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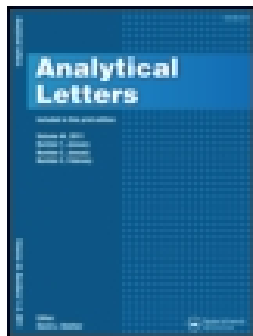
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Determination of Volatile Organic Compounds by a Novel Polymer Spin-coated Thin Film and Surface Plasmon Resonance

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Abstract

Here is reported the synthesis, characterization, and volatile organic compound (VOCs) sensing of a 1, 3-dimethyl polyphenylene vinylene polymer. The synthesis was performed by a Witting condensation through the reaction of 1, 4-terphthaldehyde with the phosphonium chloride of

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meta-xylene. The material was characterized by infrared spectroscopy, elemental analysis, and thermogravimetric analyses. Thin films of the polymer were prepared by spin coating at speeds from 1000 to 5000 rpm. Ultraviolet-visible spectroscopy and surface plasmon resonance were used to characterize the spin coated films. The thicknesses of the films were estimated by fitting the curves and were between 4.5 to 24.5 nm depending on the speed. The refractive index of the new polymer was 1.72. The polymer spin coated films were exposed to volatile organic vapors in order to characterize their sensing properties by surface plasmon resonance as a function of time. The results showed that the new material responded rapidly, sensitively, and reversibly to volatile organic compounds.

INTRODUCTION

Polymer thin films have an important role for technological applications such as electromechanics (Robert 1985; Zhang et al. 2006; Konry et al. 2008), biocompatible coatings (Subr et al. 2006), novel drug delivery systems (Lynch, Gregorio, and Dawson 2005), chemical and biochemical sensors (Badr and Meyerhoff 2005; Park et al. 2008), lenses (Sokuler and Gheber 2006), waveguides (Kim et al. 2001), and other optical devices (Huang et al. 2004; Matsui et al. 2004). Polymers provide remarkable advantages in optical applications owing to their low cost, lightweight, durability, and practicality for making thin films using different techniques. Polymer thin films can also be used in high temperature and space survivable coating applications (Hoflund, Gonzalez, and Phillips 2001). These applications often require ultrathin films such as nanoscale thickness while maintaining or improving the stability of the material.

There are a wide range of thin film preparation techniques to prepare solid state thin films of organic materials such as Langmuir-Blodgett deposition (Capan, Tarımcı, and Capan 2010), Langmuir-Schaefer deposition (Spadavecchia et al. 2006), self-assembly (Cao et al. 2013), and spin coating (Spadavecchia et al. 2004; Korczyc et al. 2017).

Spin coating is one of the most common coating processes for applying thin films on a solid substrate. It can exhibit a fast and effective deposition using a rotating substrate with high precision. Spin coating may be used to produce ultrathin organic films. Due to its interesting distinctive properties, spin coating is used for applications that include third harmonic generation (Chtouki et al. 2017), solar cells (Khavar et al. 2017), biosensors (Chou et al. 2016), photodetectors (Jacob et al. 2017), gas sensing (Berger et al. 2016; Inyawilert et al. 2017), and volatile organic compound detection (Daneshkhah et al. 2015; Evyapan and Dunbar 2016).

In recent years, new sensors have been developed for the determination of volatile organic compounds (Rella et al. 2003; Evyapan et al. 2016). Polymers have the ability to interact with volatile organic compounds and hence are suitable for their detection (Patil et al. 2015). Therefore, polymer thin films have been developed with particular interest in the detection of hazardous vapors (Hyodo et al. 2012; Öztürk et al. 2016; Wisser, Grothe, and Kaskel 2016). The sensitivity is directly related to the reactivity between vapor and polymer (Dubbe 2003). Hence, the interaction mechanism and the sensitivity are the key features for the producing efficient sensors (Evyapan and Dunbar 2016).

Here a novel 1,3-dimethyl polyphenylene vinylene polymer was employed for the sensing for volatile organic compounds (VOCs). The synthesis and characterization of the polymer are presented. Spin coating was used to control the thickness of the solid-state polymer films. Characterization of the films was performed by ultraviolet-visible spectroscopy and

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surface plasmon resonance. The reproducibility and the uniformity of the thin films were investigated, along with the thickness and refractive index. The sensing characteristics of the polymer thin films were characterized for benzene, toluene, hexane, dichloromethane, chloroform, butanol and ethanol using kinetic measurement with surface plasmon resonance. The optical sensor responses are compared based on the film thickness and the analyte.

EXPERIMENTAL

Materials and Instrumentation

Triphenylphosphene, m-xylene, hydrochloric acid, acetone, formalin solution (35%) were supplied by Fluka. Absolute ethanol, chloroform, benzene, hexane, dichloromethane, butanol, toluene and sodium metal were supplied by Reidel-De Hean A.G, Germany and 1,4-terephthaldehde was supplied by BDH, England.

Infrared spectrum were obtained using a KBr disk with a Model M8400S instrument (Shimadzu). Carbon-hydrogen-nitrogen analysis was carried out using PerkinElmer 2400 series II analyzer. Thermogravimetric analyses were performed under nitrogen at 5°C/min using a DSC Q 1000V 9.8 Build 296 analyzer.

Ultraviolet-visible spectra were recorded using Varian Cary 50 Scan spectrophotometer from 300 to 900 nm. Surface plasmon resonance measurements were carried out using the home-made setup (Kretschmann and Raether 1968) shown in **Figure 1**. The system consists of a semi-cylindrical prism (refractive index of 1.515) and a He-Ne laser at 632.8 nm (Nabok et al. 1997). The thickness and the refractive index of thin films were evaluated by fitting the SPR curves to Fresnel equations using Winspall 3.02 software from the Max-Planck Institute (Evyapan et al. 2016).

Synthesis

Chloromethylation of m-xylene (I)

10 g of m-xylene, 72 g of 35% formalin, and 150 ml of concentrated hydrochloric acid were refluxed for 5 h and the product was present in the organic phase. The product was separated and washed several times with water and recrystallized in methanol to obtain a white powder (yield 78%) with a melting point of 91°C.

Synthesis of m-xylene bis (Triphenyle Phosphonium Chloride Salts) (II)

2.21 g of compound (I) and 7.34 g of triphenylphosphene in 100 ml xylene were refluxed for 24 h. After cooling to room temperature, the white precipitate was washed with ether and acetone, filtered, and dried under vacuum in order to obtain the product (yield 83%).

Synthesis of 1,3-dimethyl Polyphenylene Vinylene (III)

The polymerization was carried out by a Witting condensation in stirred 1, 4-terephthaldehyde (10 mmole) and the phosphonium chloride product (II) (10 mmole) in 50 ml of 3:1 anhydrous ethanol:chloroform. 0.1 g sodium metal in 10 ml absolute ethanol was added dropwise at ambient temperature with stirring for 24 hrs at room temperature. Subsequently 15 ml of 2% hydrochloric acid was added to obtain a pastelike product that was washed with 3:1 ethanol:water and dried under vacuum in order to obtain the yellow powdered product.

Preparation of Spin Coated Polymer Films

The 1, 3-dimethyl polyphenylene vinylene was dissolved in chloroform at 1 mg ml^{-1}. Thin films were prepared via spin coating at spin speeds from 1000 to 5000 rpm to characterize the thickness dependence. Spin films were transferred on 76×26 mm glass slides for ultraviolet-

visible spectroscopy and 35 nm gold coated glass substrates for surface plasmon resonance. The gold layers were deposited by thermally evaporation for surface plasmon resonance. Pre-cleaned glass slides were used for evaporation of gold and the speed of evaporation was 0.2 nm s^{-1} at 10^{-6} mbar. 100 µl f polymer solution was dispensed on the rotating substrate and allowed to spin for 30 seconds. The thickness of thin films was controlled by changing the spin speed while monitoring by UV-visible spectroscopy and surface plasmon resonance.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymer

Figure 2 summarizes the synthesis of the 1, 3-dimethyl polyphenylene vinylene polymer. The dichloromethylation of m-xylene compound (I) was performed in presence of formalin solution and concentrated hydrochloric acid under reflux for 5 h. Several papers describe the preparation of this compound using different methods (Hu et al. 2010; Bakoz 2015). The chloromethylated groups were introduced by Friedel-Craft alkylation. It is generally accepted that the electrophilic reagent is formaldehyde protonated hydroxyl carbenium ion ($^{+}CH_2 = OH$). The compound (II) is called a Witting reagent and was obtained from the reaction of compound (I) with triphenylphosphene through a S_N2 mechanism. The polymer was prepared through a Witting reaction which is commonly used for the synthesis of alkenes. This method uses a carbonyl compound as an electrophilic reagent in the presence of base as the catalyst.

