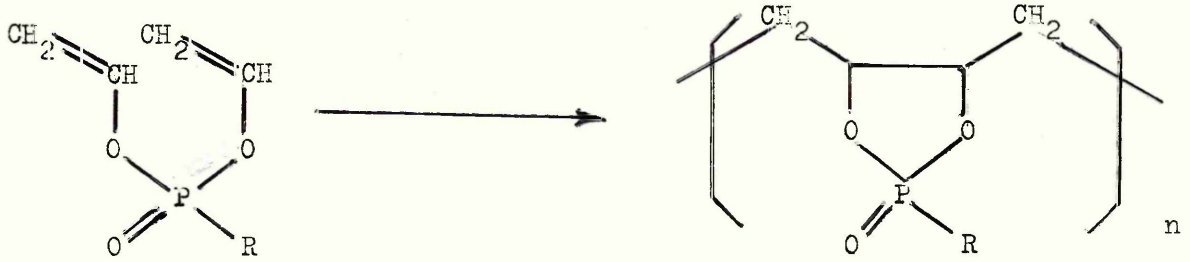
Determination of Ring Size in Cyclopolymers from Divinyl Phosphonates

CHAPTER 6

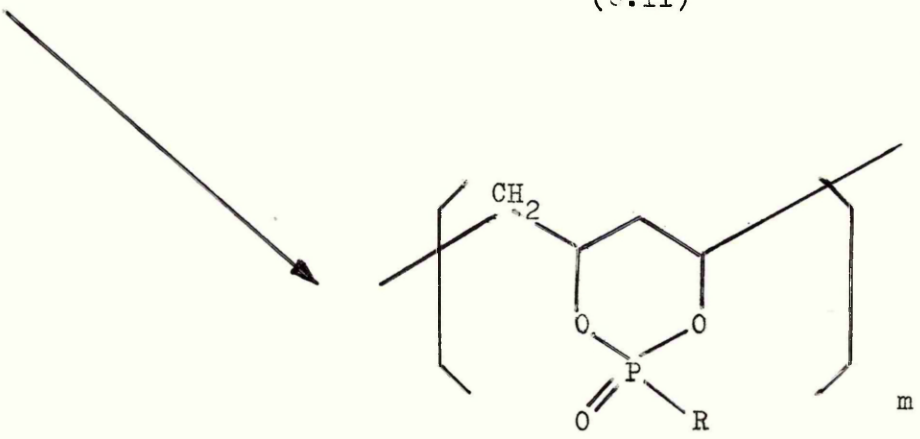
Monomer Synthesis and Cyclopolymerisation

6.1 Introduction

Divinyl phosphonates (6.I) are further examples of 1,6-dienes; if cyclopolymerisation of these monomers could be achieved, polymers with five- (6.II) and/or six-membered ring repeating units (6.III) would be expected.



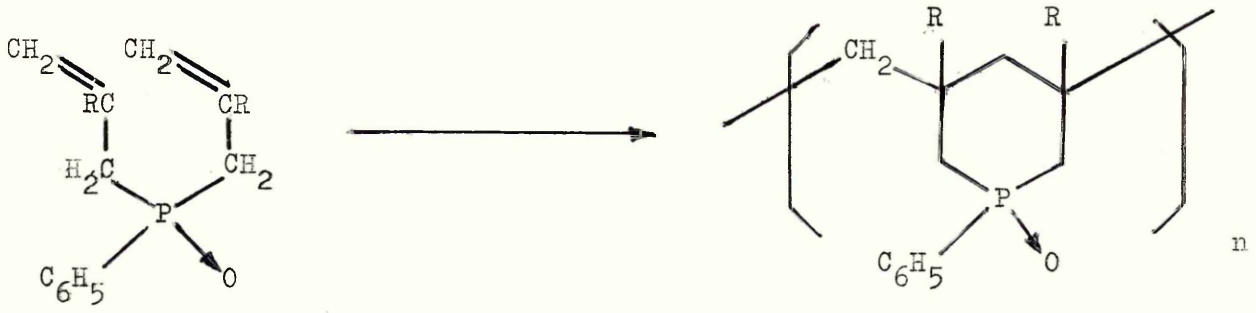
(6.I) (6.II)



(6.III)

Other phosphorus containing 1,6-dienes have been reported to yield cyclopolymers[114-116]. Butler and Berlin[114] described the polymerisation of diallylphenylphosphine oxide (6.IV) and dimethallylphenylphosphine oxide (6.V) and suggested that the cyclopolymers produced contained only six-membered rings (6.VI). They noted the possibility that five-membered rings could be formed but rejected this theory on the grounds that such a structure would necessitate formation of a primary radical rather than a secondary

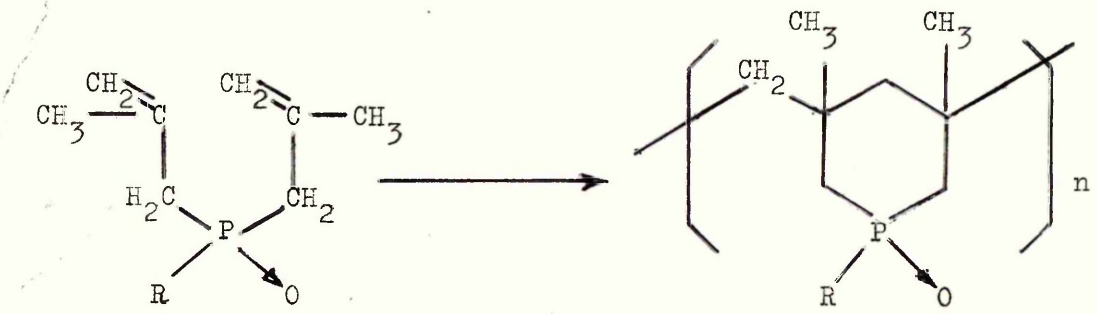
(or tertiary) radical. They also stated, at that time (1960), that a five-membered ring had never been reported in cyclic polymerisations involving symmetrical 1,6-diene systems with terminal methylene groups.



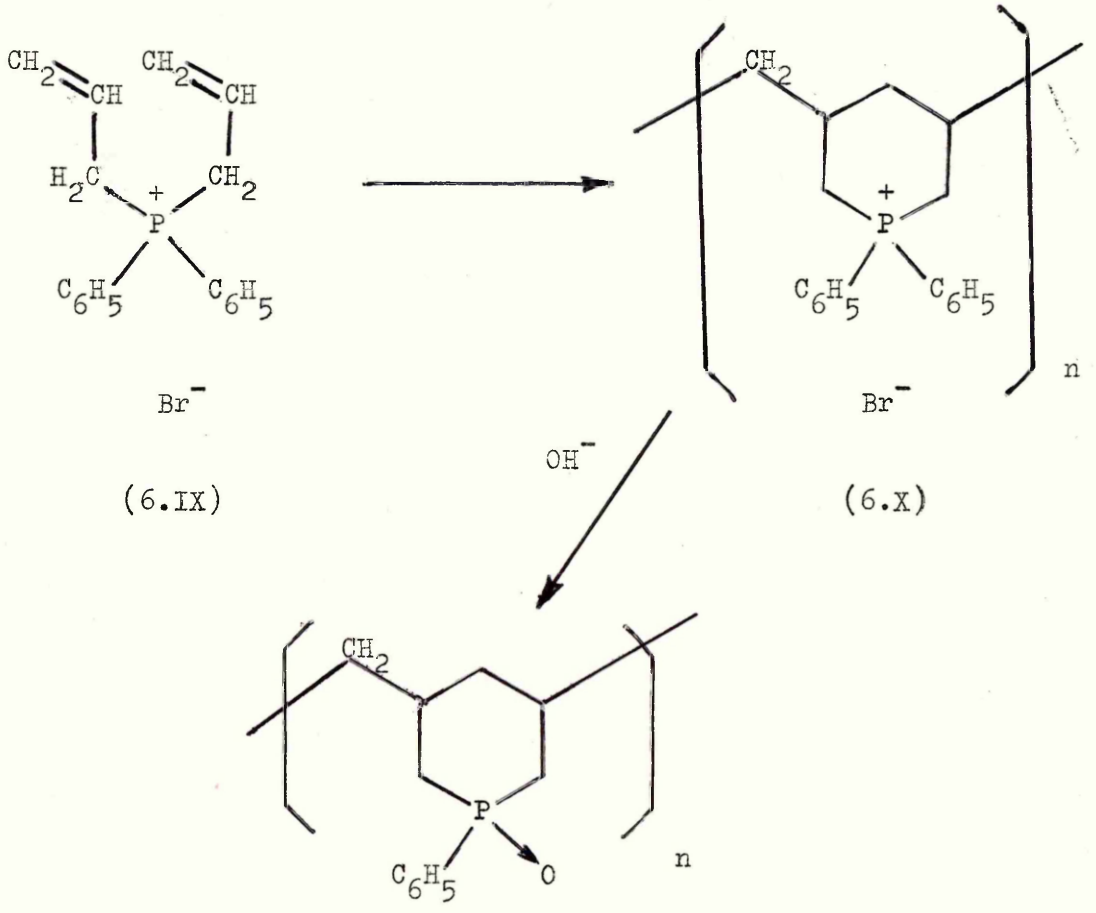
(6.IV, R=H; 6.V, R=CH_3) (6.VI)

More recent investigations of the cyclopolymerisation reaction (discussed in the INTRODUCTION to this thesis) have shown that five-membered rings are formed in addition to six-membered rings.

Butler and Berlin[115] again proposed six-membered cyclic units (6.VIII) for the cyclopolymers from dimethallylmethylphosphine oxide (6.VII, R=CH_3) and dimethylallylethylphosphine oxide (6.VII, R=C_2H_5). The polymerisations of diallyldiphenylphosphonium bromide[116] (6.IX) was also reported to yield a six-membered ring cyclopolymer (6.X) which when treated with sodium hydroxide gave a polymer with an identical infrared spectrum to poly(diallylphenylphosphine oxide) (6.XI) prepared by cyclopolymerisation of diallylphenylphosphine oxide.



(6.VII) (6.VIII)



(6.IX) (6.X) (6.XI)

All the phosphorus containing cyclopolymers mentioned previously have intrinsic viscosities of 0.04 - 0.08 dl.g^{-1}, which suggests that the polymers have a low molecular weight. The failure of unsaturated phosphorus containing monomers to yield high molecular weight polymers is not only a feature of the cyclopolymerisation reaction. Rabinowitz[117] et.al. found molecular weights of about 1200 for the homopolymers from diphenylvinyl-phosphine oxide and 4470 for those from diphenylvinylphosphine sulphide. These polymers had intrinsic viscosities of 0.027 dl.g^{-1} (in chloroform) and 0.040 dl.g^{-1} (in benzene) respectively. Murray[118], found molecular weights of up to 5500 for diethyl vinylphosphate.

Ionising radiation has been used by Tsetlin[119] and co-workers to polymerise diethyl- and diphenylvinylphosphine oxides and products with molecular weights of 30,000 have been obtained. Pellon and Valan[120] used X-rays to produce polymers of molecular weight 270,000 from tributylvinylphosphonium bromide in aqueous solutions. These two examples are from the few cases reported where high molecular weight polymers have been obtained from phosphorus containing monomers.

Thus, high molecular weight polymers were not expected (nor were they obtained) from polymerisations of divinyl phenylphosphonate and divinyl methylphosphonate. However, the polymers obtained were soluble, fusible solids and had no residual unsaturation, in contrast to previous reports of their properties. Gefter and Kabachnik[121] reported poly(divinyl phenylphosphonate) as a black, insoluble, non-combustible solid and poly(divinyl methylphosphonate) as a light yellow, insoluble non-combustible solid. Previous to this Upson[122] reported poly(divinyl phenylphosphonate) as a viscous liquid or a soft tacky solid. Both papers were published before the discovery of the cyclopolymerisation reaction and hence the possibility of linear polymers was not expected, nor was it investigated. The insoluble polymers (presumably cross-linked) were obtained by polymerisations in bulk; Gefter and Kabachnik[121] heated divinyl phenylphosphonate for 150h at 50°C with benzoyl peroxide as initiator.

This work has shown that soluble polymers (proposed as cyclopolymers) can be obtained by polymerisation of divinyl phosphonates in dilute solution, especially if polymerisation is carried out at low temperature and the initiator is decomposed photolytically.

6.2 Synthesis and Polymerisation of Divinyl Phenylphosphonate

Divinyl phenylphosphonate (6.I, R=C_6H_5) was prepared by the method of Gefter and Kabachnik[121] (Chart H). Low yields were reported by these authors and only very brief experimental details were given. An alternative route to divinyl phenylphosphonate which involved dehydrochlorination of bis(2-chloroethyl) phenylphosphonate[122] (HII) was attempted many times without success. These findings agree with those of other workers[123,124] who consider the results published by Upson[122] to be erroneous.

Phenylphosphonic dichloride was added to a cooled solution of acetaldehyde and triethylamine under an atmosphere of nitrogen. After removal of triethylamine hydrochloride by filtration, the filtrate was concentrated on a rotary evaporator and then distilled under reduced pressure to give divinyl phenylphosphonate (HI). The reagents were rigorously purified to obtain the stated yield (41%); phenylphosphonic ..

dichloride was purified by repeated distillation; acetaldehyde was shaken with sodium bicarbonate, distilled from calcium sulphate and then re-distilled from hydroquinone[125]; triethylamine was treated with benzoyl chloride before being distilled from sodium metal[126].

The slightly impure product was re-distilled on a Nester-Faust spinning band column giving a sample which had the correct analysis for divinyl phenylphosphonate and gave only one peak on a gas-liquid chromatogram. The structure of divinyl phenylphosphonate was confirmed using evidence supplied by infrared, n.m.r. and mass spectrometry.

An infrared spectrum showed peaks at 3060 and 1642 cm^{-1} (vinyl group), 1280 cm^{-1} (phosphonate P=O) and at 755, 722 and 692 cm^{-1} (phenyl group). The n.m.r. spectrum of divinyl phenylphosphonate showed three sets of peaks; a low field multiplet 1.9 - 2.6 τ (phenyl protons); a multiplet 3.1 - 3.6 τ (P-O-C<u>H</u>=CH_2) and two overlapping quartets 4.9 - 5.5 τ (P-O-CH=C<u>H</u>$_2$). The relative areas of the three signals were 5:2:4, which agrees with the theoretical integration.

^{1}H N.m.r. spectra of organo-phosphorus compounds are made more complex by additional splitting caused by the phosphorus atom, which has a nuclear spin value of $\frac{1}{2}$. Thus, a sample containing a grouping such as CH_3-P has the methyl signal split into a doublet by the phosphorus atom. Atoms with a nuclear spin value of zero, ^{12}C and ^{16}O, would not affect the methyl group in compounds containing CH_3-C or CH_3-O and the methyl group would appear as a singlet. (The above example assumes that the carbon atom in the CH_3-C group would not have any hydrogen atoms directly attached to it). In the case of divinyl phenylphosphonate protons at positions 2 and 6 of the phenyl group will be further split by the phosphorus atom but the extra signals cannot be distinguished in the phenyl protons multiplet. Unlike hydrogen atoms the spin-spin splitting (coupling) of phosphorus can be transmitted over three atoms.

The mass spectrum of divinyl phenylphosphonate shows a molecular ion at $^m/_e$ 210 with a base peak of 141^+. The fragmentation pattern is consistent with the structure: 184^+ loss of C_2H_2 by a McLafferty rearrangement; 183^+ loss of CH_2=CH- and 167^+ loss of CH_2=CH-O-.

The polymerisation of divinyl phenylphosphonate was achieved using benzoyl peroxide or azobisisobutyronitrile as initiator, the results and conditions being summarised in Table 6.1. The polymers were isolated from the polymerisation reaction as white amorphous powders by dropwise addition into vigorously stirred diethyl ether or light petroleum. All the polymers shown in Table 6.1 (with the exception of the sample from

polymerisation in bulk) had softening points in the range 130-160°C.

Table 6.1

Polymerisation of divinyl phenylphosphonate

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C	Conversion[a] %
1.0	-	BP[c]	2.0	60	70	90[b]
5.0	n-hexane (15)	ABIN[d]+hν	2.0	20	20	30
2.0	DMF[e](50)	ABIN[d]+hν	2.0	16	20	26
3.0	DMF[e](40)	ABIN[d]+hν	2.0	5	20	39
5.0	n-hexane (15)	ABIN[d]	2.0	48	55	32
2.0	DMF[e](40)	ABIN[d]	2.0	20	70	50
2.0	THF[f](50)	ABIN[d]+hν	2.0	15	20	27

[a] estimated gravimetrically

[b] insoluble polymer (presumably cross-linked)

[c] benzoyl peroxide

[d] azobisisobutyronitrile

[e] N,N-dimethylformamide

[f] tetrahydrofuran

All the polymers of divinyl phenylphosphonate were soluble in N,N-dimethylformamide and dimethylsulphoxide, with the exception of the sample from polymerisation in bulk, which was presumed to be cross-linked in view of its insolubility and infusibility. After repeated re-precipitation of the soluble polymers, infrared and n.m.r. spectra were obtained. The infrared spectra showed no evidence of any residual unsaturation and bands at 1280 cm^{-1} (P=O); 755, 722 and 692 cm^{-1} (P-phenyl). The n,m.r. spectra of poly(divinyl phenylphosphonate) showed three sets of broad peaks at 2.2 - 2.7 τ, 4.8 - 5.8 τ and 7.8 - 8.8 τ, which is very different from the spectrum of the monomer. The spectra showed no evidence of residual unsaturation and the appearance of peaks which are attributed to protons in saturated systems. A sample of poly(divinyl phenylphosphonate)

had a reduced specific viscosity of 0.042 in solutions of N,N-dimethylformamide. This suggests that the polymers are of a low molecular weight.

To explain the formation of soluble, fusible and hence linear polymers from divinyl phenylphosphonate, containing no residual unsaturation, it is proposed that they are produced via a chain-growth mechanism involving alternating intramolecular and intermolecular steps. This mechanism is known as cyclopolymerisation.