Infrared Spectroscopy

The prepared compounds and polymers were characterized by infrared spectroscopy as shown in **Figures 3–5**. For the compound (I), the spectrum indicates the presence of an aromatic

ring since the absorption bands appear between 900 and 650 cm^{-1}. The characteristic band at 3010 cm^{-1} is from the stretching of C-H bonds of the aromatic ring. The peaks at 2974 and 2961 cm^{-1} correspond to the aliphatic C-H bond stretching of the methyl group. The bands at 472 and 520 cm^{-1} confirm the extended C-Cl bond.

For the compound (II), there are characteristic bands at 505 cm^{-1} and 1103–1112 cm^{-1} due to P-Cl and CH$_2$-P, respectively. **Figure 5** shows infrared spectrum of the prepared 1, 3-dimethyl polyphenylene vinylene. The band at 3051 cm^{-1} is due to the stretching of the alkenyl C-H bond. The band at 999 cm^{-1} is due to trans-vinylene out of plane C-H bending. The characteristic band at 1701 cm^{-1} corresponds to the stretching of the vinylene bond while the band at 1598 cm^{-1} is due to the phenyl ring C-H.

Elemental Analysis

The structure of synthesized polymer was also confirmed by the carbon-hydrogen-nitrogen analysis. The calculated carbon ratio was 93.103% compared to 92.624% obtained experimentally. The calculated hydrogen ratio was 3.712% with a measured value of 3.801%. There are small differences between calculated and experimental values due to the high molecular weight of polymer. However, the results confirm the chemical structure of the repeating unit of the polymer.

Thermogravimetric Analysis

Thermogravimetric analysis monitors the change in mass of a material as a function of increasing temperature or time. Thermogravimetric analysis is used to determine the composition of materials and predict their thermal stability. It is beneficial for the investigation of polymers

and commonly used to characterize their stability (Alidagi et al. 2017; Ganapathi, Kalyon, and Fisher 2017; Li et al. 2017). Polymeric materials commonly exhibit physical and chemical changes when heat is applied. The thermal stability of polymers is defined as the resistance towards thermochemical degradation and is expressed as functions of temperature or time.

The 1,3-dimethyl polyphenylene vinylene was characterzied by thermogravimetric analysis. 5.08 mg was heated from 35°C to 700°C at a rate of 10°C/min. The mass change of was recorded as a function of temperature and time and the results are shown in **Figure 6**. The ratio of char-content was determined to be 10% at 400°C and the half-weight loss temperature was estimated to be 303°C. The decomposition of the polymer was obtained from the derivative of the thermogram and defined as optimum decomposition temperature. 1, 3-Dimethyl polyphenylene vinylene exhibits one decomposition temperature at 318°C which demonstrates the stability of the polymer.

Spin Coated Film Characterization

Polymer spin coated films have been prepared from 1000 to 5000 rpm to obtain various film thickness. **Figure 7** shows the ultraviolet-visible absorption spectra of 1, 3-dimethyl polyphenylene vinylene spin coated films obtained at various speeds and compared with solution spectra. The solution exhibits two bands at 273 and 315 nm that are attributed to the conjugation of the double bond of the vinylene group with the benzene and with dimethyl benzene ring. These transitions involve π-π^* transitions.

The spectra of spin coated films exhibit similar characteristics with the solution spectra. The peak at 315 nm for solution is broadened and red-shifted to 340 nm. The shift is caused by molecular aggregation following the organization of molecules on a solid substrate. The

ultraviolet-visible absorbance was employed to compare the thicknesses of the thin films. An increase in absorbance indicates increasing film thickness. The spin speed changes the thickness of spin coated films according to an inverse proportional relationship (Evyapan et al. 2013; Evyapan et al. 2016). Similar results have been obtained in this study as shown in **Figure 7**.

In order to characterize the reproducibility of spin coated thin films, surface plasmon resonance was also utilized. **Figure 8** shows the SPR curves of spin coated polymer films as the reflected light intensity versus the angle of incidence. The minimum reflected light intensity value corresponds to the SPR angle (θ_{SPR}). Coating a thin film on a gold substrate causes a shift of θ_{SPR} compared with bare gold. This shift is directly related with the thickness and the optical constants of thin film on gold surface as given by (Nabok et al. 1997):

$$\Delta\theta = \frac{(2\pi/\lambda)(|\varepsilon_m|\varepsilon_i)^{3/2}d}{(n_p\cos\theta)(|\varepsilon_m|-\varepsilon_i)^2\varepsilon}(\varepsilon-\varepsilon_i)$$

(1)

where λ is the wavelength of the laser beam (632.8 nm), n_p is the refractive index of the semi-cylindrical prism, $|\varepsilon_m|$ is the modulus of the complex dielectric constant of the gold film, ε_i is the dielectric constant of the medium in contact with thin film which was air for this work, ε is the dielectric constant, and d is the thickness of thin film.

Figure 8 shows that the biggest shift belongs to 1000 rpm spin coated film which is the lowest speed. If the speed is increased, SPR curves approach bare gold. Thinner films are produced by the fastest spin speed which was also obtained from ultraviolet-visible spectra. **Table 1** lists the angle shift ($\Delta\theta°$) values of the spin coated films. At higher spin speeds, the angle changes regularly, while for lower spin speeds such as 1000 and 2000 rpm, the shifts are larger and the SPR curves are broadened. The changes of the width of SPR curves are provided

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in **Table 1** as the change in the full width of half-maximum. The broadening of the SPR curves is due to the damping of resonance with increasing film thickness (Ray et al. 2000). The curves are also affected by the homogeneity and uniformity of thin film surface (Nabok et al. 1997). These undesirable results are more likely seen for thicker films due to the accumulation of molecules. **Table 1** shows that the broadening of SPR curve is 0.8° for 5000 rpm spin coated film and 2.3° for the 1000 rpm film. The surface plasmons are sensitive to the morphology of the dielectric layer because higher spin speeds increase the thin film homogeneity. Thus, good agreement between the ultraviolet-visible and surface plasmon resonance results are observed.

Another advantage of surface plasmon resonance is estimation of thickness and refractive index of the thin films. These parameters are estimated using Fresnel refraction theory by fitting SPR curves (Nabok, Hassan, and Ray 1999) using bare gold and its parameters. **Table 1** gives the thicknesses for the spin coated films, showing higher speed produces thinner and more uniform spin coated films. The refractive index of the spin coated film is 1.72 which is in agreement with organic materials (Evyapan et al. 2013).

Vapor Sensing

Surface plasmon resonance system was also used for to investigate the sensing properties of spin coated films. Gas sensing measurements were carried out using a polytetrafluoroethylene gas cell. Volatile organic compounds used as analyte included benzene, toluene, hexane, dichloromethane, chloroform, butanol and ethanol. The volatile organic compounds were introduced into the gas cell using a 10 ml syringe and were mixed with dry air to obtain various concentrations. The SPR response of a spin coated film was obtained before and after exposure

to volatile organic compounds. The interaction between thin film and analyte vapor causes a shift in the SPR curve.

The kinetic response of sensor film as a function of time was also investigated. A fixed angle was selected from the linear part near to the minimum of SPR curve and the kinetic response was recorded as the reflected light as a function of time. The organic vapors to interacted with the sample for 2 min and dry air was introduced into the gas cell for 2 min. Exposure to the organic vapors was 25% with dry air up to 100% in 25% increments. **Figure 9** shows the response of the 3000 rpm spin coated film exposed to several volatile organic compounds. Fast and reversible responses were obtained with all of the compounds. The response and the recovery times were a few seconds. The recovery is nearly complete because dry air causes the intensity to return to its initial value. The responses increased with the vapor concentration, as shown in **Figure 10**.

The strongest response was obtained for dichloromethane followed by chloroform. There are several reports of the determination of dichloromethane and chloroform (Acikbas et al. 2017; Acikbas et al. 2016) that provide the same trend in sensitivity.

The response is produced from the interaction of the film with the vapor and depends on physical properties of the analytes. The molecular size affects the response. Smaller molecules more easily diffuse into the film (Evyapan and Dunbar 2015; Evyapan and Dunbar 2016). Dichloromethane and chloroform are the smallest analytes and therefore have the largest responses. Furthermore, the viscosity of dichloromethane (0.32cSt) is lower than the other compounds. Lower viscosity causes faster diffusion into the film and a higher response. The viscosity of butanol (3.64cSt) is the highest, resulting in the lowest response.

The analyte vapor pressure also influences the sensor response. Higher vapor pressures suggest rapid movement of the analytes that increase the size and speed of the response. The dichloromethane vapor pressure of 47.06 kPa is highest value for the analytes in the study. The lowest vapor pressure (0.63 kPa) is for butanol which has lowest response.

The interaction between vapor and thin film involves two steps. The first causes a sharp response and then the sensor is saturated. The initial sharp response is a surface effect due to adsorbed vapor on the surface of thin film. Secondly, the analytes diffuse into the film structure in the diffusion effect (Evyapan and Dunbar 2015) that causes the setting of the response. In order to investigate the diffusion of the analytes, various spin coated films were treated with dichloromethane vapor.

Figure 11 shows the kinetic response of various spin coated films in the presence of saturated dichloromethane. The response increased with a decrease in the spin speed. However, the sensor increased with film thickness due to the diffusion of the analytes into the film. Larger film thicknesses provide more cavities for analytes to diffuse and interact with the 1, 3-dimethyl polyphenylene vinylene polymer. **Figure 11** shows a decrease in the sensor response with time. The diffusion is dynamic that includes the adsorption and desorption of the analytes. During the diffusion into the film, some molecules are adsorbed by the film and some adsorbed molecules are desorbed. When the rates of adsorption and desorption are equal, the sensor is saturated. The penetration of analyte into film structure also swellings the thin film (Evyapan et al. 2016).

In order to monitor the film thickness after swelling, SPR curves of spin coated films were recorded before and after vapor exposure. **Figure 12** shows the shift of the SPR curves following exposure to saturated dichloromethane on a 3000 rpm spin coated film. The SPR curve shifts to higher angles as the film increases in thickness. The interaction between

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dichloromethane and the thin film causes a shift of $\Delta\theta_{SPR} = 0.4°$ from its original value of $\theta_{SPR} = 46.1°$. Dichloromethane penetrates the film leading to swelling by 2.3 nm. Despite the adsorption of organic vapors and swelling of the thin film, the refractive index of the spin coated film is still approximately 1.7.

In order to control the recovery of the sensor, dry air was introduced and the response was recorded as the recovery cycle. After the recovery cycle, the resonance angle was $\theta_{SPR} = 46.2°$ indicating suitable recovery. Large differences following recovery may be due to the trapped analyte in the film structure.

CONCLUSIONS

A synthesized 1, 3-dimethyl polyphenylene vinylene polymer was used for thin film preparation by spin coating. Characterization of the polymer was carried out using infrared spectroscopy and thermogravimetric analysis. Thin films of the polymer were produced by spin coating at various speeds. Ultraviolet-visible spectroscopy and surface plasmon resonance were performed in order to control the reproducibility of spin coated films. The thicknesses of thin films were evaluated by surface plasmon resonance fitting and were dependent upon the spin speed between 4.5 and 24.5 nm.

Polymer thin films were exposed to different concentrations of benzene, toluene, hexane, dichloromethane, chloroform, butanol, and ethanol. The response of sensor material was monitored by surface plasmon resonance as the optical changes. Polymer thin films were found to be sensitive to dichloromethane vapor in the presence of other VOCs. The response was dependent upon the concentration of exposed vapor. The results showed that the physical characteristics influence the interaction with the thin film. The molecular size influences the

interlayer diffusion and penetration. Small molecules easily diffuse into thin film and provide a rapid response.

The viscosity, vapor pressure, and polarity also influence the response. The low viscosity and high vapor pressure of dichloromethane produce a rapid strong response. Butanol has a higher viscosity and lower vapor pressure that reduces diffusion into the thin film. The thickness of thin film also influences the sensor response. Increasing film thickness provides more cavities for the vapor and increases the response. The interaction between the thin film and vapor increased with the film thickness and caused swelling of the thin film. Exposure to dichloromethane for the 3000 rpm spin coated film increased the thickness by 2.3 nm. The synthesized 1, 3-dimethyl polyphenylene vinylene is sensitive and selective for dichloromethane.

References

Acikbas, Y., R. Capan, M. Erdogan, L. Bulut, and C. Soykan. 2017. Optical characterization and swelling behaviour of Langmuir–Blodgett thin films of a novelpoly[(Styrene (ST)-co-Glycidyl Methacrylate (GMA)]. *Sensors and Actuators B: Chemical* 241:1111–20. doi:10.1016/j.snb.2016.10.025

Acikbas, Y., R. Capan, M. Erdogan, N. Cankaya, and C. Soykan. 2016. Characterization of N-cyclohexylmethacrylamide LB thin films for room temperature vapor sensor application. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 53:132–39. doi:10.1080/10601325.2016.1132907

Alidagi, H. A., F. Hacıvelioglu, S. O. Tümay, B. Çosut, and S. Yesilot. 2017. Synthesis and spectral properties of fluorene substituted cyclic and polymeric phosphazenes. *Inorganica Chimica Acta* 457:95–102. doi:10.1016/j.ica.2016.12.013

Badr, I. H. A., and M. E. Meyerhoff. 2005. Highly selective optical fluoride ion sensor with submicromolar detection limit based on Aluminum(III) octaethylporphyrin in thin polymeric film. *Journal of the American Chemical Society* 127:5318–19. doi:10.1021/ja0500153

Bakoz, P. Y. 2015. Chloromethylation of meta xylene by phase transfer catalysis. *IOSR Journal of Applied Chemistry* 8:31–46. doi:10.9790/5736-08313946

Berger, D., A. P. de Moura, L. H. Oliveira, W. B. Bastos, F. A. La Porta, I. L. V. Rosa, M. S. Li, S. M. Tebcherani, E. Longo, and J. A. Varela. 2016. Improved photoluminescence emission and gas sensor properties of ZnO thin films. *Ceramics International* 42:13555–61. doi:10.1016/j.ceramint.2016.05.148

Cao, J., J. Liu, W. Deng, R. Li, and N. Jin. 2013. A novel self-assembly with zinc porphyrin coordination polymer forenhanced photocurrent conversion in supramolecular solar cells. *Electrochimica Acta* 112:515–21. doi:10.1016/j.electacta.2013.08.131

Capan, I., C. Tarımcı, and R. Capan. 2010. Fabrication of Langmuir–Blodgett thin films of porphyrins and investigation on their gas sensing properties. *Sensors and Actuators B: Chemical* 144:126–30. doi:10.1016/j.snb.2009.10.046

Chou, Y. N., F. Sun, H. C. Hung, P. Jain, A. Sinclair, P. Zhang, T. Bai, Y. Chang, T. C. Wen, Q. Yu, and S. Jiang. 2016. Ultra-low fouling and high antibody loading zwitterionic hydrogel coatings for sensing and detection in complex media. *Acta Biomaterialia* 40:31–37. doi:10.1016/j.actbio.2016.04.023

Chtouki, T., Y. El Kouari, B. Kulyk, A. Louardi, A. Rmili, H. Erguig, B. Elidrissi, L. Soumahoro, and B. Sahraoui. 2017. Spin-coated nickel doped cadmium sulfide thin films for third harmonic generation applications. *Journal of Alloys and Compounds* 696:1292–97. doi:10.1016/j.jallcom.2016.12.089

Daneshkhah, A., S. Shrestha, M. Agarwal, and K. Varahramyan. 2015. Poly(vinylidene fluoride-hexafluoropropylene) composite sensors for volatile organic compounds detection in breath. *Sensors and Actuators B: Chemical* 221:635–43. doi:10.1016/j.snb.2015.06.145

Dubbe, A. 2003. Fundamentals of solid state ionic micro gas sensors. *Sensors and Actuators B: Chemical* 88:138–48. doi:10.1016/S0925-4005(02)00317-9

Evyapan, M., R. Capan, M. Erdogan, H. Sarı, T. Uzunoglu, and H. Namlı. 2013. Electrical conductivity properties of boron containing Langmuir–Blodgett thin films. *Journal of Materials Science: Materials in Electronics* 24:3403–11. doi:10.1007/s10854-013-1262-7

Evyapan, M., and A. D. F. Dunbar. 2015. Improving the selectivity of a free base tetraphenylporphyrin based gas sensor for NO2 and carboxylic acid vapors. *Sensors and Actuators B: Chemical* 206:74–83. doi:10.1016/j.snb.2014.09.023

Evyapan, M., and A. D. F. Dunbar. 2016. Controlling surface adsorption to enhance the selectivity of porphyrin based gas sensors. *Applied Surface Science* 362:191–201. doi:10.1016/j.apsusc.2015.11.210