6.3 Synthesis and Polymerisation of Divinyl Methylphosphonate.

Divinyl methylphosphonate (6.I, R=CH_3) was prepared by the method outlined by Gefter and Kabachnik[121] and given in greater detail in a later publication by Gefter[124]. The first steps in the method were towards the synthesis of methylphosphonic dichloride (Chart J).

The diethyl ester of methylphosphonic acid (JI) was prepared by an Arbuzov reaction involving triethylphosphite and methyl iodide according to the method of Ford-Moore and Williams[127]. The ester was obtained in good yield (95%) by vacuum distillation of the residue after ethyl iodide had been removed. Hydrolysis of diethyl methylphosphonate with hydrochloric acid gave methylphosphonic acid (JII) which was converted into methylphosphonic dichloride (JIII) by heating with a slight excess of phosphorus pentachloride[128].

For the synthesis of divinyl methylphosphonate only carefully purified starting materials were used: methylphosphonic dichloride was fractionally distilled; acetaldehyde and triethylamine were purified as before (6.2). A solution of methylphosphonic dichloride in benzene was added to a cooled mixture of acetaldehyde and triethylamine under a nitrogen atmosphere. After removal of triethylamine hydrochloride by filtration, the filtrate was concentrated and then distilled under reduced pressure to give divinyl methylphosphonate (KI). Redistillation of the product gave a sample which had only one peak in a gas-liquid chromatogram and gave the correct analysis for divinyl methylphosphonate. The structure of divinyl methylphosphonate was confirmed by infrared, n.m.r. and mass spectrometry.

The infrared spectrum showed peaks at 3010 and 1643 cm^{-1} (C=C), 1265 cm^{-1} (P=O) and 1308 cm^{-1} (P-CH_3)[129]. The n.m.r. spectrum of divinyl methylphosphonate shows three sets of peaks at 3.1 - 3.6 τ (multiplet C$\underline{H}$=CH_2), 5.0 - 5.6 τ (quartet CH=C$\underline{H}_2$) and 8.3 - 8.6 τ (doublet CH_3). The doublet observed for the methyl group is due to the phosphorus atom splitting the methyl signal. The multiplicity of the signal due to the C$\underline{H}$=CH_2 protons is also due to coupling with the phosphorus atom.

The mass spectrum of divinyl methylphosphonate showed a weak molecular ion at $^{m}/e$ 148 (relative abundance 1.8%) with a base peak at $^{m}/e$ 79. The fragmentation pattern is consistent with the structure; peaks at 133^{+} loss of CH_3; 121^{+} loss of CH_2=CH- and 105^{+} loss of CH_2=CH-O. The weak molecular ion ($^{m}/e$ 148) is typical of dialkyl and dialkenyl phosphonates[130], but this behaviour is not found in the mass spectra of phosphonates having aromatic substituents[130] (divinyl phenylphosphonate had a molecular ion of relative abundance 26%).

Divinyl methylphosphonate was polymerised in solution using azobisisobutyronitrile as initiator, the results and conditions are summarised in Table 6.2. The polymers were isolated from the polymerisation reaction by dropwise addition into vigorously stirred ether or light petroleum. All the polymers in Table 6.2 had softening points in the range 105-120°C.

Table 6.2

Polymerisation of divinyl methylphosphonate

Wt of monomer g	Solvent (% w/w)	Initiator	mol %	Time h	Temperature °C	Conversion[a] %
1.48	DMF[b] (45)	ABIN[c]	2.0	10	70	20
1.48	THF[d] (50)	ABIN[c] +hν	2.0	17	20	30
1.48	DMF[b] (50)	ABIN[c]	2.0	14	70	27
1.48	THF[d] (50)	ABIN[c]	2.0	20	70	15

[a] estimated gravimetrically

[b] N,N-dimethylformamide

[c] azobisisobutyronitrile

[d] tetrahydrofuran

All the polymers given in Table 6.2 were soluble in N,N-dimethylformamide and had infrared and n.m.r. spectra which indicated the absence of residual unsaturation. The n.m.r. spectra again showed a considerable difference between the spectrum of the polymer and that of the monomer.

The polymers had peaks in the ranges 4.4 - 5.1 τ , 7.0 - 7.5 τ and 8.2 - 8.7 τ . A reduced specific viscosity of 0.08 (N,N-dimethylformamide) was measured for one sample of the polymer.

The cyclopolymerisation mechanism must again be used to explain the formation of soluble, fusible and hence linear polymers from divinyl methylphosphonate. Thus, both divinyl methylphosphonate and divinyl phenylphosphonate can yield cyclopolymers under suitable conditions.

CHAPTER 7

Analysis of Ring Size in Poly(divinyl phosphonates)

7.1 Introduction

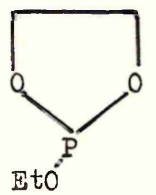
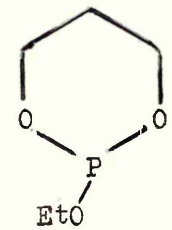
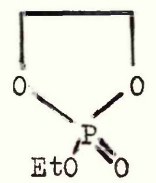
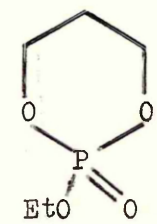
Although a six-membered ring repeating unit has been proposed most often for the structure of cyclopolymers from 1,6-dienes, it is now becoming clear that the polymers probably contain some, if they are not all, five-membered rings. Determination of the distribution of five- and six-membered ring units in cyclopolymers from 1,6-dienes has been effected by spectroscopic and chemical methods. In such cases the analysis is carried out directly on the cyclopolymer. Other workers have used the indirect method of relating the products of telomerisation reactions of 1,6-dienes with various chain-transfer agents to the cyclopolymerisation reaction. These methods are outlined in the INTRODUCTION section of this thesis. However, a systematic study of the effect of temperature, solvent, initiator, molecular weight and structure of the monomer on the ring size distribution in cyclopolymerisation reactions or cyclotelomerisation reactions of 1,6-dienes has yet to be investigated. Also, the relationship, if any exists, between cyclotelomerisation and cyclopolymerisation reactions needs to be studied. For such work to be carried out, it is necessary to find a method which will enable the ring size to be determined in both cyclotelomers and cyclopolymers directly. This Chapter describes the use of ^{31}P n.m.r. as a means of estimating the amount of five- and/or six-membered rings in poly(divinyl phosphonates). Also described are the results of several telomerisation reactions.

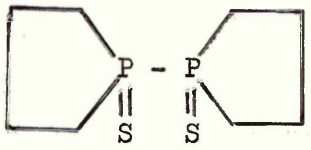
^{31}P N.m.r. spectra are simpler to interpret than ^{1}H n.m.r. spectra. For the majority of phosphorus compounds containing one phosphorus atom the spectrum consists of a single peak. This peak is usually related to a standard reference compound (85% orthophosphoric acid). Peaks which occur at a lower field than the reference are given negative p.p.m. (δ) values and those occuring at a higher field than the reference are given positive p.p.m. values. The position of the peak (chemical shift with respect to the reference) depends on the environment of the phosphorus atoms. Thus, for different chemical environments the chemical shift alters markedly, even for compounds which would normally be thought of as similar. A difference in ring size in various cyclic phosphorus compounds often gives ^{31}P n.m.r. chemical shifts which are quite different to each other and to similar acyclic phosphorus compounds. Many workers have investigated the ^{31}P n.m.r.

spectra of five- and six-membered ring phosphorus compounds. Table 7.1 shows some of the compounds studied and gives the ^{31}P chemical shifts obtained. The compounds listed in Table 7.1 are extracted from the references quoted, these and many more compounds are given in an extensive compilation of ^{31}P chemical shifts by Mark, Dungan, Crutchfield and Van Wazer[135].

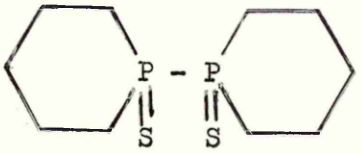
Table 7.1

^{31}P Chemical shifts for some cyclic phosphorus compounds.

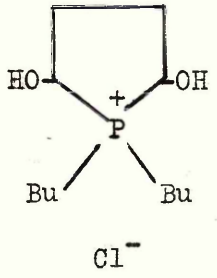
Compound	^{31}P Chemical Shift δ (p.p.m.)	Compound	^{31}P Chemical Shift δ (p.p.m.)	Reference
	-134		-132	131
	-17.2 -17		+7.7 +7	131 132
	-139		-125	131
	-12.2		+8.5	131



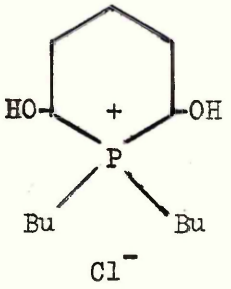
-61.2



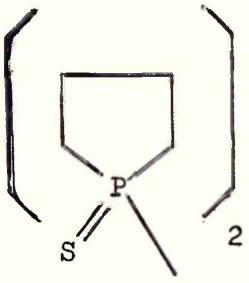
-37.5 133



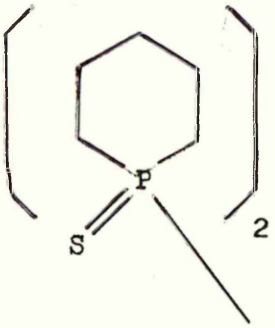
-46



-20 134



-61.2



-37.2 134

A phosphorus compound (or mixture of compounds) containing two or more phosphorus atoms in different chemical environments gives rise to two or more signals in the ^{31}P n.m.r. spectrum. Also, the areas under the peaks of an n.m.r. spectrum are proportional to the relative number of ^{31}P nuclei producing them. Van Wazer et al.[136] states that the relative molar ratios of ^{31}P nuclei in different environments can be calculated to within $\pm$ 1-2% for reasonably concentrated solutions. Considerable use of ^{31}P n.m.r. for quantitative purposes has been made by Van Wazer et al.[137-140] in measuring equilibrium constants for substituent exchange in phosphorus compounds. Measurements of peak areas for ^{31}P spectra with phosphorus atoms in different chemical environments can be done graphically or by the use of electronic integration.

^{31}P N.m.r. is therefore directly applicable to recognition of phosphorus atoms in different chemical environments (ring size) and is

able to give a quantitative measure of the relative amounts of nuclei in these different environments. The cyclopolymers obtained from divinyl phosphonates were studied in this way with a view to determining the relative amounts of six- and/or five-membered ring content.

7.2 Synthesis of Model Compounds.

The synthesis and polymerisation of divinyl phenylphosphonate and divinyl methylphosphonate are described in Chapter 6. This section describes the synthesis of some phosphonates which were used as model compounds for the assignment of ^{31}P chemical shifts in the polymers.

A number of cyclic phosphonate esters were synthesised by either (a) addition of an acid chloride to a solution of a diol in the presence of pyridine, or (b) the method of Toy[141] which consisted of heating a diol with an acid chloride under vacuum. Table 7.2 shows the conditions employed and the physical constants of the esters obtained. The cyclic esters are named using the nomenclature proposed by Mann[142].

Table 7.2

Synthesis of some phosphonate esters

Acid Chloride	Alcohol	Method	Chart Ref.	b.p.°/mm Hg (m.p.°)	Phosphonate	literature b.p.°/mm Hg (m.p.°)
Phenylphos-phonic dichloride	1,2-ethane-diol	a	HIV	169-71/0.7	2-phenyl-1,3,2-dioxaphospholane-2-oxide	210-15/6-7[141] 182-85/0.3[143]
"	1,3-propan-ediol	a	HV	148-9/0.02 (33)	2-phenyl-1,3,2-dioxaphosphorin-ane-2-oxide	212-14/7.5[141] 170-74/0.1[143]
"	2,3-butane-diol	a	HVI	130-1/0.02	4,5-dimethyl-1,3,2-dioxaphosphol-ane-2-oxide	210-15/15[141]
"	1,3-butane-diol	a	HVII	158-60/0.3 (64)	4-methyl-1,3,2-dioxaphosphorin-ane-2-oxide	
"	ethanol	a	HIII	126-8/1.0	diethyl phenyl-phosphonate	267[144]
Methylphos-phonic dichloride	1,2-ethane-diol	b	KII	130-2/2.0	2-methyl-1,3,2-dioxaphospholane-2-oxide	109-11/5 (40-1) [145]
"	1,3-propan-ediol	b	KIII	122-4/0.4 (98-100)	2-methyl-1,3,2-dioxaphosphorin-ane-2-oxide	(98-9)[146]
"	2,3-butane-diol	b	KIV	126-8/4.0 (42-4)	2,4,5-trimethyl-1,3,2-dioxaphos-pholane-2-oxide	86-8/0.5 (42-4) [146]
"	1,3-butane-diol	b	KV	70-1/0.2 (40-1)	2,4-dimethyl-1,3,2-dioxaphosphor-inane-2-oxide	71/0.25 (40)[147]

7.3 ^{31}P N.m.r. Spectra of Poly(divinyl phosphonates) and Related Compounds

The ^{31}P n.m.r. spectrum of certain samples of poly(divinyl phenylphosphonate) showed two regions of absorption for 20% solutions of the polymer in N,N-dimethylformamide. The chemical shifts of the regions of absorption are shown in Table 7.3 along with the conditions used in the polymerisations. Figures 7.1, 7.2, 7.3 and 7.4 show the ^{31}P n.m.r. spectra obtained for the samples quoted in Table 7.3.

Table 7.3

^{31}P Chemical shifts of some samples of poly(divinyl phenylphosphonate).

Polymerisation Conditions	Chemical Shift δ p.p.m.	Figure
40% solution in DMF[a] using 2 mol % ABIN[b] as initiator for 20h at 70°C	-28.0	7.1
50% solution in THF[c] using 2.0 mol % ABIN[b] + hν as initiator for 15h at 20°C	-28.2, -13.0	7.2
40% solution in DMF[a] using 2.0 mol % ABIN[b] + hν as initiator for 16h at 20°C	-28.5, -13.8	7.3
20% solution in DMF[a] using 2 mol % ABIN[b] +hν as initiator for 20h at 20°C	-28.0, -12.8	7.4

[a] N,N-dimethylformamide

[b] azobisisobutyronitrile

[c] tetrahydrofuran

If the two chemical shift values of the soluble polymer are due to phosphorus atoms in different chemical environments, then compounds with similar structural units (five- and six-membered rings) should show similar chemical shifts. This assumes that cyclopolymerisation has occurred in the soluble polymers obtained. Evidence which suggests that this is the case is given in Chapter 6. Table 7.4 shows the structure and ^{31}P chemical shifts of some cyclic five- and six-membered phenylphosphonates along with certain acyclic phenylphosphonates.

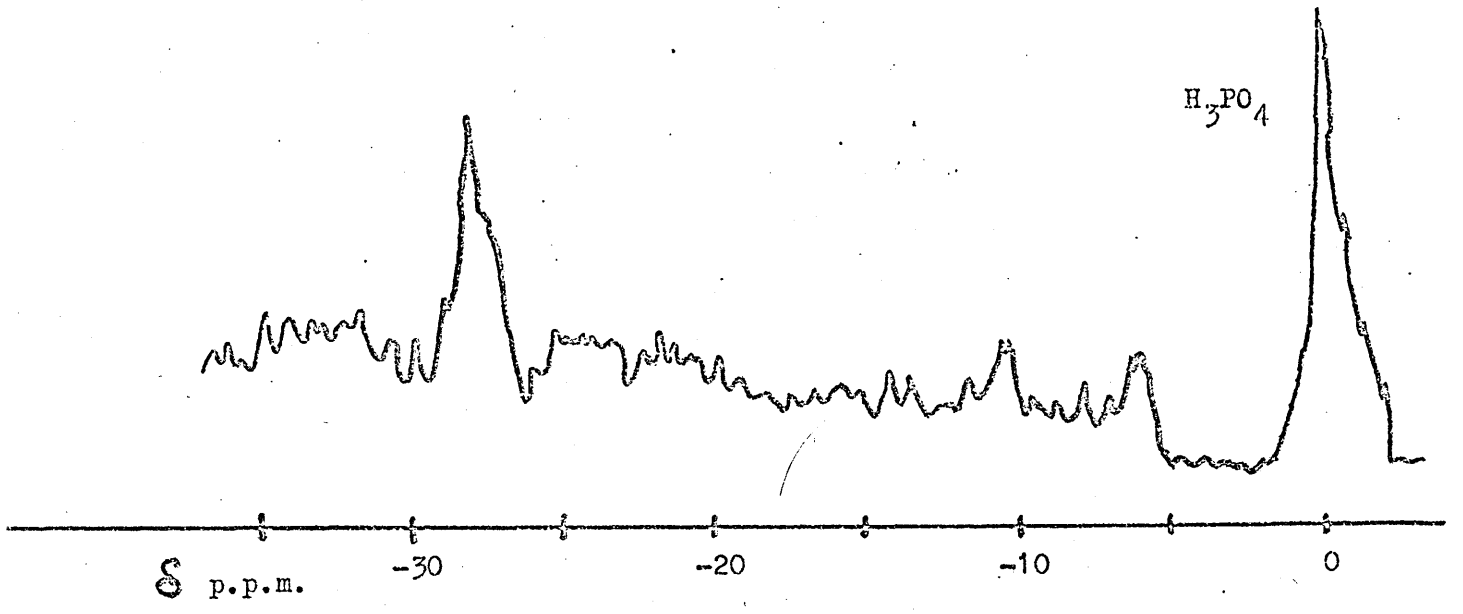


Figure 7.1

^{31}P N.m.r. spectrum of a sample of poly(divinyl phenylphosphonate).

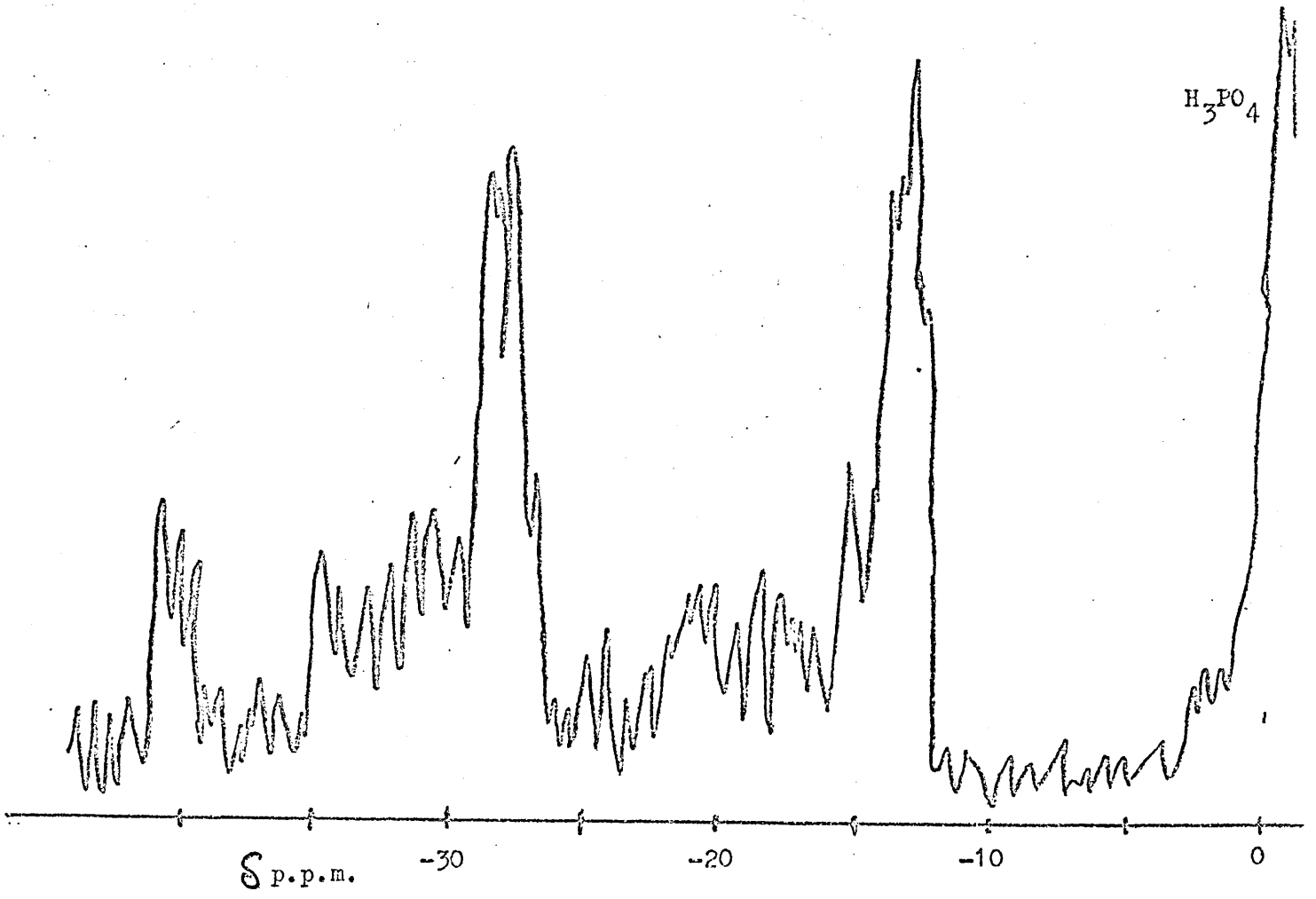


Figure 7.2

^{31}P N.m.r. spectrum of a sample of poly(divinyl phenylphosphonate).

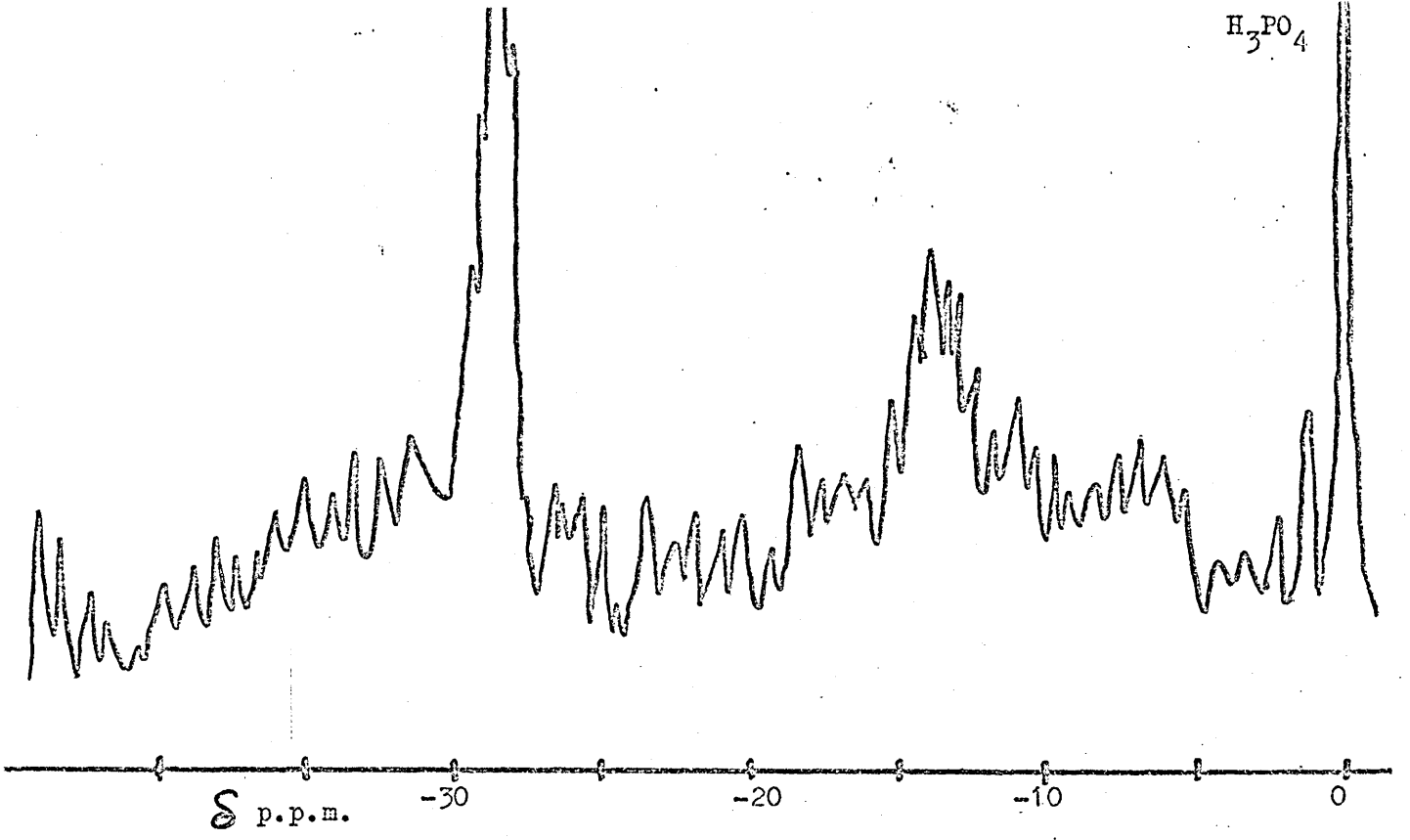


Figure 7.3

^{31}P N.m.r. spectrum of a sample of poly(divinyl phenylphosphonate).

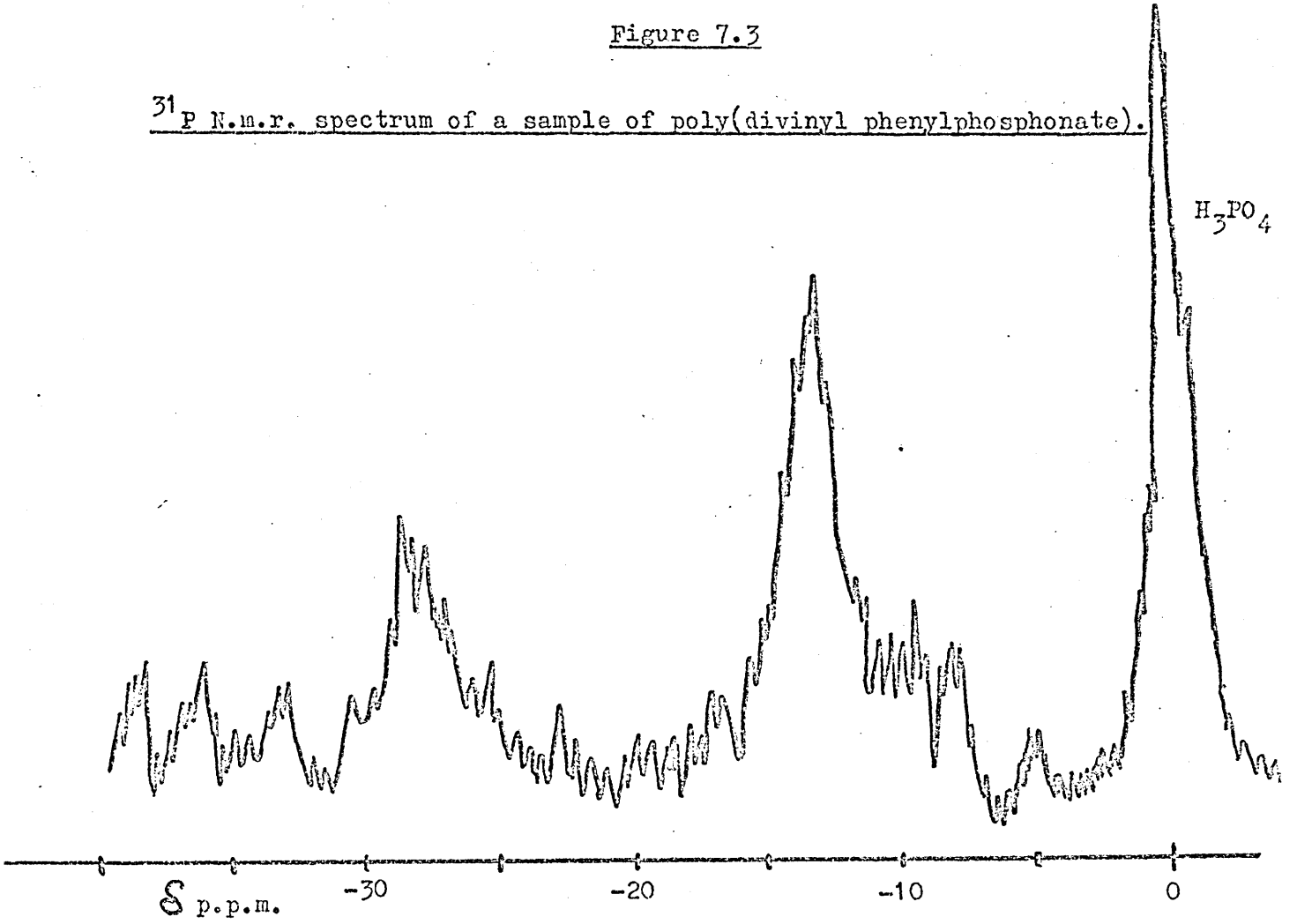
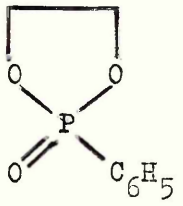
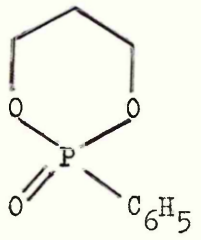
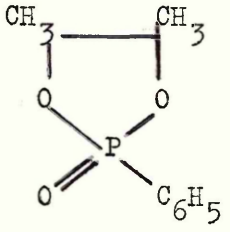
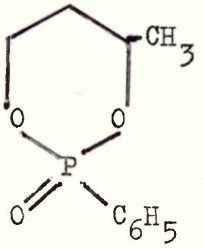


Figure 7.4

^{31}P N.m.r. spectrum of a sample of poly(divinyl phenylphosphonate).

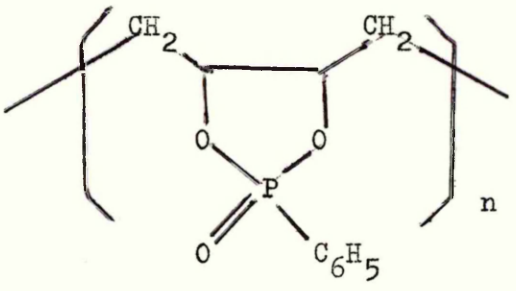
Table 7.4

^{31}P chemical shifts of some phenylphosphonates

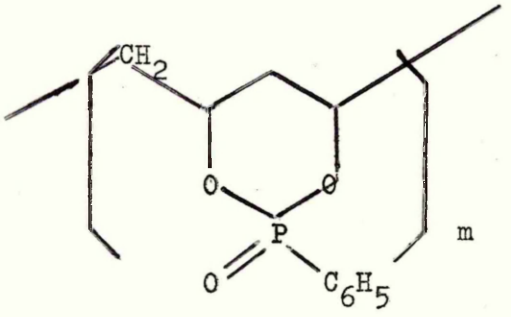
Compound	Structure	^{31}P Chemical Shift δ p.p.m.
2-Phenyl-1,3,2-dioxaphospholane-2-oxide		-31.0
2-Phenyl-1,3,2-dioxaphosphorinane-2-oxide		-11.2
4,5-Dimethyl-1,3-2-dioxaphospholane-2-oxide		-28.0
4-Methyl-1,3,2-dioxaphosphorinane-2-oxide		-13.0
Divinyl phenylphosphonate	$C_6H_5PO(OCH=CH_2)_2$	-11.4
Diethyl phenylphosphonate	$C_6H_5PO(OCH_2CH_3)_2$	-16.9
Bis(2-chloroethyl) phenylphosphonate	$C_6H_5PO(OCH_2CH_2Cl)_2$	-17.2

All the ^{31}P n.m.r. spectra of poly(divinyl phenylphosphonate) given in Table 7.3 showed peaks with chemical shifts near +28 p.p.m. (Figures 7.1 - 7.4) which by comparison with chemical shift values of five-membered cyclic phosphonates given in Table 7.4 suggests that the polymers contained phosphorus atoms in environments very similar to phosphorus atoms in five-membered rings. On this basis it is proposed that divinyl phenylphosphonate does polymerise to give products with five-membered rings (7.I). Figures 7.2 - 7.4 also show peaks with chemical shifts near -14 p.p.m. this value is similar to the six-membered cyclic phosphonates, especially 4-methyl-2-phenyl-1,3,2-dioxaphosphorinane-2-one which is very similar structurally to the six-membered ring repeating unit proposed for cyclopolymerisation of divinyl phenylphosphonate (7.II).

Apparently therefore, divinyl phenylphosphonate can cyclopolymerise to give products containing predominantly five-membered rings or a mixture of five- and six-membered rings dependant on the polymerisation conditions.



(7.I)



(7.II)

Before using the ^{31}P n.m.r. spectra of poly(divinyl phenylphosphonate) in a quantitative manner to calculate the amount of five- and six-membered rings in the polymer, the method was tried using known mixtures of cyclic phosphonates. The results (EXPERIMENTAL section) show that, in general, the precision limits for calculating the amount of five- and six-membered rings are $\pm$ 2%. In view of the degree of noise in some ^{31}P n.m.r. spectra this limit is raised to $\pm$ 5%. Table 7.5 gives the calculated amount of five- and six-membered rings in poly(divinyl phenylphosphonate).

Table 7.5

Calculated amount of five- and six-membered rings in various samples of poly(divinyl phenylphosphonate).

Figure	Polymerisation conditions solvent	initiator	Five-membered rings %	Six-membered rings %
7.1	DMF[a]	ABIN[c]	100	-
7.2	THF[b]	ABIN[d]	46	54
7.3	DMF[a]	ABIN[d]	63	37
7.4	DMF[b]	ABIN[d]	32	68

[a] N,N-dimethylformamide

[b] tetrahydrofuran

[c] azobisisobutyronitrile, thermally at 70°C

[d] azobisisobutyronitrile, photochemically at 20°C

Similarly the ^{31}P spectra of samples of poly(divinyl methylphosphonate) were obtained (Figures 7.5 and 7.6). However, these spectra showed only one region of absorption at approximately -24 p.p.m. (Table 7.6). By comparison with the chemical shifts of some cyclic and acyclic methylphosphonates (Table 7.7) a six-membered ring (7.III) is proposed as the repeating unit in the cyclopolymers from divinyl methylphosphonate.

Table 7.6

^{31}P Chemical shifts for some samples of poly(divinyl methylphosphonate).