Evyapan, M., B. Kadem, T. V. Basova, I. V. Yushina, and A. K. Hassan. 2016. Study of the sensor response of spun metal phthalocyanine films to volatile organic vapors using surface plasmon resonance. *Sensors and Actuators B: Chemical* 236:605–13. doi:10.1016/j.snb.2016.05.070

Ganapathi, J. I., D. M. Kalyon, and F. T. Fisher. 2017. Effect of multistage sonication on dispersive mixing of polymer nanocomposites characterized via shear-induced crystallization behavior. *Journal of Applied Polymer Science* 134:44681. doi:10.1002/app.44681

Hoflund, G. B., R. I. Gonzalez, and S. H. Phillips. 2001. In situ oxygen atom erosion study of a polyhedral oligomeric silsesquioxane-polyurethane copolymer. *Journal of Adhesion Science and Technology* 15:1199–211. doi:10.1163/156856101317048707

Hu, Y. L., M. Lu, X. B. Liu, S. B. Zhang, Z. H. Ji, and T. T. Lu. 2010. An inexpensive and efficient synthetic method for the preparation of pyromellitic dianhydride promoted by ionic liquid. *Arkivoc* 9:63–74. doi:10.3998/ark.5550190.0011.907

Huang, Y., G. T. Paloczi, A. Yariv, C. Zhang, and L. R. Dalton. 2004. Fabrication and replication of polymer integrated optical devices using electron-beam lithography and soft lithography. *Journal of Physical Chemistry B* 108:8606–13. doi:10.1021/jp049724d

Hyodo, T., C. Ishibashi, K. Matsuo, K. Kaneyasu, H. Yanagi, and Y. Shimizu. 2012. CO and CO2 sensing properties of electrochemical gas sensors using an anion-conducting polymer as an electrolyte. *Electrochimica Acta* 82:19–25. doi:10.1016/j.electacta.2012.03.142

Inyawilert, K., A. Wisitsoraat, A. Tuantranont, S. Phanichphant, and C. Liewhiran. 2017. Ultra-sensitive and highly selective H2sensors based on FSP-madeRh-substituted SnO2sensing films. *Sensors and Actuators B: Chemical* 240:1141–52. doi:10.1016/j.snb.2016.09.094

Jacob, A. A., L. Balakrishnan, S. R. Meher, K. Shambavi, and Z. C. Alex. 2017. Structural, optical and photodetection characteristics of Cd alloyed ZnO thin film by spin coating. *Journal of Alloys and Compounds* 695:3753–59. doi:10.1016/j.jallcom.2016.11.265

Khavar, A. H. C., A. Mahjoub, F. S. Samghabadi, and N. Taghavinia. 2017. Fabrication of selenization-free superstrate-type CuInS2 solar cells based on all-spin-coated layers. *Materials Chemistry and Physics* 186:446–55. doi:10.1016/j.matchemphys.2016.11.017

Kim, J. P., W. Y. Lee, J. W. Kang, S. K. Kwon, J. J. Kim, and J. S. Lee. 2001. Fluorinated Poly(arylene ether sulfide) for polymeric optical waveguide devices. *Macromolecules* 34:7817–21. doi:10.1021/ma010439r

Konry, T., Y. Heyman, S. Cosnier, K. Gorgy, and R. S. Marks. 2008. Characterization of thin poly(pyrrole-benzophenone) film morphologies electropolymerized on indium tin oxide coated optic fibers for electrochemical and optical biosensing. *Electrochimica Acta* 53:5128–35. doi:10.1016/j.electacta.2008.02.022

Korczyc, A. B., A. Reszka, K. Sobczak, T. Wojciechowski, and K. Fronc. 2017. The synthesis, characterization and ZnS surface passivation of polycrystalline ZnO films obtained by the spin-coating method. *Journal of Alloys and Compounds* 695:1196–204. doi:10.1016/j.jallcom.2016.08.334

Kretschmann, E., and H. Raether. 1968. Radiative decay of non radiative surface plasmons excited by light. *Zeitschrift für Naturforschung* 23a:2135–36.

Li, M., J. Zhang, J. Xin, K. Huang, S. Li, M. Wang, and J. Xia. 2017. Design of green zinc-based thermal stabilizers derived from tung oil fatty acid and study of thermal stabilization for PVC. *Journal of Applied Polymer Science* 134:44679. doi:10.1002/app.44679

Lynch, I., P. Gregorio, and K. A. Dawson. 2005. Simultaneous release of hydrophobic and cationic solutes from thin-film "Plum-Pudding" gels: a multifunctional platform for surface drug delivery? *The Journal of Physical Chemistry B* 109:6257–61. doi:10.1021/jp0502149

Matsui, J., M. Mitsuishi, A. Aoki, and T. Miyashita. 2004. Molecular optical gating devices based on polymer nanosheets assemblies. *Journal of the American Chemical Society* 126:3708–09. doi:10.1021/ja039871+

Nabok, A. V., A. K. Hassan, A. K. Ray, O. Omar, and V. I. Kalchenko. 1997. Study of adsorption of some organic molecules in calix[4]resorcinolarene LB films by surface plasmon resonance. *Sensors and Actuators B: Chemical* 45:115–21. doi:10.1016/S0925-4005(97)00282-7

Nabok, A. V., A. K. Hassan, and A. K. Ray. 1999. Optical and electrical characterisation of polyelectrolyte self-assembled thin films. *Materials Science and Engineering C* 8–9:505–08. doi:10.1016/S0928-4931(99)00009-0

Öztürk, S., A. Kösemen, Z. Sen, N. Kılınç, and M. Harbeck. 2016. Poly(3-Methylthiophene) thin films deposited electrochemically on QCMs for the sensing of volatile organic compounds. *Sensors* 16:423–33. doi:10.3390/s16040423

Park, T., N. Mirin, J. B. Lassiter, C. L. Nehl, N. J. Halas, and P. Nordlander. 2008. Optical properties of a nanosized hole in a thin metallic film. *ACS Nano* 2:25–32. doi:10.1021/nn700292y

Patil, U. V., N. S. Ramgir, N. Karmakar, A. Bhogale, A. K. Debnath, D. K. Aswal, S. K. Gupta, and D. C. Kothari. 2015. Room temperature ammonia sensor based on copper nanoparticle intercalated polyaniline nanocomposite thin films. *Applied Surface Science* 339:69–74. doi:10.1016/j.apsusc.2015.02.164

Ray, A. K., O. Omar, C. S. Bradley, N. A. Bell, D. J. Simmonds, C. S. Thorpe, and R. A. Broughton. 2000. Langmuir–Blodgett film forming properties of substituted TCNQ molecules. *Vacuum* 57:253–58. doi:10.1016/S0042-207X(00)00119-6

Rella, R., J. Spadavecchia, G. Ciccarella, P. Siciliano, G. Vasapollo, and L. Valli. 2003. Optochemical vapour detection using spin coated thin films of metal substituted phthalocyanines. *Sensors and Actuators B: Chemical* 89:86–91. doi:10.1016/S0925-4005(02)00447-1

Robert, G. G. 1985. An applied science perspective of Langmuir-Blodgett films. *Advances in Physics* 34:475–512. doi:10.1080/00018738500101801

Sokuler, M., and L. A. Gheber. 2006. Nano fountain pen manufacture of polymer lenses for nano-biochip applications. *Nano Letters* 6:848–53. doi:10.1021/nl060323e

Spadavecchia, J., G. Ciccarella, P. Siciliano, S. Capone, and R. Rella. 2004. Spin-coated thin films of metal porphyrin–phthalocyanine blend for an optochemical sensor of alcohol vapors. *Sensors and Actuators B: Chemical* 100:88–93. doi:10.1016/j.snb.2003.12.027

Spadavecchia, J., G. Ciccarella, L. Valli, and R. Rella. 2006. A novel multisensing optical approach based on a single phthalocyanine thin films to monitoring volatile organic compounds. *Sensors and Actuators B: Chemical* 113:516–25. doi:10.1016/j.snb.2005.03.110

Subr, V., C. Konak, R. Laga, and K. Ulbrich. 2006. Coating of DNA/Poly(l-lysine) complexes by covalent attachment of Poly[N-(2-hydroxypropyl)methacrylamide]. *Biomacromolecule* 7:122–30. doi:10.1021/bm050524x

Wisser, F. M., J. Grothe, and S. Kaskel. 2016. Nanoporous polymers as highly sensitive functional material in chemiresistive gas sensors. *Sensors and Actuators B: Chemical* 223:166–71. doi:10.1016/j.snb.2015.09.074

Zhang, J., M. Luo, H. Xiao, and J. Dong. 2006. interferometric study on the adsorption-dependent refractive index of silicalite thin films grown on optical fibers. *Chemistry of Materials* 18:4–6. doi:10.1021/cm0525353

Table 1. Surface plasmon resonance parameters of the 1,3-dimethyl polyphenylene vinylene spin coated films as a function of spin speed.