Polymerisation conditions	Chemical shift δ p.p.m.	Figure
20% solution in DMF[a] using 2 mol % ABIN[b] as initiator for 16h at 70°C	-24.2	7.5
20% solution in DMF[a] using 2 mol % ABIN[b] + hν as initiator for 20h at 20°C	-25.0	7.6

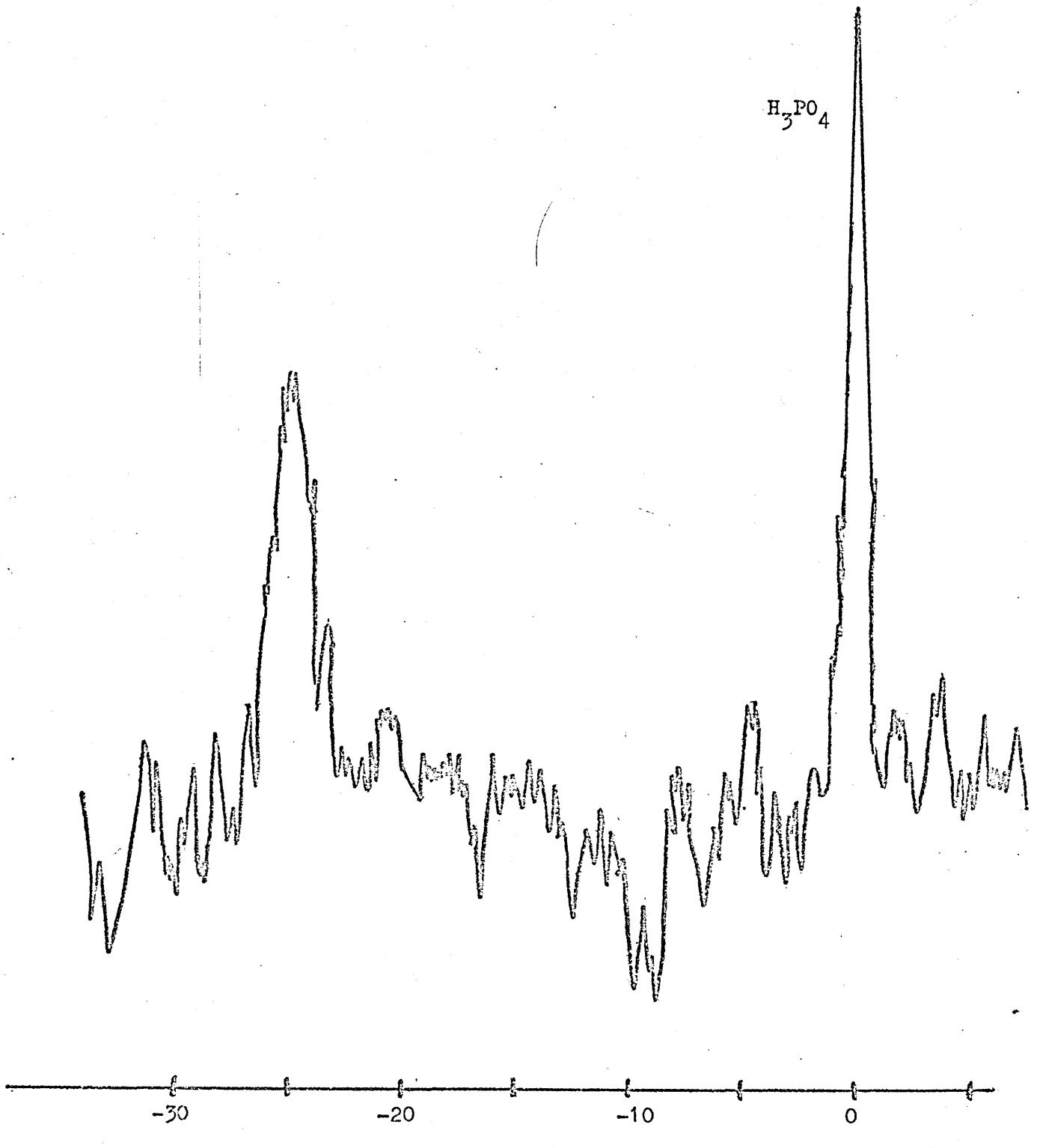


Figure 7.5

^{31}P N.m.r. spectrum of a sample of poly(divinyl methylphosphonate).

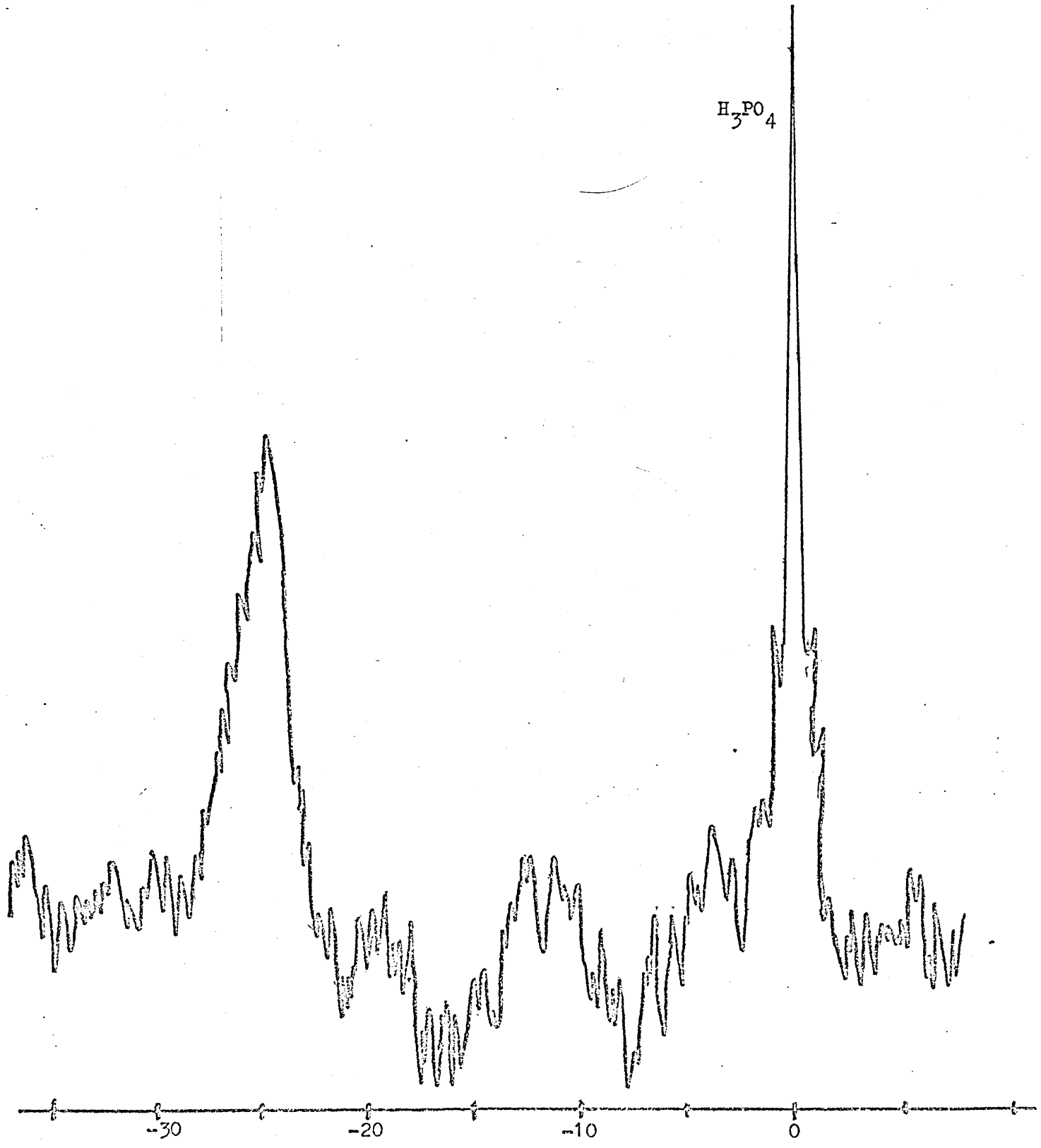


Figure 7.6

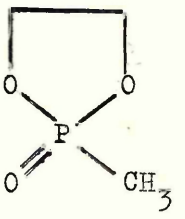
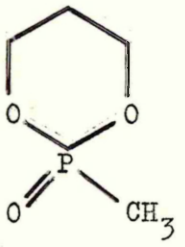
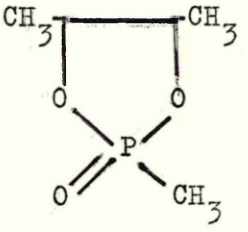
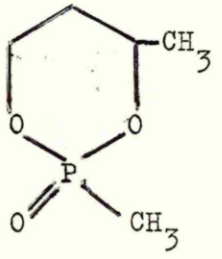
^{31}P N.m.r. spectrum of a sample of poly(divinyl methylphosphonate).

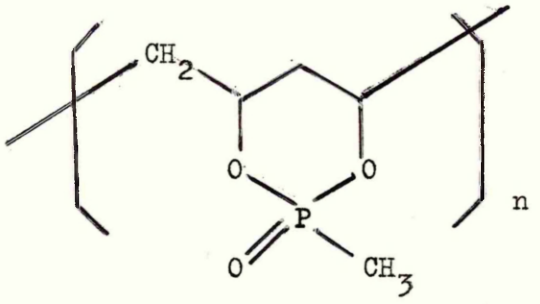
[a] N,N-dimethylformamide

[b] azobisisobutyronitrile

Table 7.7

^{31}P chemical shifts of some methylphosphonates.

Compound	Structure	^{31}P Chemical shift δ p.p.m.
2-Methyl-1,3,2-dioxaphospholane-2-oxide		-42.6
2-Methyl-1,3,2-dioxaphosphorinane-2-oxide		-23.2
2,4,5,Trimethyl-1,3,2-dioxaphospho-lane-2-oxide		-39.2
2,4-Dimethyl-1,3,2-dioxaphosphor-inane-2-oxide		-26.4
Divinyl methylphosphonate	$CH_3PO(OCH=CH_2)_2$	-22.8
Diethyl methylphosphonate	$CH_3PO(OCH_2CH_3)_2$	-26.0



(7.III)

This work has shown that the ring size in cyclopolymers of divinyl phosphonates is dependant on the solvent, method of initiation and the structure of the monomer. In the case of divinyl phenylphosphonate the five- and six-membered ring content in the polymer is markedly altered when the solvent or initiation technique is changed. Divinyl methylphosphonate does not give variations in ring size content when conditions are altered. However, this work has indicated that these factors are important and should enable a more systematic study to be completed in view of the ease of assignment of ^{31}P chemical shifts to five- and/or six-membered rings.

7.4 Telomerisation of Divinyl phosphonates

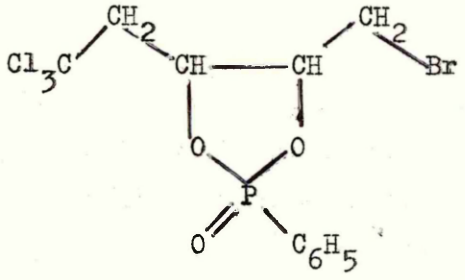
Chapters 6 and 7 have shown that divinyl phosphonates can yield cyclopolymers containing both five- and six-membered rings. This section of the Chapter reports attempts to cyclotelomerise these monomers in order to compare the results with the cyclopolymerisation reaction.

Many attempts to react divinyl phenylphosphonate with perfluoroalkyl iodides were made without success, using identical techniques to those of Brace[41-45]. Similarly, thioacetic acid failed to react with divinyl phenylphosphonate under a variety of initiation techniques. These reactions gave an almost quantitative recovery of monomer and perfluoroalkyl iodide or thioacetic acid. When divinyl phenylphosphonate was heated with bromotrichloromethane and 2 mol % azobisisobutyronitrile a vigorous exothermic reaction occurred resulting in a charred, black product. However, bromotrichloromethane is known to add to double bonds in the presence of ultraviolet light,[148,149] the energy of the quanta being sufficient to cleave the C-Br bond giving a trichloromethyl radical and a bromine radical. Using this technique, addition of bromotrichloromethane

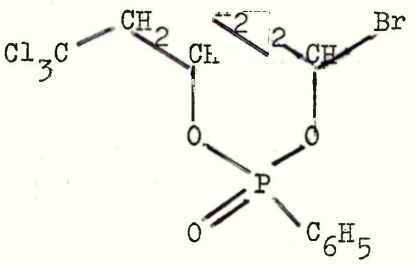
to divinyl phosphonates was possible and the reaction proceeded without any experimental problems.

Irradiation of a mixture of bromotrichloromethane and divinyl phenylphosphonate (mole ratio 3:1) using a medium pressure mercury discharge lamp gave a pale yellow viscous product. The product would not distill without extensive decomposition, neither would it crystallise from a variety of solvents. Thin layer chromatography indicated that the product, after removal of excess bromotrichloromethane, was essentially a single compound. Consequently, in view of the difficulty experienced in attempting to further purify the product, evidence for the structure of the compound was obtained from samples of the reaction mixture after removal of excess bromotrichloromethane.

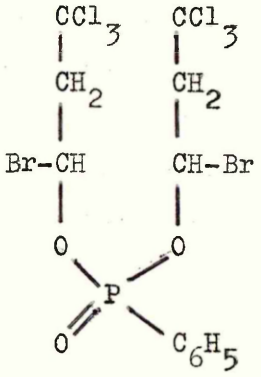
Infrared and n.m.r. spectra showed no residual unsaturation thus three possibilities exist for the structure: a five-membered ring mono-adduct (7.IV); a six-membered ring mono-adduct (7.V); or a di-adduct (7.VI).



(7.IV)



(7.V)



(7.VI)

The cyclic compounds (7.IV) and (7.V) would be expected to have molecular weights of 408.4 whereas the di-adduct (7.VI) would have a molecular weight of 608.6. The product from the reaction of bromotrichloromethane and divinyl phenylphosphonate had many peaks around m/e 600 in its mass spectrum, This suggests the formation of a di-adduct of molecular formula $C_{12}H_{11}PO_3Br_2Cl_6$. Since the formula proposed has eight halogen atoms then these will produce characteristic ions at two mass unit intervals (Cl has isotope masses of 35 and 37, Br has isotope masses of 79 and 81).

If the atomic weight of Cl is 35 and Br is 79, the molecular ion will be at m/e 602 and a series of peaks at 602, +2, +4, +6, +8, etc. will be expected and their relative proportions can be calculated from a knowledge of isotope abundances. This neglects the effect of isotopes of carbon, hydrogen phosphorus and oxygen^{150}. Table 7.8 shows the theoretical fraction of each molecular ion along with the fraction found, together with the same details for the major fragmentation (loss of HBr) from the molecular ion. There is quite close agreement between the two values, especially for the molecular ion. These results support the suggestion that a di-adduct is formed in the reaction of divinyl phenylphosphonate and bromotrichloromethane.

Table 7.8

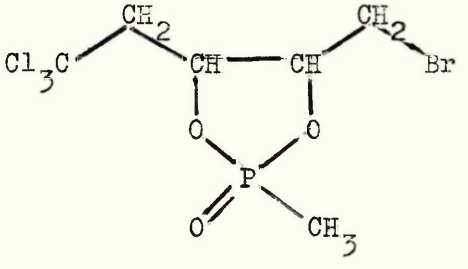
Theoretical probabilities and relative proportions found for peaks at masses M, M+2, M+4, M+6 etc. for molecules containing bromine and chlorine atoms.

m/e		Theoretical (fraction of total)	Found (fraction of total)
		$C_{12}H_{11}PO_3Br_2Cl_6$ M.W.(Br,79;Cl,35) = 602	
M	602	0.0470	0.0481
M+2	604	0.1839	0.1925
M+4	606	0.2998	0.2885
M+6	608	0.2672	0.2595
M+8	610	0.1435	0.1441
M+10	612	0.0478	0.0481
M+12	614	0.0097	0.0102
		$C_{12}H_{10}PO_3BrCl_6$ (loss of H-Br,- 80) M.W. = 522	
P	522	0.0929	0.080
P+2	524	0.272	0.265
P+4	526	0.326	0.308
P+6	528	0.209	0.198
P+8	530	0.078	0.070
P+10	532	0.017	0.015

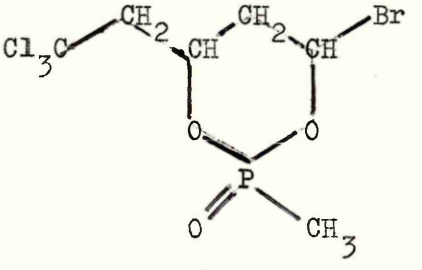
Conclusive proof of the formation of a di-adduct was obtained from the microanalysis of the product which was determined directly on the reactio mixture after removal of excess bromotrichloromethane. The analysis gave the values: Br,26.04%; Cl,33.72%; which agree closely with the calculated values for $C_{12}H_{11}PO_3Br_2Cl_6$: Br,26.34%; Cl,35.06%. The cyclic products would both have a molecular formula of $C_{12}H_{11}PO_3BrCl_3$ for which the calculated values are Br,19.75%; Cl,26.04%. The ^{31}P n.m.r. spectra of the di-adduct showed only one peak with a chemical shift of - 16.0p.p.m. which is similar to the acyclic saturated phosphonates, diethyl phenylphosphonate (- 16.9 p.p.m.) and bis(2-chloroethyl) phenylphosphonate (- 17.2 p.p.m.).

Thus, all the chemical and spectroscopic methods of analysis and structure determination indicate that the product from the photochemical addition of bromotrichloromethane and divinyl phenylphosphonate is bis(1-bromo-3,3,3-trichloropropyl) phenylphosphonate.

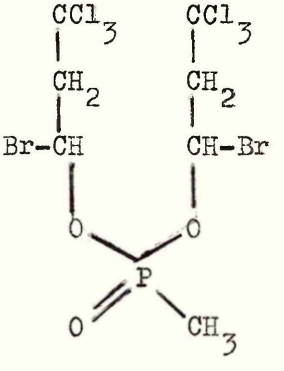
Under identical conditions, a mixture of divinyl methylphosphonate and bromotrichloromethane was irradiated with ultraviolet light from a medium pressure mercury discharge lamp. The product was a pale yellow viscous liquid but unlike the di-adduct from divinyl phenylphosphonate, this product was less stable and darkened on storage. Again, three possibilities for the structure of the product are proposed: a five-membered ring mono-adduct (7.VII); a six-membered ring mono-adduct (7.VIII) or a di-adduct (7.IX).



(7.VII)



(7.VIII)



(7.IX)

The product had a single peak in a ^{31}P n.m.r. spectrum suggesting that only one type of phosphorus species was present with a chemical shift value of -27.4 p.p.m. This value suggests that the product is either a six-membered ring (two model cyclic six-membered ring methylphosphonates

have chemical shift values of -23.2 and 26.4 p.p.m. Table 7.7) or a di-adduct (7.IX) (diethyl methylphosphonate has a chemical shift of -26.0 p.p.m.). A six-membered ring product (7.VIII) would agree with the results of cyclopolymerisation of the monomer. No conclusive evidence could be obtained from microanalysis of the adduct since unlike the product obtained from divinyl phenylphosphonate this adduct decomposed on standing.