Parameter	1000 (rpm)	2000 (rpm)	3000 (rpm)	4000 (rpm)	5000 (rpm)
Angle shift ($\Delta\theta°$)	2.5	2.1	1.5	1.4	1.2
Change of full width of half max ($\theta°$)	2.3	1.5	0.8	0.7	0.8
Thickness, d (nm)	24.5	22.4	7.7	6.6	4.5

Figure 1. Schematic diagram of the Kretschmann (1968) configuration for surface plasmon resonance using a semi-cylindrical prism (refractive index of 1.515) and a He-Ne laser (632.8 nm).
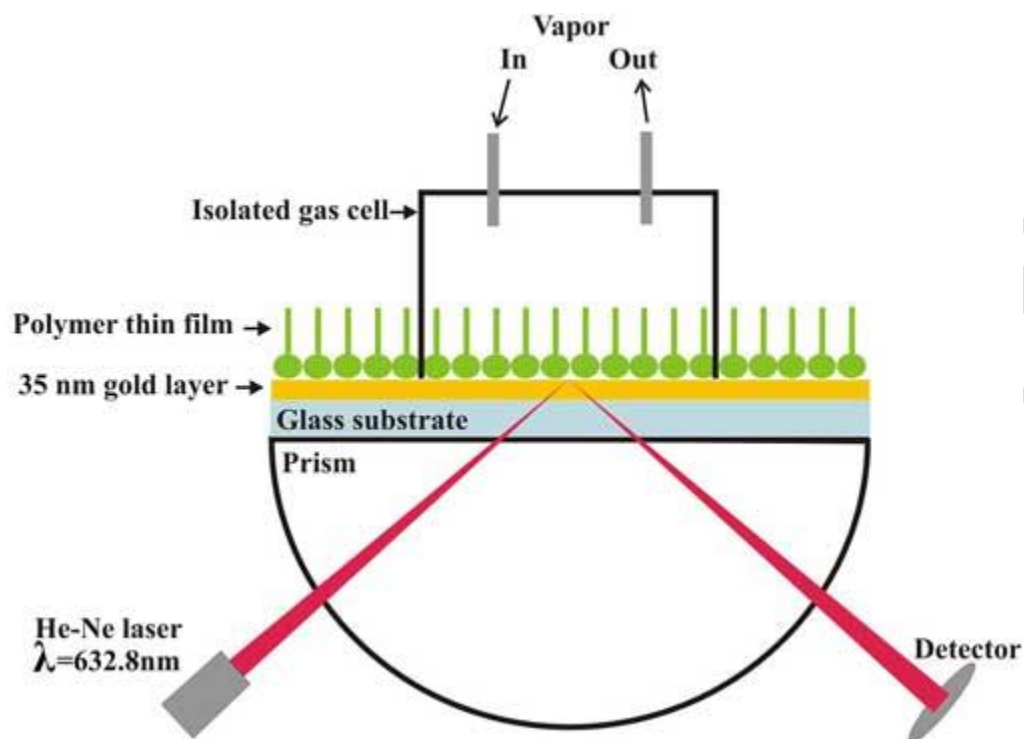
Figure 2. Synthesis of 1, 3-dimethyl polyphenylene vinylene.
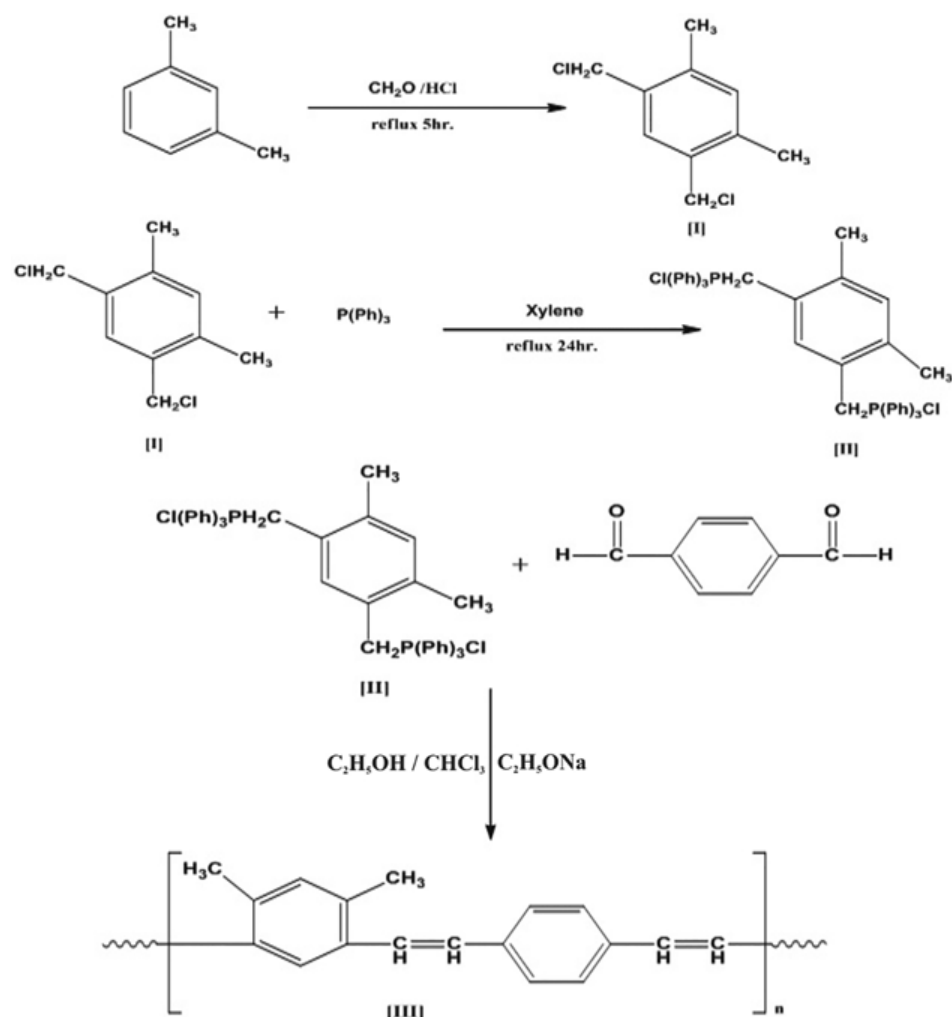
Figure 3. Infrared spectrum of compound (I).
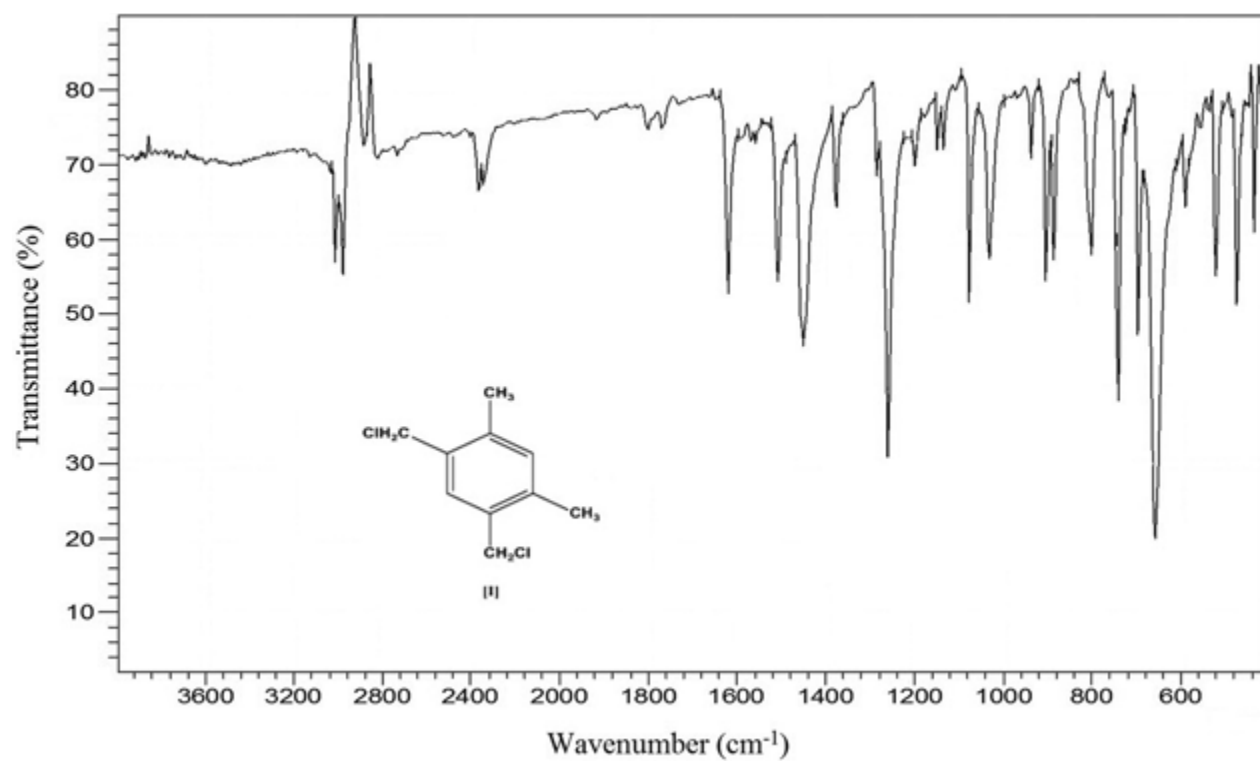
Figure 4. Infrared spectrum of compound (II).
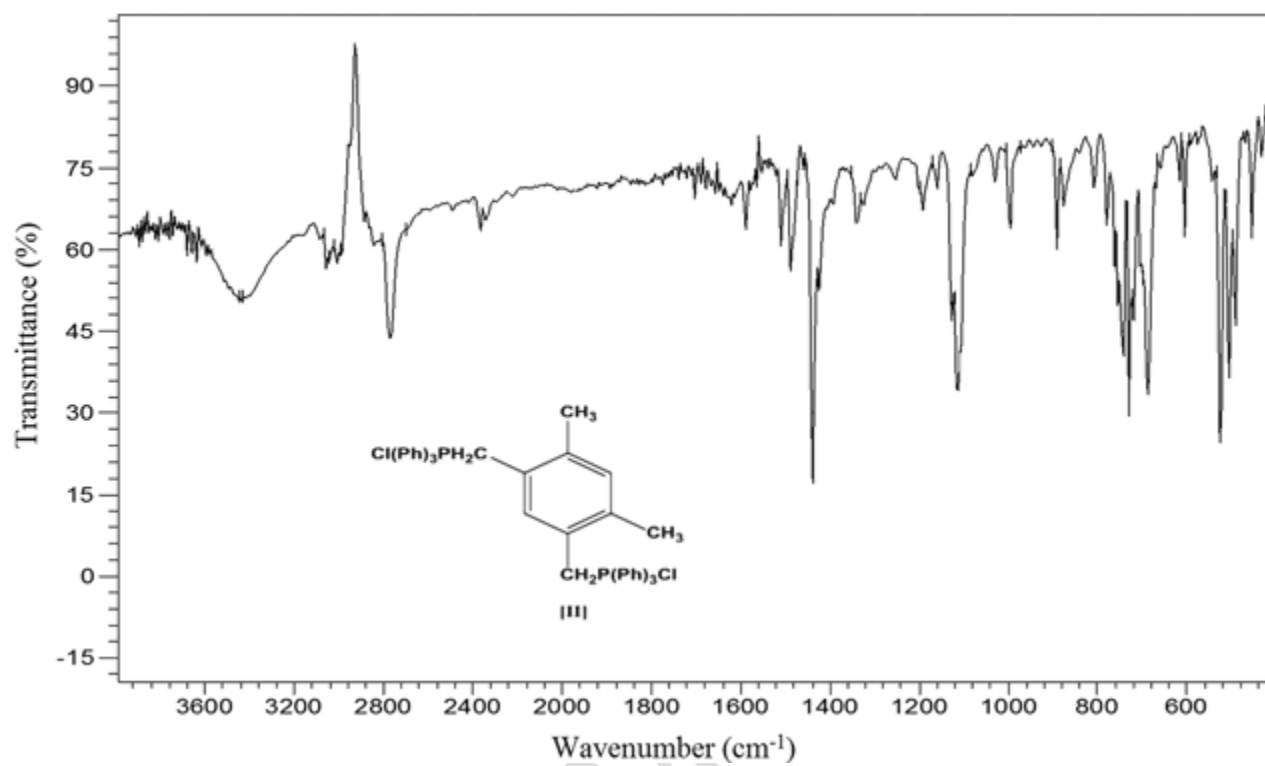
Figure 5. Infrared spectrum of infrared spectroscopy result of the 1, 3-dimethyl polyphenylene vinylene polymer.
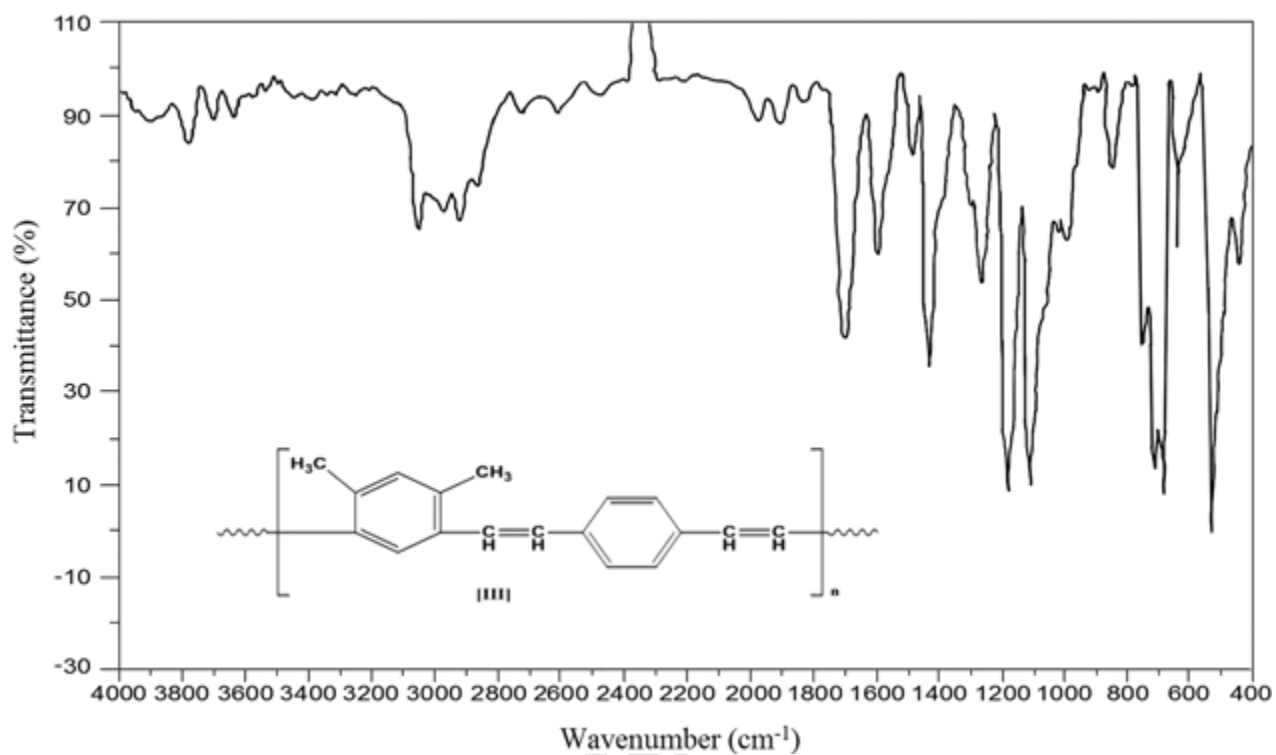
Figure 6. Thermogravimetric analysis of 5.08 mg of 1,3-dimethyl polyphenylene vinylene polymer from 35°C to 700°C: (a) thermogram and (b) derivative of the thermogram.
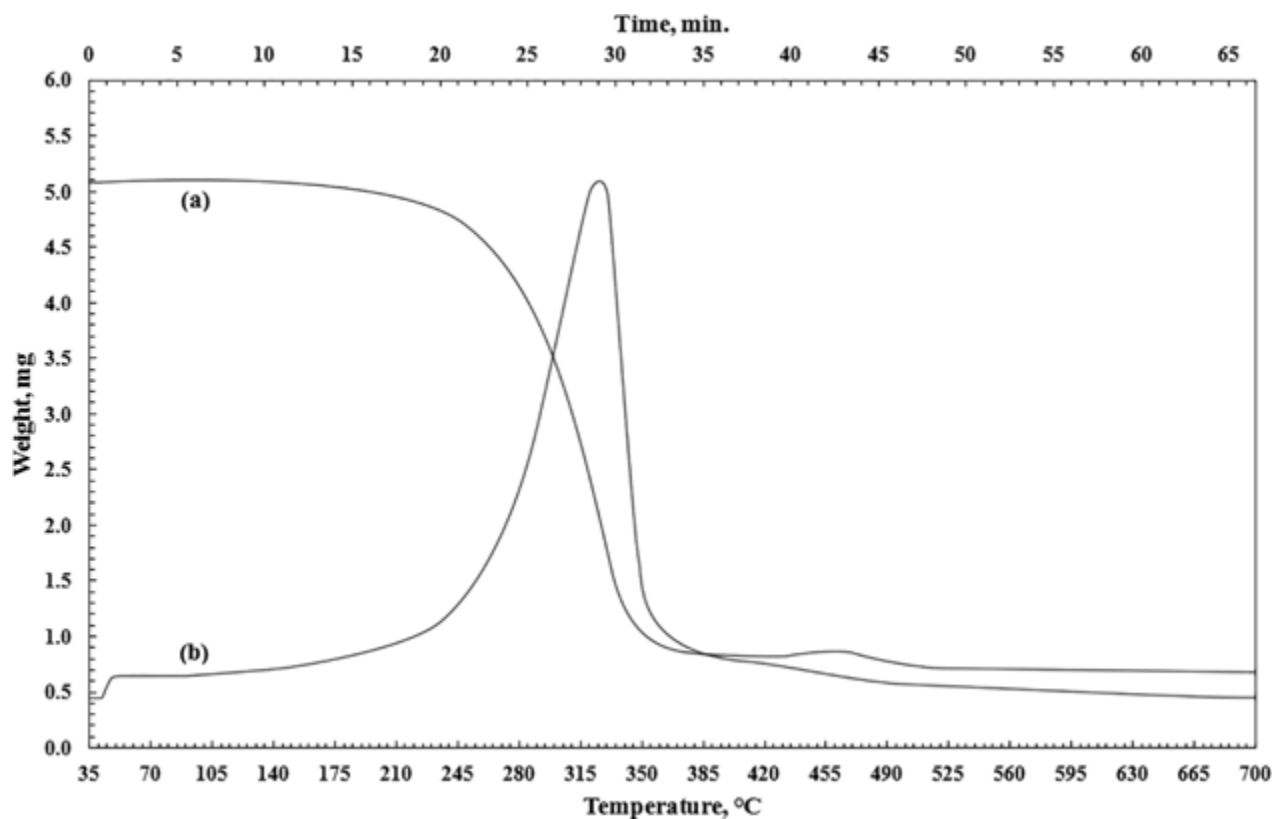
Figure 7. Ultraviolet-visible absorption spectra of the 1,3-dimethyl polyphenylene vinylene: (a) in chloroform, (b) 1000 rpm spin coated film, (c) 2000 rpm spin coated film, (d) 