The ^{1}H n.m.r. spectrum of a sample of the adduct had three areas of absorption at 2.9 - 3.4 τ (multiplet), 6.3 - 6.5 τ (doublet) and 8.2 and 8.5 τ (doublet). The relative intensities of these peaks were in the ratio 2:4:3. The signal at 8.3 and 8.5 τ is caused by the methyl protons being split into a doublet by the phosphorus atom. Such a signal would be expected whether the adduct was a six-membered ring or an acyclic product. The six-membered ring adduct (7.VIII) would be expected to have four further sets of signals: $-CH_2-$ ring protons; $-C\underline{H}_2-CCl_3$ protons; $C\underline{H}-CH_2CCl_3$ protons; and Br-C$\underline{H}$- proton. However, the di-adduct (7.IX) would give rise to only two further signals ($-C\underline{H}_2-CCl_3$ and $C\underline{H}$-Br) in addition to the methyl signal. The chemical shifts of the two peaks found in the sample are very similar to those obtained from the n.m.r. spectrum of the di-adduct of divinyl phenylphosphonate, which gave peaks at 2.8 - 3.3 τ ($C\underline{H}$-Br) and 6.2 - 6.4 τ ($C\underline{H}_2-CCl_3$). These results suggest that the product from the photochemical addition of bromotrichloromethane and divinyl methylphosphonate is bis(1-bromo-3,3,3-trichloropropyl) methylphosphonate.

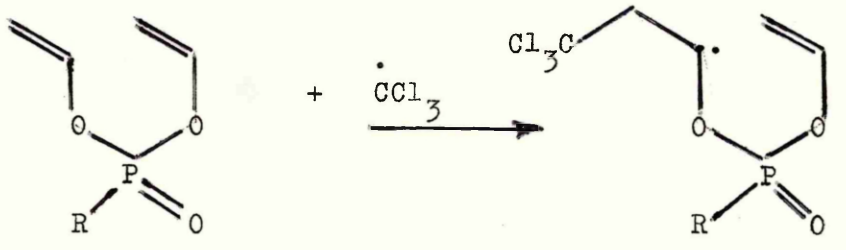
No conclusive evidence could be obtained from the mass spectrum of a sample of the product. However, the molecular ion which was found at $^{m}/e$ 355, could have occurred by fragmentation of the di-adduct (molecular weight 528) but not from the six-membered cyclic adduct (molecular weight 344). Apparently, therefore, the radicals formed from the fission of bromotrichloromethane give only di-adducts with divinyl phosphonates. This observation contradicts the results which might be expected in view of the ability of these monomers to undergo cyclopolymerisation.

The reaction of divinyl phosphonates with bromotrichloromethane under the influence of ultraviolet light is a chain reaction. The first step being undoubtedly the formation of trichloromethyl and bromine radicals (7.X)

$$BrCCl_3 \xrightarrow{h\nu} \dot{C}Cl_3 + \dot{B}r$$

(7.X)

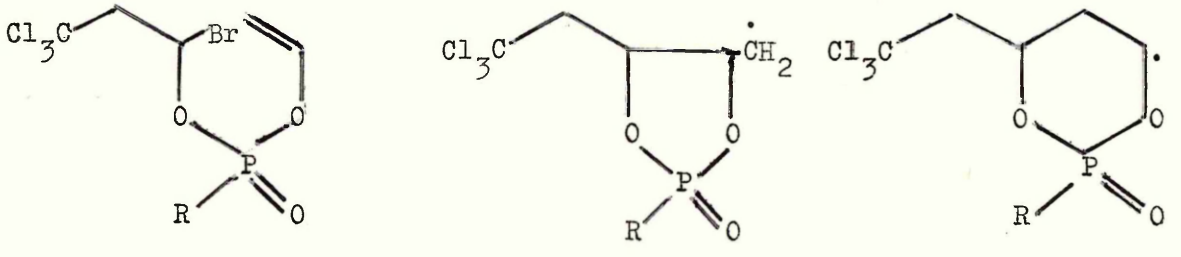
Addition of $\dot{C}Cl_3$ to a divinyl phosphonate molecule (7.XI) would form the radical (7.XII)



(7.XI) (7.XII)

The radical (7.XII) can react by either (a) propagation with bromotrichloromethane to form (7.XIII) or (b) intramolecular propagation to give a five- or six-membered ring radical (7.XIV) a (7.XV). Further addition of bromotrichloromethane across the remaining double bond in (7.XIII) gives the experimentally obtained di-adducts. Propagation of (7.XIV) or (7.XV) with bromotrichloromethane would yield five- or six-membered ring mono-adducts.

Excess addendum has been used in order to avoid the polymerisation reactions. Clearly, cyclisation would be favoured by a lower molar ratio of bromotrichloromethane to divinyl phosphonate and by dilution of the reactants in a relatively inert solvent such as cyclohexane.



(7.XIII) (7.XIV) (7.XV)

Another reason why telomerisation of divinyl phosphonates produces di-adducts is, almost certainly, that bromotrichloromethane is a very effective chain transfer agent which terminates an initiated molecule (7.XII) before the intramolecular propagation can occur. The chain transfer constants of bromotrichloromethane to various other monomers are very high (Table 7.9)

and since divinyl phosphonates do not readily propagate (Chapter 6) the rate of termination of initiated divinyl phosphonate molecules will be high.

Table 7.9

Transfer constants for bromotrichloromethane with various monomers.

Monomer	Temperature °C	$C_s \times 10^4$	Remarks	Reference
Methyl methacrylate	30	830	a, b(C_3)	151
-	-	45000	a, b(C_4)	-
Styrene	30	76000	a, b(C_2)	152
-	-	77000	a, b(C_2)	153
-	-	2400000	a, b(C_3)	152
-	-	2780000	a, b(C_3)	153
Vinyl acetate	25	>> 10000	a	148

[a] photoinitiation

[b] telomerisation (C_i; i = number of monomer units in transferring chain)

Thus, it will be necessary to use a less effective chain transfer agent if the mode of the cyclotelomerisation reaction is to be studied. However, a suitable agent would apparently have to be more reactive than either perfluoroalkyl iodides or thioacetic acid. The chain transfer constants of iodobutane and thioacetic acid with styrene and vinyl acetate are given in Table 7.10. (Although iodobutane was not one of the radical addenda considered for divinyl phosphonates, reaction with the fluorinated derivative iodononafluorobutane was attempted).

Table 7.10

Transfer constants for iodobutane and thioacetic acid with various monomers.

Additive	Monomer	Temperature °C	$C_s \times 10^4$	Remarks	Reference
Iodobutane	styrene	60	1.85	a	154
"	vinyl acetate	60	500	b	155
Thioacetic acid	styrene	99	>14.7	-	156

[a] thermal initiation

[b] peroxide initiation

Obviously, further investigation of the reaction of divinyl phosphonates with bromotrichloromethane and other chain transfer agents is necessary in order to produce cyclotelomers under a variety of conditions. If this can be achieved, this work has shown that ^{31}P n.m.r. would be a very useful technique for the determination of ring size in such products. This approach will facilitate a comparitive study of the products of the cyclotelomerisation and cyclopolymerisation reactions which should provide valuable information on the mechanism of cyclopolymerisation.

CONCLUSIONS - PART 2

Divinyl phenylphosphonate and divinyl methylphosphonate have been synthesised using modifications of the method of Gefter and Kabachnik[121]. In contrast to the results reported by these authors, it has been possible to obtain soluble, fusible, linear polymers (cyclopolymers) from both monomers by polymerisation in dilute solution.

By ^{31}P nuclear magnetic resonance spectroscopy it is possible to distinguish and quantitatively determine phosphorus atoms in five- and six-membered ring environments. Using a series of phosphonates as model compounds, this technique has shown that poly(divinyl phenylphosphonate) contains both five- and six-membered ring repeating units, in amounts which depend upon the method of polymerisation, whereas poly(divinyl methylphosphonate) produced under a variety of conditions contains only six-membered rings. This work has established that ^{31}P n.m.r. can be used to determine the ring size in cyclopolymers from divinyl phosphonates by direct analysis of the polymers.

Telomerisation of divinyl phosphonates with bromotrichloromethane gave products, which from the evidence are di-adducts. Cyclic mono-adducts were not formed presumably due to the concentration of addendum used and its effectiveness as a chain transfer agent.

A more detailed investigation and correlation of the two methods of determining ring size in cyclopolymers: (i) direct analysis, and (ii) cyclotelomerisation, could be developed from an extension of this work.

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus (design no. 889,339) using a 35mm immersion thermometer (0-360°) graduated in degrees, and are uncorrected.

Infrared spectra were recorded as liquid films or as potassium bromide discs using Pye-Unicam SP 200, SP 1000 or SP 1200 instruments. Peak positions are recorded in frequency units (cm^{-1}) using a polystyrene film absorption peak 1603 cm^{-1} as a calibration.

Ultraviolet spectra were recorded as solutions in methanol (unless otherwise stated) using Pye-Unicam SP 500 or SP 800 instruments.

^{1}H Nuclear magnetic resonance spectra were determined at normal temperatures for deutrochloroform or carbon tetrachloride solutions (unless otherwise stated) containing tetramethylsilane (τ = 10.0) as an internal standard using a JEOL C-60 HL high resolution 60 MHz instrument.

^{31}P Nuclear magnetic resonance spectra were determined at normal temperatures for chloroform or N,N-dimethylformamide solutions (unless otherwise stated) containing 85% phosphoric acid (δ = 0.0 p.p.m.) in a sealed capillary as an internal standard, using a JEOL C-60 HL high resolution 24 MHz instrument.

Mass spectra were determined on an AEI MS-30 instrument.

Refractive indices were determined using a Bellingham and Stanley Ltd. Abbé 60 refractometer.

Vapour phase chromatograms were recorded on a Pye 104 chromatograph using Apiezon L, 30/80 mesh Celite column 2 metres long, unless otherwise stated.

Microanalyses were carried out by Dr. F.B.Strauss, Microanalytical Laboratory, 10 Carlton Road, Oxford.

1,3-Divinylimidazolid-2-one (AIV)

1,3-Divinylimidazolid-2-one was prepared by the method of Crawshaw and Jones[55] (Chart A) as a crystalline solid m.p.64-65°(white flakes from light petroleum b.p. 40-60°)

Found: C,60.45; H,7.2; N,20.05%; M^+,138;

Calc. for $C_7H_{10}N_2O$: C,60.85; H,7.3; N,20.25%; M,138;

ν_{max} 3100 (C-H alkene), 2900 (C-H aliphatic), 1725 (C=O), 1635 (C=C), 1320(=CH-), 1275 (Amide III), 983,842cm^{-1}(N-CH=CH_2); τ (CCl_4) 2.8 - 3.3 (2H,q,N-CH = CH_2), 5.7-6.1(4H,q,NCH=CH_2), 6.4(4H,s,ring protons); λ_{max} 251 nm(ε 37,800).

Poly (1,3-divinylimidazolid-2-one)

Conditions and results are given in Table 1.1. A typical free radical initiated polymerisation was carried out as follows. 1,3-Divinylimidazolid-2-one (0.5g,3.6x10^{-3}mol) was placed in a pyrex tube which was purged with dry nitrogen and sealed with a rubber serum cap. Di-tert.-butylperoxide (10μL.,5.1x10^{-5}mol,1.41mol%) was injected through the serum cap using a syringe and the tube heated at 130° ± 0.5° for 3h. The white solid was removed, ground to a powder and Soxhlet extracted with methanol giving poly(1,3-divinylimidazolid-2-one),(0.45g,90%) m.p. > 360°; ν_{max} 1690-1710 (C=O),1270(Amide III) with residual peaks at 1635(C=C),980,830 cm^{-1} (N-CH=CH_2).

1,3-Divinylhexahydropyrimid-2-one (BV)

1,3-Divinylhexahydropyrimid-2-one was prepared by the method of Crawshaw and Jones[55] (Chart B) as a crystalline solid m.p.65-66°(white flakes from light petroleum b.p. 40-60°)

Found: C,63.15; H,8.2; N,18.25%; M^+,152;

Calc. for $C_8H_{12}N_2O$: C,63.15; H,7.95; N,18.4%; M,152;

ν_{max} 3100 (C-H alkene), 2900 (C-H aliphatic), 1660 (C=O), 1630 (C=C), 1325 (=CH-), 978,837cm^{-1}(N-CH=CH_2); τ ($CDCl_3$) 2.3-2.7(2H,q,N-CH=CH_2), 5.6-5.9(4H,q,N-CH=CH_2), 6.5-6.7(4H,t,N-CH_2-CH_2-CH_2-N), 7.7-8.2(2H,m,CH_2-CH_2-CH_2); λ_{max} 254 nm(ε 40,800).

Poly (1,3-divinylhexahydropyrimid-2-one)

Conditions and results are given in Table 1.2.A typical free radical initiated polymerisation was carried out as follows. 1,3-Divinylhexahydropyrimid-2-one (0.5g,3.3x10^{-3}mol) was placed in a pyrex tube which was purged with dry nitrogen and sealed with a rubber serum cap. Di-tert-butylperoxide (10μL.,5.1x10^{-5}mol,1.54mol%) was injected through the

serum cap with a syringe and the tube heated at 130° ± 0.5° for 3h. The white solid was removed, ground to a powder and Soxhlet extracted with methanol giving poly(1,3-divinylhexahydropyrimid-2-one),(0.38g,72%) m.p. > 360°; ν_{max} 1660-1650(C=O) with residual peaks at 1630(C=C),978,837, cm^{-1}(N-CH=CH_2).

1,3-Diphenyl-1,3-divinylurea (CIV)

1,3-Diphenyl-1,3-divinylurea was prepared by the method of Crawshaw and Jones [55] (Chart C) as a crystalline solid m.p.115-116°(white needles from light petroleum b.p. 60-80°)

Found: C,77.65; H,6.3; N,10.85%; M^+,264;

Calc. for $C_{17}H_{16}N_2O$: C,77.25; H,6.1; N,10.6%; M,264;

ν_{max} 1675(C=O),1630(C=C),1300(Amide III)1595,1494,750,697,(C_6H_5-)972, 845cm^{-1}(N-CH=CH_2); τ ($CDCl_3$)2.5-3.1(6H,m,m-and p-C_6H_5-),3.3-3.5(2H,m,CH =CH_2),5.7-6.3(8H,q,o-C_6H_5-and CH=CH_2); λ_{max} 253 nm(ε 18,200).

N,N-dimethyl-2-chloroethylamine

Aqueous sodium hydroxide (30% $^w/_v$,280ml) was added to N,N-dimethyl-2-chloroethylamine hydrochloride (300g,2.08mol) in water (280ml).The liberated base was extracted with ether to give N,N-dimethyl-2-chloroethylamine (200g,89%) as a colourless liquid, b.p. 108-110°, after removal of ether under reduced pressure and distillation . The base was stored at -20° in the dark to avoid dimerisation to N,N,N',N'-tetramethylpiperazinium chloride.

1,3-Bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (DI)

Dry 1,3-dimethylurea (15.0g,0.17mol) was dissolved with stirring in anhydrous N,N-dimethylformamide (200ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide / acetone cold finger. Sodium hydride (60% dispersion in oil,20.0g) was added with stirring,followed by dropwise addition of N,N-dimethyl-2-chloroethylamine (39.6g,0.37mol). The mixture was heated to 60° on a water bath when a vigorous exothermic reaction commenced. After the initial reaction had subsided the solution was maintained at 90-95°for a further 20h. The solution was cooled ,poured into dilute hydrochloric acid (1200ml) and extracted with chloroform to remove the oil introduced with the sodium hydride. The aqueous layer was made alkaline with aqueous sodium hydroxide (30% $^w/_v$), extracted with chloroform and the extract dried over anhydrous calcium chloride. Chloroform was removed under reduced pressure to give 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea

(28.1g,72%) as a deep red liquid; ν_{max} 2950(C-H), 1680(C=O), 1262cm^{-1} (Amide III).

Dimethiodide of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea(DII)

Methyl iodide (8.5g,0.06mol) in anhydrous ether (50ml) was added dropwise over 1h to a solution of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (6.9g,0.03mol) in anhydrous ether (75ml). The precipitated solid was crystallised giving the dimethiodide of 1,3-bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (12.3g,80%) m.p.224-225° (white needles from methanol);

Found: C,30.2; H,6.3; N,10.8%;

$C_{13}H_{32}N_4OI_2$ requires: C,30.35; H,6.25; N,10.9%;

ν_{max} 2900(C-H),1620(C=O),1315cm^{-1}(Amide III); τ (D_2O)6.4(8H,s,CO-N-CH_2-CH_2-$\overset{+}{N}$),6.8(18H,s,$\overset{+}{N}(CH_3)_3$),7.0(6H,s,CH_3-N-CO-N-CH_3).

1,3-Dimethyl-1,3-divinylurea (DIV)

1,3-Bis(N,N-dimethylaminoethyl)-1,3-dimethylurea (23.0g,0.1mol) was dissolved in methanol (150ml), cooled to 5° and hydrogen peroxide (100 vol.,60g) was added dropwise with stirring over 1h. The solution was allowed to warm to room temperature and stirring maintained for 15h, after which time the solution no longer turned phenolphthalein paper red. Manganese dioxide (1.0g) was added and the solution stirred until the supernatant liquid did not colour starch iodide paper. The solution was filtered and water and methanol removed under reduced pressure. The syrupy product was distilled and the fraction b.p.80-100° at 5.0mm Hg collected which after redistillation from solid sodium hydroxide yielded 1,3-dimethyl-1,3-divinylurea (4.1g,29%),b.p.52-54° at 1.0mm Hg as a colourless liquid, n_D^{25} 1.5067;

Found: C,60.25; H,8.75; N,20.1%; M^+,140;

$C_7H_{12}N_2O$ requires: C,60.05; H,8.7; N,20.05%; M,140;

ν_{max} 3100(C-H),2910(C-H),1675(C=O),1620(C=C),1270(Amide III),1320,978, 845cm^{-1}(N-CH=CH_2); τ (CCl_4)3.2-3.7(2H,q,N-C$\underline{H}$=CH_2),5.7-6.1(4H,t,N-CH=C$\underline{H}_2$), 7.1(6H,s,N-CH_3); λ_{max}245 nm(ε 15,700).