3000 rpm spin coated film, (e) 4000 rpm spin coated film, (f) 5000 rpm spin coated film, and (g) absorbance change as a function of speed.
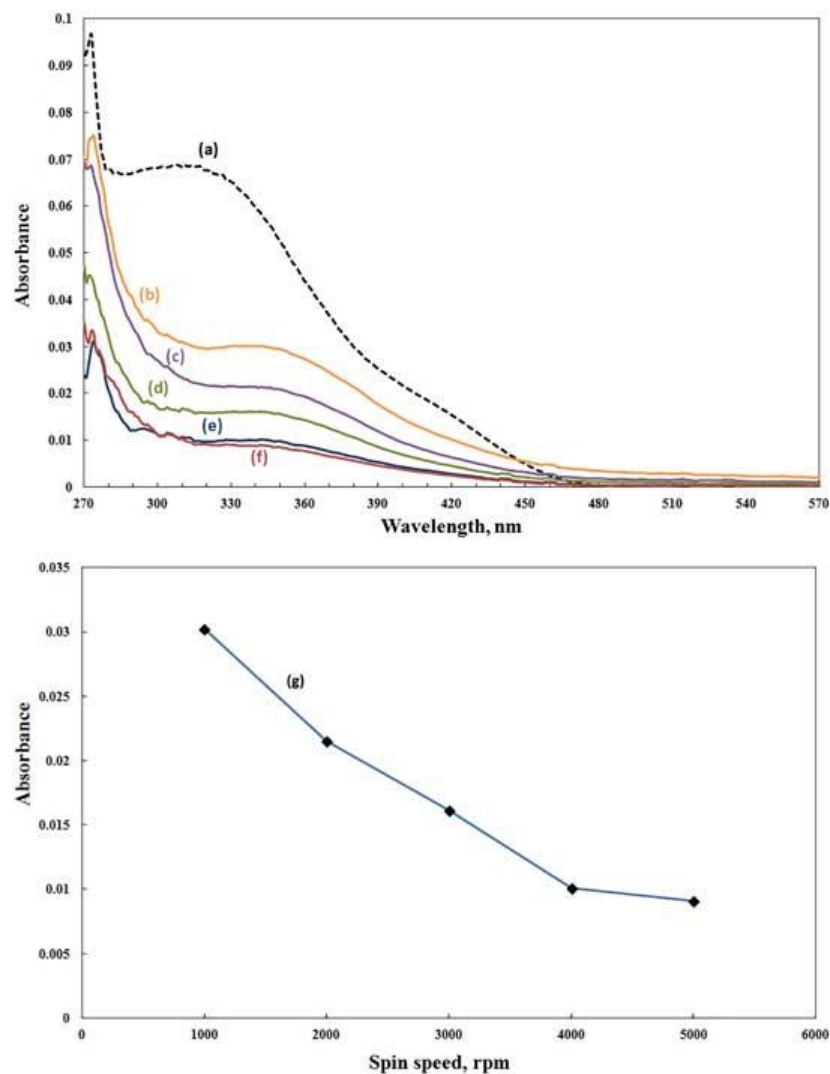
Figure 8. Surface plasmon resonance curves of 1, 3-dimethyl polyphenylene vinylene spin coated films: (a) bare gold, (b) 5000 rpm, (c) 4000 rpm, (d) 3000 rpm, (e) 2000 rpm, and (f) 1000 rpm.
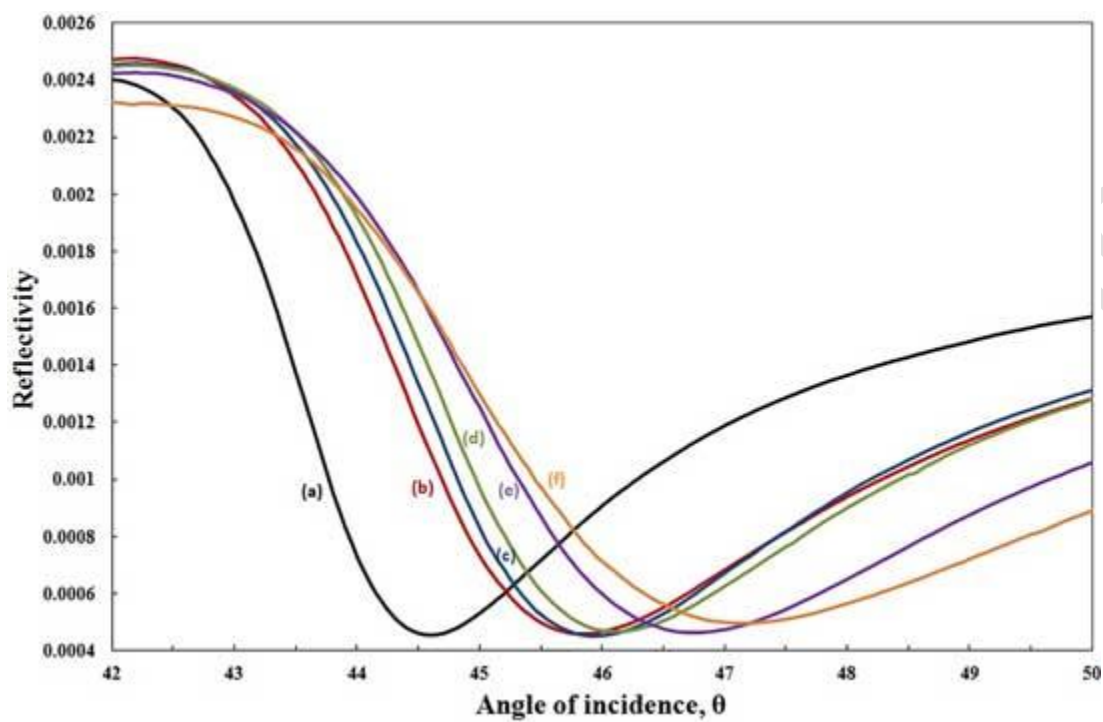
Figure 9. Kinetic response of the 3000 rpm spin coated film of the 1, 3-dimethyl polyphenylene vinylene to the presence of: (a) butanol, (b) toluene, (c) hexane, (d) benzene, (e) ethanol, (f) chloroform, and (g) dichlorormethane.