2-Bromoethylamine hydrobromide (EI)

2-Bromoethylamine hydrobromide was prepared essentially by the method of Cortesse.[66]

Ethanolamine (100g,1.64mol) was added dropwise with stirring to ice-cold hydrobromine acid (700ml,sp.gr.1.42). A fractionating column was attached to the flask and 185ml of distillate collected. The rate of heating was

then diminished until the liquid refluxed in the column. Refluxing was continued for 1h then a further 70ml of distillate collected, followed by a 1h reflux. This cycle was repeated for 60,50,25ml portions of distillate followed by 3h reflux before distillation of crude hydrobromic acid (230ml), the total volume of distillate being 630ml. When the residue had cooled to 70°, acetone (350ml) was added with stirring and the solution was cooled in ice giving 2-bromoethylamine hydrobromide (260g, 77%) m.p. 172-173° (white flakes from acetone).

N-Ethylethylenediamine (EII)

2-Bromoethylamine hydrobromide (102.5g, 0.5mol) in water (100ml) was added to ethylamine (70%, 155g, 2.5mol) in water (300ml). The mixture was refluxed for 12h, using water cooled to 5° in the condenser, after which solid sodium hydroxide was added with stirring until no more would dissolve. The upper layer was removed and the lower layer extracted with ether; the upper layer plus ether extracts were dried over solid sodium hydroxide, then sodium metal. Distillation through a fractionating column from fresh sodium gave N-ethylethylenediamine (18.5g, 42%), b.p. 128-130° as a colourless liquid n_D^{25} 1.4383; characterised as the dipicrate m.p. 220-221° (yellow needles from ethanol).

1-Ethylimidazolid-2-one (EIII)

N-Ethylethylenediamine (17.6g, 0.2mol) was dissolved with stirring in water (80ml) in an evaporating basin. Potassium cyanate (16.2g, 0.2mol) was added and the solution neutralised with hydrochloric acid (1N) using litmus paper as an indicator. The solution was warmed on a water bath for 2h and then evaporated to a pasty solid which was distilled under reduced pressure yielding 1-ethylimidazolid-2-one (17.0g, 75%), b.p. 120-122° at 0.5mm Hg which crystallised on standing m.p. 43-44° (white flakes from chloroform); ν_{max} 3300-3350(N-H), 1680(C=O), 1275cm^{-1} (Amide III); τ (CCl_4) 6.7(4H, s, ring protons), 6.7-7.0(2H, q, N-CH_2-CH_3), 8.8-9.1(3H, t, N-CH_2-CH_3).

1-Ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (EIV)

1-Ethylimidazolid-2-one (19.4g, 0.17mol) was dissolved with stirring in anhydrous N,N-dimethylformamide (200ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil, 10.0g) was added with stirring followed by dropwise addition of N,N-dimethyl-2-chloroethylamine (19.8g, 0.185mol). The mixture was heated to 60° when a vigorous exothermic reaction commenced. After the initial reaction had subsided the solution

was maintained at 90-95° for a further 8h. The mixture was cooled, poured into water (1000ml) and extracted with chloroform. The extract was dried over anhydrous calcium chloride and the chloroform was removed under reduced pressure yielding 1-ethyl-3-(N,N-dimethylaminoethyl) imidazolid-2-one (26.4g,81%) as a deep red liquid; ν_{max} 2800(N-$(CH_3)_2$), 1690(C=O),1270cm^{-1}(Amide III).

Methiodide of 1-ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (EV)

Methyl iodide (17.0g,0.12mol) in anhydrous ether (50ml) was added dropwise over 1h to a solution of 1-ethyl-3-(N,N-dimethylaminoethyl)imidazolid-2-one (19.8g,0.12mol) in anhydrous ether (200ml). The precipitate was crystallised giving the methiodide of 1-ethyl-3-(N,N-dimethylaminoethyl) imidazolid-2-one (34.0g,86%)m.p.200-201°(white needles from methanol);

Found: C,36.4; H,7.0; N,12.4%;
$C_{10}H_{22}N_3OI$ requires: C,36.7; H,6.8; N,12.85%;

ν_{max} 1700(C=O),1270cm^{-1}(Amide III); τ (D_2O)6.2-7.0(19H,m,all CH_2 and $\overset{+}{N}(CH_3)_3$),8.8-9.1(3H,t,N-CH_2-CH_3).

1-Ethyl-3-vinylimidazolid-2-one (EVII)

The methiodide of 1-ethyl-3(N,N-dimethylaminoethyl)imidazolid-2-one (32.7g.0.1mol) was dissolved in a mixture of ethanol (200ml) and water (60ml). Silver oxide (23.2g,0.1mol) was added and the mixture stirred at 40° until the supernatant liquid was free from iodide ions. The solution was filtered and water and ethanol were removed under reduced pressure to give the quaternary ammonium hydroxide as a pale yellow syrup. The syrup was decomposed at 120-130° at 1.5mm Hg yielding 1-ethyl-3-vinyl-imidazolid-2-one (9.0g,64%)b.p.116-118° at 1.5mm Hg as a colourless liquid n_D^{25} 1.4991;

Found: C,60.1; H,8.9; N,20.2%; M^+,140;
$C_7H_{12}N_2O$ requires: C,60.05; H,8.7; N,20.05%; M,140;

ν_{max} 3120(C-H vinyl),2990-2900(C-H),1705(C=O).1635(C=C),1503(Amide II), 1278(Amide III),990,838cm^{-1}(N-CH=CH_2); τ ($CDCl_3$),2.8-3.3(1H,q,N-CH=CH_2), 5.8-6.2(2H,m,N-CH=CH_2),6.6(4H,s,CH_2 ring),6.6-6.9(2H,q,N-CH_2-CH_3),8.7-9.0(3H,t,N-CH_2-CH_3); λ_{max}230 nm(ε 20,000).

Poly(1-ethyl-3-vinylimidazolid-2-one)

Table 1.5 shows representative polymerisation conditions and results. The following is a typical procedure for a free radical initiated polymerisation. 1-Ethyl-3-vinylimidazolid-2-one (1.00g,7.14x10^{-3}mol) was dissolved in anhydrous benzene (4.0g), in a pyrex tube.

Azobisisobutyronitrile (20mg, 1.22×10^{-4}mol, 1.75mol%) was added and the tube purged with dry nitrogen, sealed with a rubber serum cap, vigorously agitated and placed in a thermostat bath at $70^{\circ} \pm 0.1^{\circ}$ for 4h. The contents of the tube were slowly added to vigorously stirred diethyl ether (200ml). The precipitated polymer was collected by filtration, washed repeatedly with diethyl ether and dried at 55°/0.1mm Hg for 8h to give poly(1-ethyl-3-vinylimidazolid-2-one (0.46g, 46%), softening point 165° (white amorphous solid);

Found: C, 58.9; H, 8.8; N, 18.95%;

$(C_7H_{12}N_2O)_n$ requires: C, 60.05; H, 8.65; N, 20.05%;

ν_{max} 2970-2900(C-H), 1690(C=O), 1503(Amide II), 1270cm^{-1}(Amide III); τ (C_6D_6)6.3-7.2(br), 8.6-9.3(br).

Solution viscosity of poly(1-ethyl-3-vinylimidazolid-2-one)

Viscosity measurements were carried out at 25° in an Ostwald viscometer B.S.U. -A; the results are summarised below.

Solvent	Concentration % (c)	Flowtimes s[a] t	t_o	η_{rel}	η_{sp}	η_{sp}/c	$[\eta]$
Toluene	0.922	215.0	183.0	1.174	0.174	0.188	0.19
	0.737	207.8	-	1.135	0.135	0.183	
	0.294	193.4	-	1.056	0.056	0.190	
	0.108	190.2	-	1.039	0.039	0.361	

[a] Mean value of three times whose difference did not exceed $\pm$ 0.2s.

Purification of monomers and solvents for copolymerisation.

1,3-Divinylimidazolid-2-one was crystallised twice from light petroleum b.p.40-60° (Analytical Reagent) dried at reduced pressure and stored at -5°.

1,3-Divinylhexahydropyrimid-2-one was crystallised twice from light petroleum b.p.40-60° (Analytical Reagent) dried at reduced pressure and stored at -5°.

1-Ethyl-3-vinylimidazolid-2-one was distilled through a Nester-Faust spinning band distillation column equipped with an 18" stainless steel band and partial take off head, b.p.110° at 1.0mm Hg and stored at -5°.

Ethyl acrylate (mid.cut) was redistilled through a 30cm column packed with glass helicies equipped with a partial take off head (reflux ratio 3:1) b.p.98.8-99.0° and stored at -5°.

Benzene (Analytical Reagent) was redistilled b.p.80.5°.
Azobisisobutyronitrile was crystallised twice from methanol (Analytical Reagent) dried over phosphorus pentoxide under reduced pressure and stored at -5°.

Copolymerisation of 1,3-divinylimidazolid-2-one, 1,3-divinylhexahydropyrimid-2-one or 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate.

Corresponding amounts of vinylurea monomer and ethyl acrylate (total weight 2.000g) were weighed into stoppered bottles, transferred using two aliquots of benzene (5ml each) to polymer tubes containing azobisisobutyronitrile (0.13 mol %). The contents of each polymer tube was made up to 20.0g with benzene, purged with dry nitrogen and sealed with a rubber serum cap. The tubes were vigorously agitated and placed in a thermostatted water bath at 60° ± 0.1°. When the reaction was judged to have proceeded to a few percent conversion the contents of the tube were slowly poured into vigorously stirred light petroleum b.p.40-60° (200ml). The precipitate was collected by filtration, washed repeatedly with light petroleum and dried at 55°/0.1mm Hg for 6h. The polymers were ground to a fine powder, washed repeatedly with light petroleum and dried at 55°/0.1mm Hg for 24h. The nitrogen content of the copolymer gave the percentage of vinylurea in the copolymer. The results are given in Tables 2.1, 2.5, 2.9.

Effect of 1,3-diphenyl-1,3-divinylurea on the polymerisation of styrene.

1. Rate of polymerisation -Qualitative experiments have shown that 1,3-diphenyl-1,3-divinylurea acts as an inhibitor or retarder of the polymerisation of vinyl acetate, ethyl acrylate, acrylic anhydride and styrene. The rate of polymerisation of a solution of 1,3-diphenyl-1,3-divinylurea (5.0%, $^{w}/_{w}$) in styrene was measured using a dilatometer, and compared with the rate of polymerisation of styrene alone.
1,3-Diphenyl-1,3-divinylurea (0.500g) was dissolved in freshly distilled styrene (9.500g) and introduced into a calibrated dilatometer under an atmosphere of dry nitrogen. The dilatometer was placed in a thermostat bath at 70° ± 0.1° and after allowing 3min. for equilibration and expansion of the solution the decrease in height of the column was measured at 1min. intervals. When the solution had traversed the length of the column the dilatometer was washed, dried and refilled with fresh styrene/1,3-diphenyl-1,3-divinylurea mixture and the experiment repeated. The mean values of three experiments are shown in Table 2.16 and Fig. 2.10.

along with the mean values for styrene alone under identical conditions.

The dilatometer was calibrated by calculating the cross-sectional area of the capillary ($4.25 \times 10^{-3} cm^2$) from the weight of a mercury thread, by measuring the total volume of the dilatometer ($5.74 cm^3$) using water and hence calculating that each 1cm decrease in the capillary height represents 0.406% polymerisation.

2. Viscosity and molecular weight -- Corresponding amounts of 1,3-diphenyl-1,3-divinylurea and freshly distilled styrene (total wt. 1.000g) were dissolved in benzene (2.00ml) in a pyrex tube containing azobisisobutyronitrile (5mg, 0.5% $^{w}/_{w}$). The tube was purged with dry nitrogen, sealed with a rubber serum cap, vigorously agitated, placed in a water bath at $70^{\circ} \pm 0.5^{\circ}$ for 5h and given periodic agitation. The contents of the tube were slowly poured into vigorously stirred methanol (300ml) and the precipitated polymer collected by filtration, washed repeatedly with methanol and dried at 55°/0.5mm Hg for 10h. The dilute solution viscosity was determined at 25° using an Ostwald viscometer (B.S.U-A) and the results are summarised below.

DPDVU in mixture % a	DPDVU in mixture % b	Conversion[d] %	Concentration in toluene % (c)	Flowtimes s[e] t	Flowtimes s[e] t_o	η_{rel}	η_{sp}	η_{sp}/c
0.0	0.0	22	0.254	198.1	186.0	1.065	0.065	0.256
5.0	1.5	20	0.242	196.3	-	1.055	0.055	0.228
10.0	2.3	18	0.236	193.3	-	1.039	0.039	0.166
20.0	2.7	16	0.228	191.3	-	1.028	0.028	0.124
30.0	3.5	14	0.228	190.5	-	1.025	0.025	0.109

[a] Amount of 1,3-diphenyl-1,3-divinylurea (DPDVU) in mixture before polymerisation.

[b] Amount of DPDVU in polymer after polymerisation, calculated from nitrogen analysis.

[d] Estimated gravimetrically by precipitation in methanol.

[e] Mean value of three runs differing by less than $\pm$ 0.2s.

Hydrolysis of 1,3-divinylimidazolid-2-one or 1,3-divinylhexahydropyrimid-2-one.

Hydrochloric acid (30ml, N/100) was added to 0.20g of 1,3-divinylimidazolid-2-one or 1,3-divinylhexahydropyrimid-2-one under a slow stream of dry nitrogen. The exit tube from the flask was immersed in a solution of

2,4-dinitrophenylhydrazine (alcohol/sulphuric acid). After passing nitrogen for 1h the precipitated 2,4-dinitrophenyldrazone (0.35g) was collected and crystallised to give acetaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p.166° (orange needles from ethanol) with an identical infrared spectrum to an authentic sample. Water was removed under reduced pressure from the residual hydrolysis mixture leaving a crystalline solid of imidazolid-2-one m.p.130-131°(white needles from ethanol)having an identical infrared spectrum to an authentic sample. Similarly 2-ketohexahydropyrimidine m.p.274-276°(white needles from water) having an identical infrared spectrum to an authentic sample was the residue from the hydrolysis of 1,3-divinylhexahydropyrimid-2-one.

Hydrolysis of 1,3-diphenyl-1,3-divinylurea.

Hydrochloric acid (20ml,6N) was added to 0.15g of 1,3-diphenyl-1,3-divinylurea under slow stream of dry nitrogen. The exit tube from the flask was immersed in a solution of 2,4-dinitrophenylhydrazine (alcohol/sulphuric acid). After passing nitrogen for 4h the precipitated 2,4-dinitrophenylhydrazone was collected, and crystallised to give acetaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p.166°(orange needles from ethanol) with an identical infrared spectrum to an authentic sample. Water was removed under reduced pressure from the residual hydrolysis mixture leaving a white solid of 1,3-diphenylurea m.p. and mixed m.p.239-240°(long white needles from methanol) having an identical infrared spectrum to an authentic sample.

1-Acetylimidazolid-2-one (FI)

Imidazolid-2-one (17.4g,0.2mol) was dissolved with stirring in a mixture of acetic anhydride (21.0g.0.2mol) and glacial acetic acid (80ml). The solution was refluxed for 4h,cooled and poured into diethyl ether (200ml). The precipitate was crystallised giving 1-acetylimidazolid-2-one (14.6g, 57%)m.p.177-178°(white prisms from ethanol),

Found: C,46.6; H,6.15; N,21.9%; M^+,128;

Calc. for $C_5H_8N_2O_2$: C,46.9; H,6.3; N,21.85%; M,128;

ν_{max}3,300(N-H),3000,2930(C-H),1750(C=O),1655(C=O),1265cm^{-1}(Amide III); $\tau(D_2O)$6.0-6.7(4H,m,ring protons),7.7(3H,s,N-CO-CH_3); $\lambda_{max}(H_2O)$215 nm(ε 13,000).

1,3-Diacetylimidazolid-2-one (FII)

Imidazolid-2-one (10.0g,0.116mol) was dissolved with stirring in a mixture of acetyl chloride (45.0g,0.574mol) and glacial acetic acid (50ml) The solution was refluxed for 4h,cooled and poured into diethyl ether

(200ml). The precipitate was crystallised giving 1,3-diacetylimidazolid-2-one (15.1g,77%) m.p.126-127° (white prisms from acetone),

Found: C,49.6; H,6.0; N,16.65%; M^+,170;

Calc. for $C_7H_{10}N_2O_3$: C,49.4; H,5.9; N,16.45%; M,170;

ν_{max} 3000-2930(C-H),1755(C=O),1695(C=O)1260cm^{-1}(Amide III); τ(D_2O) 6.2(4H,s,ring protons),7.5(6H,s,N-CO-CH_3); λ_{max}(H_2O)227nm(ε 25,500).

1-Formylimidazolid-2-one (FIII)

Imidazolid-2-one (15.0g,0.17mol) was dissolved with stirring in a mixture of formic acid (8.0g,0.17mol) and acetic anhydride (17.0g,0.17mol), refluxed for 3h,cooled and poured into diethyl ether (200ml). The precipitate was crystallised giving 1-formylimidazolid-2-one (13.2g,68%) m.p.151-152° (white prisms from acetone);

Found: C,42.05; H,5.25; N,24.75%;

$C_4H_6N_2O_2$ requires: C,42.1; H,5.3; N,24.55%;

ν_{max} 3300(N-H),1725(C=O),1680(C=O),1268cm^{-1}(Amide III); τ(D_2O)1.4 (1H,s,H-C=O),6.1-6.7(4H,m,ring protons); λ_{max}(H_2O)214nm(ε 14,250).

1,3-Diethylimidazolid-2-one (FIV)

Imidazolid-2-one (7.5g,0.085mol) was dissolved with stirring in anhydrous N,N-dimethylformamide (100ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil,10.0g) was added with stirring followed by dropwise addition of ethyl iodide (28.0g,0.17mol). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction subsided the solution was maintained at 90° for a further 18h. The solution was cooled,poured into water (600ml),extracted with chloroform and the extract dried over anhydrous calcium chloride. Chloroform was removed under reduced pressure and the residue distilled yielding 1,3-diethylimidazolid-2-one (8.2g,68%),b.p.83-84° at 0.5mm Hg as a colourless liquid n_D^{25} 1.4678;

Found: C,58.85; H,10.0; N,19.6%; M^+,142;

Calc. for $C_7H_{14}N_2O$: C,59.15; H,9.9; N,19.7%; M,142;

ν_{max} 2970,2870(C-H),1685(C=O),1263cm^{-1}(Amide III); τ(CCl_4)6.8(4H,s, ring protons),6.8-7.3(4H,q,N-CH_2-CH_3),8.8-9.1(6H,t,N-CH_2CH_3).

1,3-Dibenzylimidazolid-2-one (FVII)

Imidazolid-2-one (7.5g,0.085mol) was dissolved with stirring in anhydrous N,N-dimethylformamide (100ml) in a flask equipped with an efficient

reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride(60% dispersion in oil,10.0g) was added with stirring followed by dropwise addition of benzyl chloride (22.0g,0.17mol). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction had subsided the solution was maintained at 90° for a further 14h. The solution was cooled,poured into water (600ml) and the solid which separated collected by filtration. Crystallisation of the solid gave 1,3-dibenzylimidazolid-2-one (18.5g,82%) m.p.92-93°(white flakes from light petroleum b.p.60-80°);

Found: C,76.5; H,6.85; N,10.5%; M^+,266;

Calc. for $C_{17}H_{18}N_2O$: C,76.65; H,6.8; N,10.5%; M,266;

ν_{max}3020(C-H aromatic),2920-2860(C-H aliphatic),1690(C=O),1493,1450 (C=C),1255cm^{-1}(Amide III); τ(CS_2)3.1(10H,s,phenyl protons),5.9(4H,s, N-CH_2-C_6H_5),7.1(4H,s,ring protons); λ_{max}260nm (ε 400).

1,3-Diphenylimidazolid-2-one (CIA)

During the synthesis of 1,3-diphenyl-1,3-divinylurea,1,3-diphenylimidazolid -2-one was isolated from the reaction of N,N-dimethyl-2-chloroethylamine with the di-sodium salt of 1,3-diphenylurea; the major product of the reaction being 1,3-bis(N,N-dimethylaminoethyl)-1,3-diphenylurea (CI).[55] Crystallisation gave 1,3-diphenylimidazolid-2-one (5.1g,12% based on diphenylurea)m.p.215-216°(silvery-white flakes from ethanol);

ν_{max}1680(C=O),1300(Amide III),1598,1498,754,694cm^{-1}(monosubstituted benzene); τ($(CD_3)_2CO$)2.1-3.0(10H,m,phenyl protons),6.0(4H,s,ring protons);

λ_{max}266nm(ε 37,000).

1,3-Diethylhexahydropyrimid-2-one (GI)

2-Ketohexahydropyrimidine (8.7g,0.085mol) was dissolved with stirring in anhydrous N,N-dimethylformamide (100ml) in a flask equipped with an efficient reflux condenser topped with a solid carbon dioxide/acetone cold finger. Sodium hydride (60% dispersion in oil,10.0g) was added with stirring,followed by dropwise addition of ethyl iodide (28.0g,0.17mol). A vigorous exothermic reaction occurred with evolution of hydrogen. After the reaction had subsided the solution was maintained at 90° for a further 6h. The solution was cooled,poured into water (600ml),extracted with chloroform and the extract dried over anhydrous calcium chloride. Removal of chloroform under reduced pressure followed by distillation gave 1,3-diethylhexahydropyrimid-2-one (10.1g,77%)b.p.95-96° at 0.5mm Hg

as a colourless liquid n_D^{25} 1.4774;

Found: C,61.2; H,10.15; N,17.6%; M^+,156;

Calc. for $C_8H_{16}N_2O$: C,61.5; H,10.3; N,17.9%; M,156;

ν_{max} 2960,2890(C-H),1645(C=O),1296cm^{-1}(Amide III); τ (CCl_4)6.6-7.0 (8H,m,CH_2 protons adjacent nitrogen),8.0-8.4(2H,m,N-CH_2-CH_2-CH_2-N),9.0-9.2(6H,t,N-CH_2-CH_3).

Purification of acetaldehyde

Acetaldehyde (reagent grade) was shaken with sodium bicarbonate for 1h, filtered and stood over anhydrous calcium sulphate for 2h before distillation through a 100cm Vigreux column. The middle fraction was collected, stood over a small amount of hydroquinone for 2h at 0° before redistillation through a 100cm Vigreux column equipped with a partial take off head (reflux ratio 3:1). The fraction having b.p.20.5° was collected.

Purification of triethylamine

Triethylamine (reagent grade) was allowed to stand over molecular sieve (Type 4A) for 48h. Benzoyl chloride (30ml) was added dropwise to a 500ml portion of triethylamine, the solution was filtered, refluxed with a further portion of benzoyl chloride (30ml) and then distilled. The middle fraction was redistilled from sodium through a 100cm Vigreux column equipped with a partial take off head (reflux ratio 5:1) and the fraction having b.p.89.5° was collected.

Divinyl phenylphosphonate (HI)

Freshly distilled phenylphosphonic dichloride, b.p.86-88° at 0.5mm Hg, (138.0g,0.70mol) was added dropwise over 2h to a stirred solution of acetaldehyde (230.0g,5.2mol) and triethylamine (196.0g,1.94mol) which was previously cooled to -15° and swept with dry nitrogen. The solution was maintained at -15° for 5h during which time the precipitate and solution slowly darkened in colour. The solution was allowed to warm to room temperature, stirred for a further 15h then light petroleum b.p.40-60° (200ml) was added with stirring. The precipitate (triethylamine hydrochloride m.p.253° from alcohol) was removed by filtration and the volatile fractions removed under reduced pressure. Distillation of the residue gave divinyl phenylphosphonate b.p.116-118° at 1.5mm Hg, which was redistilled through a Nester-Faust spinning band column with an 18" stainless steel band and partial take off head (60.0g,41%) b.p.107-108° at 0.5mm Hg as a colourless liquid n_D^{25} 1.5149;

Found: C,57.4; H,5.25; P,14.8%; M^+,210;

Calc. for $C_{10}H_{11}PO_3$: C,57.15; H,5.25; P,14.75%; M,210;

ν_{max} 3060(C-H phenyl and vinyl),1642(C=C vinyl),1593,1443(C=C phenyl), 1280(P=O),1020(P-O-CH=CH_2),980-960(CH=C <),792(P-O-C assym.),755,722, 692cm^{-1}(C-H phenyl); τ (CCl_4)1.9-2.6(5H,m,P-phenyl),3.1-3.6(2H,q,P-O-C$\underline{H}$=CH_2),4.9-5.5(4H,t,P-O-CH=C$\underline{H}_2$); δ^{31}P($CHCl_3$)-11.4p.p.m.

Poly (divinyl phenylphosphonate)

Conditions and results are given in Table6.1. A typical example of a free radical initiated polymerisation was carried out as follows. Divinyl phenylphosphonate (2.10g,0.01mole) was dissolved in freshly distilled N,N-dimethylformamide (2.10g,b.p.44-45° at 20mm Hg),added to a pyrex tube containing azobisisobutyronitrile (30mg,$2x10^{-4}$mol,2.0mol%) the tube purged with dry nitrogen and sealed with a rubber serum cap. The mixture was irradiated with a medium pressure mercury discharge lamp for 16h,then slowly poured into vigorously stirred diethyl ether (200ml), the precipitate collected by filtration,washed repeatedly with diethyl ether and dried under reduced pressure 55° at 0.5mm Hg. The solid was ground to a fine powder,Soxhlet extracted with hexane and dried under reduced pressure 55° at 0.5mm Hg giving poly(divinyl phenylphosphonate) (0.45g,21%)softening point 155-160°;

Found: C,56.5; H,5.55%;

Calc. for $(C_{10}H_{11}PO_3)_n$: C,57.15; H,5.25%;

ν_{max} 3100-2900 (br) (C-H), 1600-1550, 1450 (C=C phenyl), 1300-1250 (br) (P=O), 1040-990 (br) (P-O-C), 755-690 cm^{-1} (C-H phenyl)

τ($(CD_3)_2SO$) 2.2-2.7 (br), 4.8-5.8(br), 7.7-8.8(br); δ^{31}P (N,N -dimethylformamide) -14.2, -29.0 p.p.m. The sample had a reduced specific viscosity (η sp./c) of 0.042 (N,N-dimethylformamide).

Reaction of divinyl phenylphosphonate with bromotrichloromethane

Divinyl phenylphosphonate (4.2g,0.02mol) was dissolved in freshly distilled bromotrichloromethane (10.0g,0.05mol). The mixture was purged with dry nitrogen, sealed in a glass ampoule and irradiated with a medium pressure mercury discharge lamp for 15h. The excess bromotrichloromethane was removed under reduced pressure yielding bis(1-bromo-3,3,3-trichloropropyl) phenylphosphonate as a pale yellow highly viscous liquid, n_D^{25} 1.5635;

Found: Br,26.05; Cl,33.7%;

$C_{12}H_{10}PO_3Cl_6Br_2$ requires: Br,26.35; Cl,35.06%;

ν_{max} 2990(C-H aliphatic),1595,1443(C=C),1275(P=O),1020-1060(P-O-C),792 (P-OC assym),755,690cm^{-1}(C-H phenyl); τ (CCl_4)1.9-2.6(5H,m,P-phenyl), 2.8-3.3(2H,m,P-O-CH-Br),6.2-6.4(4H,m,-CH-CH_2-CCl_3), δ ^{31}P($CHCl_3$)-16.0 p.p.m.

Bis(2-chloroethyl)phenylphosphonate (HII)

Ethylene oxide (13.2g,0.3mol) was added through a wide bore gas inlet tube over 2h to a stirred solution of phenylphosphonic dichloride (19.5g,0.1 mol) and anhydrous aluminium chloride (1.95g) at room temperature. Distillation of the reaction mixture gave bis(2-chloroethyl) phenylphosphonate (19.8g,70%)b.p.192-194° at 2.0mm Hg as a colourless viscous liquid n_D^{25} 1.5236;

ν_{max} 3060(C-H phenyl),2980,2900(C-H aliphatic),1593,1445(C=C),1255(P=O), 1140,1030(P-O-CH_2-CH_2),760,700cm^{-1}(C-H phenyl); τ (CCl_4)2.0-2.6(5H,m,P-phenyl),4.6-4.9(4H,m,P-O-$\underline{CH}_2$-)6.3-6.5(4H,t,O-CH_2-$\underline{CH}_2$); δ ^{31}P($CHCl_3$)-17.2 p.p.m.

Diethyl phenylphosphonate (HIII)

Phenylphosphonic dichloride (9.8g,0.05mol) in anhydrous benzene (20ml) was added dropwise to a stirred refluxing solution of anhydrous ethanol (7.0g,0.15mol) and anhydrous pyridine (8.0g,0.10mol) in anhydrous benzene (60ml). When addition was complete the solution was refluxed for a further 2h, cooled and filtered to remove pyridinium chloride. The filtrate was concentrated on a rotary evaporator then distilled giving diethyl phenylphosphonate (10.7g,76%)b.p.126-128 at 1.0mm Hg as a colourless liquid n_D^{25} 1.4923;

ν_{max} 3060(C-H phenyl),2980-2900(C-H aliphatic),1593,1440(C=C),1255(P=O), 1168(P-O-CH_2-CH_3),755,700cm^{-1}(C-H phenyl); τ(CCl_4)2.1-2.6(5H,m,P-phenyl), 5.8-6.3(4H,m,O-$\underline{CH}_2$-CH_3),8.7-8.9(6H,t,O-CH_2-$\underline{CH}_3$); δ ^{31}P($CHCl_3$)-16.8p.p.m.

2-Phenyl-1,3,2-dioxaphospholane-2-oxide (HIV)

Phenylphosphonic dichloride (19.5g,0.1mol) in anhydrous dioxan (30ml) was added dropwise to a stirred solution of 1,2-ethanediol (6.2g,0.1mol) and anhydrous pyridine (16.0g,0.2mol) in anhydrous dioxan (60ml) under an atmosphere of dry nitrogen. The solution was stirred for a further 2h, filtered and dioxan removed under reduced pressure. Distillation of the residue gave 2-phenyl-1,3,2-dioxaphospholane-2-oxide (11.9g,65%)b.p.169-171° at 0.7mm Hg as a colourless liquid n_D^{25} 1.5359;

Found: C,51.9; H,5.3%;

Calc. for $C_8H_9PO_3$: C,52.2; H,4.95%;

ν_{max} 3040(C-H phenyl),2980(C-H aliphatic),1597,1445(C=C),1270(P=O),1132, 1040(P-O-C),750,713,690cm^{-1}(C-H phenyl); τ ($(CD_3)_2SO$)1.8-2.5(5H,m,P-phenyl),5.1-5.5(4H,m,O-CH_2); $\delta^{31}P$($CHCl_3$)-31.0p.p.m.

2-Phenyl-1,3,2-dioxaphorinane-2-oxide (HV)

Phenylphosphonic dichloride (19.5g,0.1mol) in anhydrous benzene (30ml) was added dropwise to a stirred refluxing solution of 1,3-propanediol (7.6g,0.1mol) and anhydrous pyridine (16.0g,0.2mol) in anhydrous benzene (60ml) under an atmosphere of dry nitrogen. The solution was refluxed for a further 2h,cooled,filtered and benzene removed under reduced pressure. Distillation of the residue gave 2-phenyl-1,3,2-dioxaphosphorinane-2-oxide (12.3g,62%)b.p.148-149° at 0.02mm Hg as a colourless liquid which crystallised on standing m.p.32-33°(white plates from hexane);

Found: C,54.3; H,5.8%;

Calc. for $C_9H_{11}PO_3$: C,54.55; H,5.6%;

ν_{max} 3040(C-H phenyl),2990(C-H aliphatic),1595,1440(C=C),1260(P=O), 1130,1050(P-O-C),760,740,685cm^{-1}(C-H phenyl); τ (CCl_4)2.0-2.4(5H,m,P-phenyl),5.3-6.1(4H,m,P-O-CH_2),7.8-8.3(2H,m,O-CH_2-CH_2-CH_2-O); $\delta^{31}P$($CHCl_3$) -11.2p.p.m.

4,5-Dimethyl-2-phenyl-1,3,2-dioxaphospholane-2-oxide (HVI)

Phenylphosphonic dichloride (19.5g,0.1mol) in anhydrous dioxan (30ml) was added dropwise to a stirred solution of 2,3-butanediol (9.0g,0.1mol) and anhydrous pyridine (16.0g,0.2mol) in anhydrous dioxan (60ml) under an atmosphere of dry nitrogen. The solution was stirred for a further 2h, filtered and dioxan removed under reduced pressure. Distillation of the residue gave 4,5-dimethyl-2-phenyl-1,3,2-dioxaphospholane-2-oxide (14.5g, 69%)b.p.130-131° at 0.02mm Hg as a colourless liquid n_D^{25} 1.5204;

Found: C,56.65; H,6.4%,

Calc. for $C_{10}H_{13}PO_3$: C,56.6; H,6.15%;

ν_{max} 3040(C-H phenyl),2980,2920(C-H aliphatic),1593,1445(C=C),1275(P=O), 1137,1050(P-O-C),755,725,700cm^{-1}(C-H phenyl); τ(CCl_4)1.9-2.6(5H,m,P-phenyl),5.6-5.8(2H,m,P-O-C<u>H</u>),8.6-8.7(6H,d,O-CH-C<u>H</u>$_3$); δ^{31}P($CHCl_3$)-28.0 p.p.m.

<u>4-Methyl-2-phenyl-1,3,2-dioxaphosphorinane-2-oxide (HVII)</u>

Phenylphosphonic dichloride (19.5g,0.1mol) in anhydrous dioxan (30ml) was added dropwise to a stirred solution of 1,3-butanediol (9.0g,0.1mol) and anhydrous pyridine (16.0g,0.2mol) in anhydrous dioxan (60ml) under an atmosphere of dry nitrogen. The solution was stirred for a further 16h, filtered and dioxan removed under reduced pressure. Distillation of the residue gave 4-methyl-2-phenyl-1,3,2-dioxaphosphorinane-2-oxide (13.2g, 62%)b.p.158-160° at 0.3mm Hg as a colourless liquid which crystallised on standing m.p.64-65°(white needles from hexane);

Found: C,56.25; H,6.4%;

Calc. for $C_{10}H_{13}PO_3$: C,56.6; H,6.15%;

ν_{max} 3040(C-H phenyl),2980-2900(C-H aliphatic),1593,1445(C=C),1270 (P=O),1135,1080(P-O-C),755,715,690cm^{-1}(C-H phenyl); τ (CCl_4)2.0-2.7 (5H,m,P-phenyl),5.0-6.2(3H,m,P-O-C<u>H</u>),8.0-8.3(2H,m,-CH_2-C<u>H</u>$_2$-CH-CH_3),8.6-8.8(3H,d,CH-C<u>H</u>$_3$); δ^{31}P($CHCl_3$)-14.0p.p.m.

<u>Calibration of the n.m.r. method for analysis of the ring size in phosphonate polymers</u>.