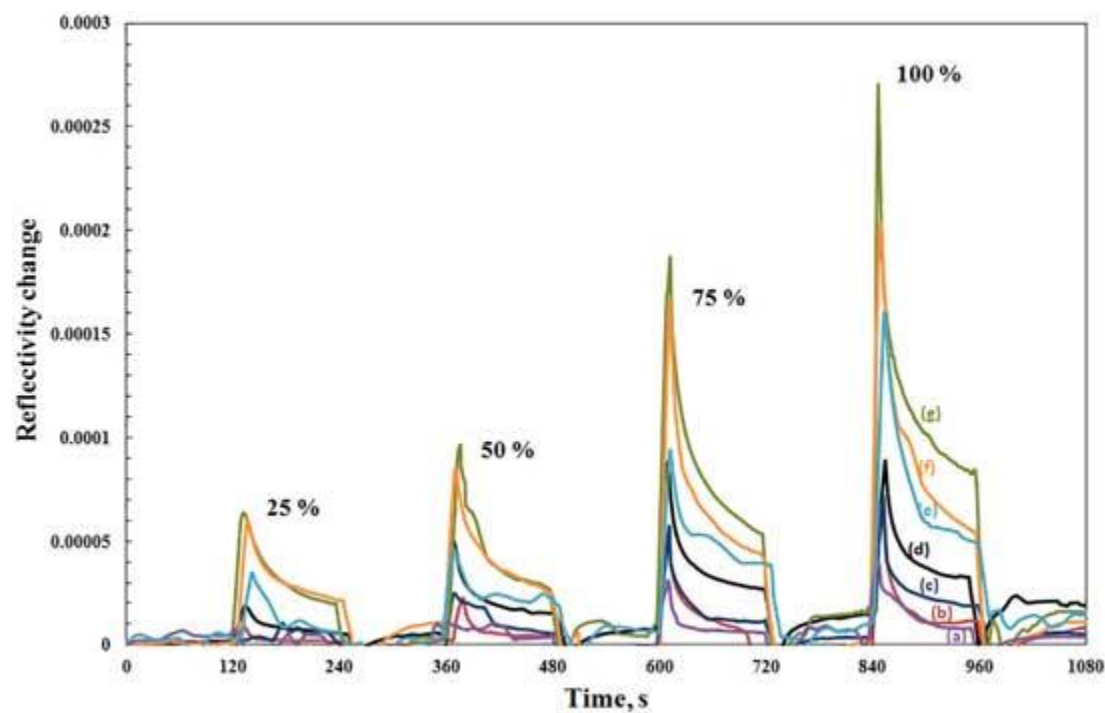
Figure 10. Maximum sensor response for 25, 50, 75, and 100% of volatile organic compounds.
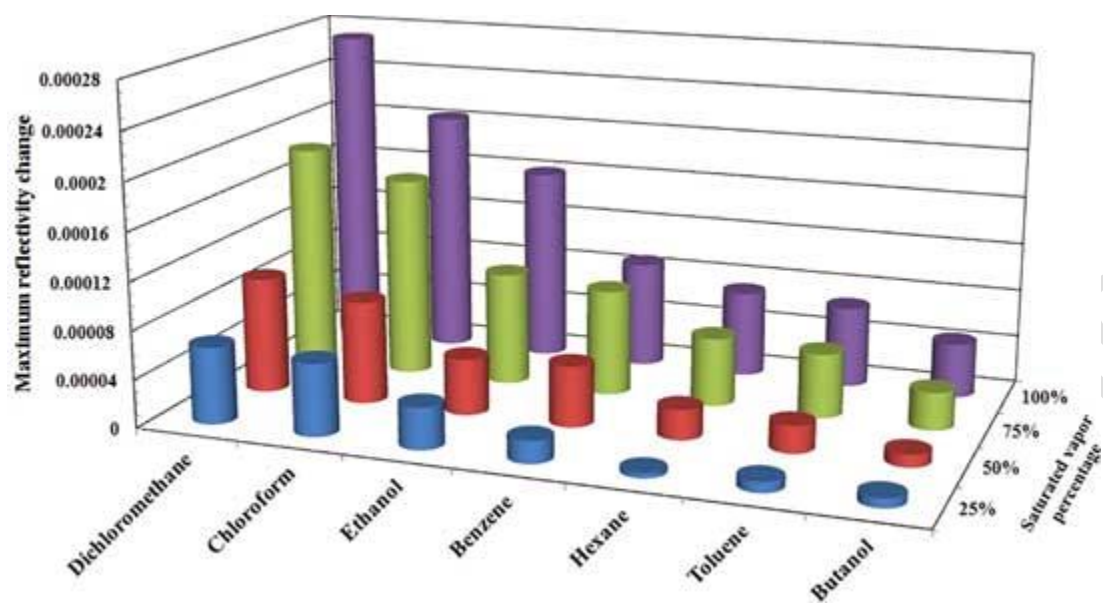
Figure 11. Kinetic response of the 1, 3-dimethyl polyphenylene vinylene spin coated films to saturated dichloromethane: (a) 1000 rpm, (b) 2000 rpm, (c) 3000 rpm, (d) 4000 rpm, and (e) 5000 rpm.
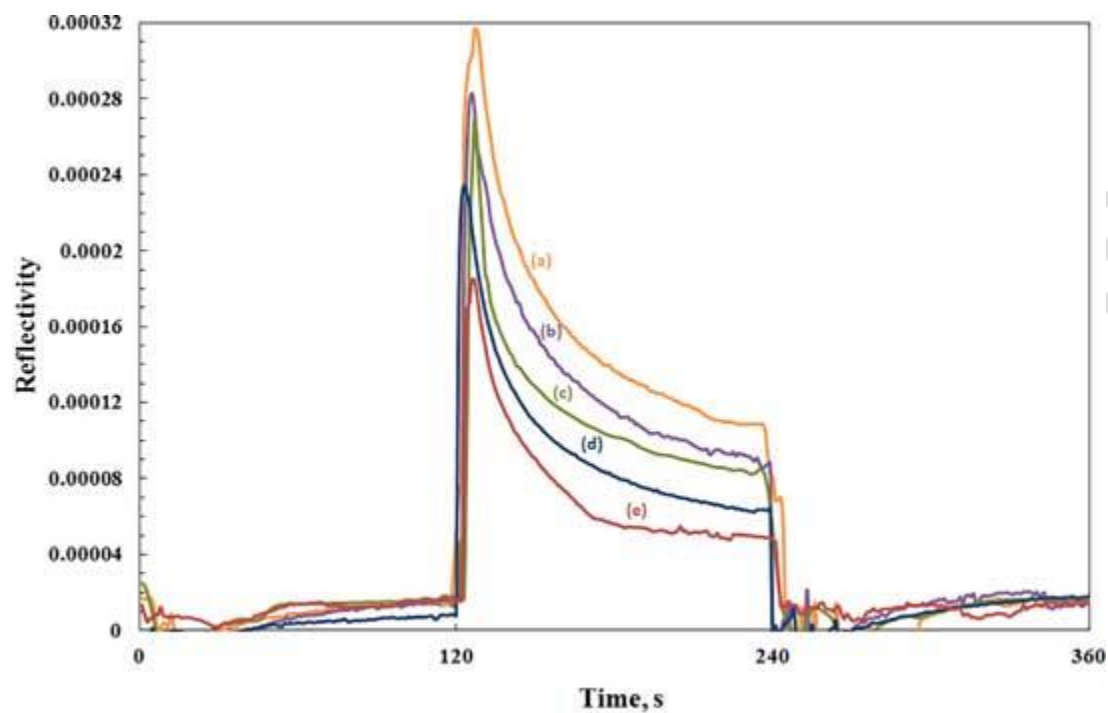
Figure 12. Surface plasmon resonance of the 3000 rpm spin coated film of the 1,3-dimethyl polyphenylene vinylene: (a) in air, (b) after exposure to saturated dickloromethane, and (c) following recovery in dry air.