Varying amounts of 2-phenyl-1,3,2-dioxaphospholane-2-oxide,2-phenyl-1,3,2-dioxaphosphorinane-2-oxide and acyclic phosphonates were dissolved in chloroform (2.0ml) and the ^{31}P n.m.r. spectrum of the mixture obtained. The results are summarised on the next page.

5-membered ring phosphonate[a] g	6-membered ring phosphonate[b] g	acyclic phosphonate g	calculated ratio 5:6: acyclic % w/w	^{31}P n.m.r. peak position p.p.m.	ratio found 5:6:acyclic peak areas
0.35	0.65	-	1:1.97	-31.0(5) -11.2(6)	1:2.01
0.50	0.50	-	1:1	-31.0(5) -11.2(6)	1:1.02
0.75	0.25	-	3:1	-31.0(5) -11.2(6)	2.94:1
0.50	0.50	0.50[c]	1:1:1	-31.0(5) -11.2(6 +acyclic)	1:1.89
0.33	0.33	0.33[d]	1:1:1	-31.0(5) -16.9 (acyclic) -11.2(6)	1:1.11:1.12

[a] 2-phenyl-1,3,2-dioxaphospholane-2-oxide

[b] 2-phenyl-1,3,2-dioxaphosphorinane-2-oxide

[c] divinyl phenylphosphonate

[d] diethyl phenylphosphonate

Diethyl methylphosphonate (JI)

Triethyl phosphite (110.0g,0.66mol) and iodomethane (100.0g,0.705mol) were refluxed for 2h on a steam bath using an efficient condenser and an anhydrous calcium chloride guard tube. Iodoethane (96g) was distilled from the reaction mixture and the residue distilled giving diethyl methylphosphonate (95.0g,95%) b.p.59-60° at 1.0mm Hg as a colourless liquid n_D^{25} 1.4128;

Found: C,39.45; H,8.6%;

Calc. for $C_5H_{13}PO_3$: C,39.45; H,8.55%;

ν_{max} 2970,2910(C-H aliphatic),1308(P-CH_3)1230(P=O),1160,1025cm^{-1}(P-O-C_2H_5); τ($CDCl_3$)5.6-6.2(4H,m,P-O-CH_2),8.4-8.8(9H,q,CH_3protons) δ ^{31}P ($CHCl_3$)-26.0p.p.m.

Methylphosphonic acid (JII)

Diethyl methylphosphonate (140.0g,0.985mol) was refluxed for 8h with hydrochloric acid (600ml) and water (600ml). Water,hydrochloric acid and ethanol were removed by distillation giving methylphosphonic acid (80.0g, 83%) as a colourless viscous liquid which crystallised on standing m.p. 103-105°(white plates from hexane/ethyl acetate).

Methylphosphonic dichloride (JIII)

Phosphorus pentachloride (180.0g,0.865mol) was added to methylphosphonic acid (36.0g,0.375mol) in a flask equipped with an efficient reflux condenser and an anhydrous calcium chloride guard tube. A vigorous exothermic reaction started on gentle heating and the contents of the flask soon became liquid. The solution was refluxed for a further 12h and distilled through a 30cm Vigreux column. Phosphoryl chloride was removed as the first fraction followed by methylphosphonic dichloride (48,0g,77%)b.p.160-162° as a colourless liquid n_D^{25} 1.4595 which crystallised on standing m.p.32-34°;

Found: Cl,53.15%;

Calc. for CH_3POCl_2: Cl,53.35%;

ν_{max} 2980,2900(C-H aliphatic),1303(P-CH_3),1268cm^{-1}(P=O).

Divinyl methylphosphonate (KI)

Methylphosphonic dichloride (26.6g,0.20mol) in anhydrous benzene (40ml) was added dropwise over 2h to a stirred solution of acetaldehyde (64.0g, 1.45mol) and triethylamine (55.5g,0.55mol) which had been previously cooled to -15° and swept with dry nitrogen. The solution was maintained at -15° for 4h with continuous stirring during which time the precipitate and solution slowly darkened in colour. The solution was allowed to warm to room temperature, stirred for a further 12h then light petroleum b.p.40-60° (200ml) was added with stirring. The precipitate (triethylamine hydrochloride m.p.253° from alcohol) was removed by filtration and the volatile fractions removed under reduced pressure. Distillation of the residue gave divinyl methylphosphonate b.p.68-70° at 6.0mm Hg,which was redistilled through a Nester-Faust spinning band column equipped with an 18" stainless steel band and partial take off head (9.3g,32%)b.p.52-53° at 1.0mm Hg as a colourless liquid n_D^{25} 1.4369;

Found: C,40.34; H,6.45; P,21.25%; M^+,148;

Calc. for $C_5H_9PO_3$: C,40.5; H,6.1; P,20.95%; M,148;

ν_{max} 3010(C-H vinyl),2920(C-H methyl),1643(C=C),1308(P-CH_3),1270(P=O), 1020(P-O-CH=CH_2),910(CH=C),818cm^{-1}(P-O-C assym); τ (CCl_4)3.1-3.6(2H,m,

P-O-C$\underline{H}$=CH_2), 5.0-5.6(4H, q, P-O-CH=C$\underline{H}_2$), 8.3-8.6(3H, d, CH_3-P=O); δ^{31}P($CHCl_3$) -22.8p.p.m.

Poly (Divinyl methylphosphonate)

Conditions and results are given in Table6.2. A typical example of a free radical initiated polymerisation was carried out as follows. Divinyl methylphosphonate (1.48g, 0.01mol) was dissolved in freshly distilled tetrahydrofuran (1.5g), added to a pyrex tube containing azobisisobutyronitrile (30mg, $2x10^{-4}$mol, 2.0mol%), the tube purged with dry nitrogen and sealed with a rubber serum cap. The mixture was irradiated with a medium pressure mercury discharge lamp for 20h, then slowly poured into vigorously stirred ether (200ml), the precipitate collected by filtration, washed repeatedly with ether and dried under reduced pressure 55° at 0.5mm Hg. The solid was ground to a fine powder, Soxhlet extracted with hexane and dried under reduced pressure giving poly (divinyl methylphosphonate)(0.41g, 30%) softening point 105-110°;

Found: C, 40.1; H, 6.9%;

Calc. for $(C_5H_9PO_3)_n$: C, 40.5; H, 6.1%;

ν_{max} 2990-2900(br)(C-H), 1310(P-CH_3), 1270-1220(br)(P=O), 1040-980(br) (P-O-C), 825-800cm^{-1}(br)(P-O-C assym); τ($(CD_3)_2SO$)4.4-5.1(br), 7.0-7.5 (br), 8.2-8.7(br); δ^{31}P(N,N-dimethylformamide) -24.6p.p.m. The sample had a reduced specific viscosity ($\eta_{sp/c}$) of 0.08 (N,N-dimethylformamide).

Reaction of divinyl methylphosphonate with bromotrichloromethane

Divinyl methylphosphonate (1.48g, 0.01mol) was dissolved in freshly distilled bromotrichloromethane (5.0g, 0.025mol). The mixture was purged with dry nitrogen, sealed in a glass ampoule and irradiated with a medium pressure mercury discharge lamp for 16h. Excess bromotrichloromethane was removed under reduced pressure yielding bis(1-bromo-3,3,3-trichloropropyl)methylphosphonate as a pale yellow viscous liquid n_D^{25} 1.5330;

Found: Br, 36.6; Cl, 50.15%;

$C_7H_9PO_3Br_2Cl_6$ requires: Br, 29.35; Cl, 39.05%;

ν_{max} 2920(C-H aliphatic), 1309(P-CH_3), 1270(P=O), 1060-1020(P-O-C), 818cm^{-1} (P-O-C assym); τ(CCl_4)2.9-3.4(2H, m, P-O-CH-Br), 6.3-6.4(4H, d, CHBr-C$\underline{H}_2$-CCl_3), 8.1-8.5(3H, d, P-CH_3); δ^{31}P($CHCl_3$) -27.4p.p.m.

2-Methyl-1,3,2-dioxaphospholane-2-oxide (KII)

1,2-Ethanediol (1.8g,0.03mol) was added to ice cold methylphosphonic dichloride (3.9g,0.03mol) in a flask connected via a cold trap to a water pump. The contents of the flask were allowed to warm to room temperature, hydrogen chloride being removed under vacuum whilst keeping the temperature at 30-40°. When most of the hydrogen chloride had been evolved, the reaction was maintained at 100-110° for 2h. Distillation of the residue gave 2-methyl-1,3,2-dioxaphospholane-2-oxide (1.5g,41%)b.p.130-132° at 2.0mm Hg as a colourless liquid n_D^{25} 1.4565;

ν_{max}2920(C-H),1309(P-CH_3),1240(P=O),1040cm^{-1}(P-O-C); τ(CCl_4)5.5-5.9 (4H,m,P-O-CH_2),8.2-8.5(3H,d,P-CH_3); δ^{31}P($CHCl_3$) -43.2p.p.m.

2-Methyl-1,3,2-dioxaphosphorinane-2-oxide (KIII)

1,3-Propanediol (2.3g,0.03mol) was added to ice cold methylphosphonic dichloride (3.9g,0.03mol) in an evacuated flask, after which the contents were kept at 30-40° whilst most of the hydrogen chloride was removed under vacuum and then the reaction was heated to 100-110° for 2h. Distillation of the residue gave 2-methyl-1,3,2-dioxaphosphorinane-2-oxide (1.6g,40%) as a colourless liquid b.p.122-124° at 0.4mm Hg which crystallised on standing m.p.98-100°(white flakes from hexane);

Found: C,35.4; H,6.95%;

Calc. for $C_4H_9PO_3$: C,35.3; H,6.65%;

ν_{max}2980(C-H),1308(P-CH_3),1250(P=O),1082(P-O-C),804cm^{-1}(P-O-C assym); τ(CCl_4)5.5-6.3(4H,m,P-O-CH_2),8.0-8.2(2H,m,P-O-CH_2-CH_2-CH_2),8.4-8.7 (3H,d,P-CH_3); δ^{31}P($CHCl_3$) -23.2p.p.m.

2,4,5-Trimethyl-1,3,2-dioxaphospholane-2-oxide (KIV)

1,2-Butanediol (2.7g,0.03mol) was added to ice cold methylphosphonic dichloride (3.9g,0.03mol) in an evacuated flask after which the contents were kept at 30-40° whilst most of the hydrogen chloride was removed under vacuum and then the reaction was maintained at 100-110° for 2h. Distillation of the residue gave 2,4,5-trimethyl-1,3,2-dioxaphospholane-2-oxide (2.3g, 47%)b.p.126-128° at 4.0mm Hg as a colourless liquid which crystallised on standing m.p.42-44°;

ν_{max}2980(C-H),1309(P-CH_3),1270(P=O)1050cm^{-1}(P-O-C); τ(CCl_4)5.6-5.9 (2H,m,P-O-CH),8.3-8.7(9H,m,all CH_3's); δ^{31}P($CHCl_3$) -39.2p.p.m.

2,4-Dimethyl-1,3,2-dioxaphosphorinane-2-oxide (KV)

1,3-Butanediol (2.7g,0.03mol) was added to ice cold methylphosphonic dichloride (3.9g,0.03mol) in an evacuated flask after which the contents were kept at 30-40° whilst most of the hydrogen chloride was removed under vacuum and then the reaction was maintained at 100-110° for 2h. Distillation of the residue gave 2,4-dimethyl-1,3,2-dioxaphospholane-2-oxide (2.2g,45%)b.p.70-71° at 0.2mm Hg as a colourless liquid which crystallised on standing m.p.40-41°;

ν_{max} 2980, 2940(C-H), 1309(P-CH_3), 1245(P=O), 1080(P-O-C), 803cm^{-1}(P-O-C assym); τ (CCl_4)5.4-6.0(3H,m,P-O-CH,P-O-CH_2),8.0-9.0(8H,m,P-CH_3,O-C-CH_2-C-O,C-CH_3); δ^{31}P($CHCl_3$)-26.4p.p.m.

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APPENDIX 1

Computer Program for Calculating Reactivity Ratios.

The program presented here is written in the FORTRAN IV programming language.

```
      COPOLYMERISATION PARAMETERS
      SUBROUTINE SLINE (X,Y,SLOPE,RCEP,NUM) DIMENSION Y(50),X(50)
      SUM X = 0.0
      SUM Y = 0.0
      SUM XX = 0.0
      SUM XY = 0.0
      ANUM = NUM
      DO 49 I=1, NUM
      SUM X = SUM X + X(I)
      SUM Y = SUM Y + Y(I)
      SUM XX = SUM XX + X(I) **2
   49 SUM XY = SUM XY + X(I) * Y(I)
      DET = SUM X * SUM X - ANUM * SUM XX
      SLOPE = (SUM X * SUM Y - ANUM * SUM XY) / DET
      RCEP = (SUM X * SUM XY - SUM Y * SUM XX) / DET
      RETURN
      END
      DIMENSION SMAF 1 (15), SMAF 2 (15), CAPF 1 (15), CAPF 2 (15),
      R1(11), R2(15,11), ORD(50), ABSC(50), EXTRA(11), SLOPE(15),
      SINT(15)
      READ (2,1) NPTS
    1 FORMAT
      READ (2,2) (SMAF 1(I), CAPF 1(I), I=1, NPTS)
    2 FORMAT (2F 10.0)
    4 DO 8 J=1, NPTS
      SMAF 2 (J) = 1.0 - SMAF 1 (J)
      CAPF 2 (J) = 1.0 - CAPF 1 (J)
      ORD (J) = (SMAF 1 (J) * (1.0-(2.0 * CAPF 1 (J))))/(SMAF 2 (J) *
      CAPF 1 (J))
    8 ABSC (J) = ((SMAF 1 (J) ** 2) * CAPF 1 (J))/((SMAF 2 (J) ** 2) *
      CAPF 1 (J))
```

```
      CALL SLINE (ORD,ABSC,ARGS,ARG1,NPTS)
      WRITE (5, 11)
11    FORMAT (1H , 20X, 'H.H.MONKS REACTIVITY RATIOS',)
      WRITE (5, 12)
12    FORMAT (1H , 10X, ' THE ARRAYS NEEDED FOR CALCULATION ARE -',)
      WRITE (5, 15)
15    FORMAT (1H , 10X, 'SMALL F1 SUB I', 4X,'CAPITAL F1 SUB I', 4X,
     'SMALL F2 SUB I', 4X,'CAPITAL F2 SUB I',)
      WRITE (5,61)(SMAF 1(M), CAPF 1 (M), SMAF 2(M), CAPF 2(M), M=1,
     NPTS)
61    FORMAT (1H , 12X, F 10.7, 8X, F 10.7, 8X, F 10.7, 8X, F 10.7)
      WRITE (5,70)
70    FORMAT (1H1,    10X, 'FITTING THE LEAST SQUARES LINE',)
      WRITE (5,17)
17    FORMAT (1H ,10X 'THE CALCULATED POINTS TO BE FITTED ARE-',)
      WRITE (5,18)
18    FORMAT (1H , 10X, 'ORDINATES', 40X, 'ABSCISSAS',)
      WRITE (5,19) (ORD (JD), ABSC (JD), JD=1,NPTS)
19    FORMAT (1H , 12X, F16.7, 30X, F16.7)
      WRITE (5,20) ARGS
20    FORMAT (1HO,10X, 'THE SLOPE OF THE FITTED LINE', 4X, F16.7)
      WRITE (5,21)ARG 1
21    FORMAT (1HO, 10X,'THE INTERCEPT OF THE FITTED LINE', 4X, F16.7)
      DO 37 K=1, NPTS
      B = 0.90
      C1 = SMAF 1 (K)/SMAF 2 (K)
      C2 = CAPF 2 (K)/CAPF 1 (K)
      CON = C1 * (C2-1.0)
      COR1 = C1 * C2 * C1
      DO 37 L=1, 11
      R1 (L) = B * ARGS
      B = B + 0.02
37    R2 (K,L) = CON + COR1 * R1 (L)
      DO 500 KR = 1, NPTS
      DO 501 LR = 1, 11
501   EXTRA (LR) = R2 (KR, LR)
      CALL SLINE (EXTRA, R1, ARGS, ARG1, NPTS)
      SLOPE (KR) = ARGS
500   SINT (KR) = ARG1
```

```
      WRITE (5,71)
   71 FORMAT (1HO,10X,'SOLUTIONS OF THE LINEAR EQUATIONS FOLLOW',)
      DO 95 JHD = 1, NPTS
      DO 90 MAC = 1, 11
      IF (MAC - 1) 300, 96, 97
   96 WRITE (5,98) SMAF1 (JHD), CAPF1 (JHD), R1(MAC), R2(JHD,MAC)
      GO TO 90
   97 WRITE (5,99) R1 (MAC), R2(JHD,MAC)
   90 CONTINUE
      WRITE (5,100)
      WRITE (5,20) SLOPE(JHD)
   95 WRITE (5,21) SINT(JHD)
  100 FORMAT (1HO, 10X, 'A STRAIGHT LINE HAS BEEN FITTED TO R(2)VS
      R(1)',)
   98 FORMAT (1H ,'WHEN SMALLF1 =', F14.7, 'AND CAPF1 =', F14.7,
      'AND R(1) =', F14.7, 'THEN R(2) =', F14.7)
   99 FORMAT (78X, F14.7, 14X,F14.7)
      WRITE (5,301)
  301 FORMAT (1H1, 'END END END END END',)
  300 CALL EXIT
      END
```

APPENDIX 2

Post-graduate Courses of Study

The following post-graduate lectures were attended.

1. At The University, Sheffield.

(a) Structure determination by mass spectrometry (6 lectures)

(b) Principles of nuclear magnetic resonance and chemical applications (6 lectures)

(c) High Polymers (6 lectures)

2. At Sheffield Polytechnic

(a) Macromolecules (11 lectures)

(b) Polymeric materials (2 day course)

H_2NCH_2-C

BI

BII

BIII

BIV

DI

DI

DIII