

Synthesis, Characterization and Electrical Conductivity of Poly(p-phenylene vinylene)

Ali ÇIRPAN, Zuhâl KÜÇÜKYAVUZ*, Savaş KÜÇÜKYAVUZ
*Department of Chemistry, Middle East Technical University,
06531 Ankara-TURKEY
e-mail: zuhal@metu.edu.tr*

Received 24.09.2002

Poly(p-phenylene vinylene) (PPV) was prepared electrochemically from p-xylene-bis(diethylsulphonium chloride) in a solvent-electrolyte couple of acetonitrile-tetrabutylammonium tetrafluoroborate (TBAFB). The polymer obtained from the electrode surface was converted to PPV by the thermal elimination of diethyl sulfide, HCl and ethyl sulfide. PPV was also obtained chemically in order to investigate the effect of the synthetic method on the structure and electrical conductivity. The characterization of the polymers was carried out by means of fourier transform infrared spectrometer (FTIR), differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) techniques. The doping effect on the conductivity of the PPV was investigated by using different agents such as H₂SO₄, I₂ and metallic Na.

It was concluded from the results of spectroscopical investigations that trans-vinylene units are formed on the backbones of polymers obtained by both chemical and electrochemical methods. Thermal analysis data confirmed that the thermal elimination of diethyl sulfide from the polymers obtained by electrochemical and chemical methods are almost complete, and therefore, the resultant product is PPV. It was evident from the TGA results that the polymer obtained chemically had a thermal stability higher than the electrochemically prepared polymer.

Although the polymers obtained were insoluble and insulating, they were successfully converted into conducting polymers with the maximum conductivity of 10⁻³ S/cm by doping in solution or in vapor.

Key Words: Conducting Polymers; Poly(p-phenylene vinylene); Electrochemical Polymerization; Doping; Electrical Conductivity.

Introduction

Poly(p-phenylene vinylene) (PPV) is a conjugated polymer, which becomes conductive by the addition of electron donors or acceptors^{1,2}. Several methods have been reported for the synthesis of PPV³⁻⁵. Direct chemical polymerization, which was the first attempt of synthesizing PPV, gave a product in the form of an insoluble powder that limited the use of the polymer in many applications³. The most popular method for the preparation of PPV is base-induced polymerization of sulfonium salt monomer in aqueous solution^{2,4,5}. In this method, PPV films are obtained from the precursor polymer after thermal elimination of the sulfonium groups. PPV has also been prepared electrochemically by reducing p-xylene-bis-(triphenylphosphonium

*Corresponding author

bromide) in acetonitrile using ITO as a working electrode at the cathode and platinum plate at the anode at a constant voltage of 5.5 V ⁶. Damlin *et al.*⁷ prepared PPV through electrochemical reduction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-p-xylene. They cycled the potential between 1.3 and -2.3 V during electrolysis.

In the present study we synthesized PPV by using p-xylene-bis- (diethylsulfonium chloride) (PXBDC) in an acetonitrile-terabutylammonium tetrafluoroborate(TBAFB) solvent-electrolyte pair at a constant potential of -2.5 V by electrochemical polymerization. Moreover, the synthesis of PPV was also achieved by the chemical polymerization method to compare to the PPV prepared electrochemically.

Experimental

α,α' -dichloro-p-xylene, diethyl sulfide, methanol and TBAFB were purchased from the Merck Company. All chemicals were used without further purification. Synthesis of the monomer, PXBDC, was achieved by reacting α,α' -dichloro-p-xylene at a concentration of 0.75 M with excess diethyl sulfide at 50°C in a methanol: water (80:20) solution for 24 h ². This monomer was purified by concentrating the reaction solution and precipitating the product in cold acetone (0°C), filtration and vacuum drying.

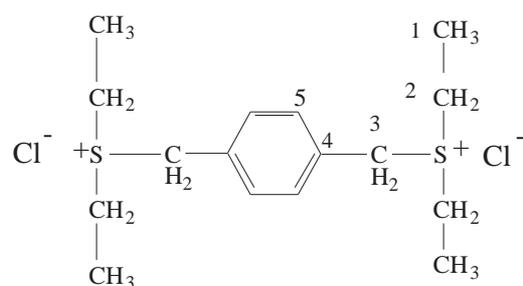
Chemical synthesis of PPV was carried out according to the procedure described by Gagnon *et al.*². Chemically polymerized PPV film was heated under vacuum at specified temperature at 180°C and 245°C for 6 h.

Cyclic voltammetry (CV) measurements were carried out under N₂ atmosphere in acetonitrile at room temperature, and 0.1 M TBAFB was used as the supporting electrolyte. The solution for the electropolymerization was obtained by dissolving 1.066 g PXBDC in 30-mL acetonitrile. Platinum plates (1.5 cm²) were employed as the working (WE) and counter electrodes (CE). A saturated calomel electrode (SCE) was used as the reference electrode (RE). The electropolymerization reaction was carried out at constant potential (+2.5 V) at room temperature.

For the characterization of the samples, a fourier transform infrared spectrometer (FTIR) (Nicolet DX 510 FTIR using KBr pellet at room temperature), differential scanning calorimetry (DSC) (910 S/TA 2000), thermal gravimetry analysis (TGA) (V.4.OD Dupont) and a ¹H and ¹³C nuclear magnetic resonance spectrometer (Bruker Instrument NMR Spectrometer DPX-400) were used. The conductivity of the samples was measured on pellets or powder by using the two probe method.

Results and Discussion

Characterization of monomer



p-xylene-bis(diethylsulphonium chloride) monomer

The characterization of the PXBDC monomer was achieved by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. $^1\text{H-NMR}$ (400 MHz, D_2O); $\delta = 1.34$ (t, 12H), $\delta = 3.20$ (q, 8H), $\delta = 4.59$ (s, 4H), $\delta = 4.72$ (s, D_2O), $\delta = 7.53$ (s, 4H). $^{13}\text{C-NMR}$ (400 MHz, D_2O); $\delta = 15.77$ (CH_3), $\delta = 40.67$ ($^2\text{CH}_2$), $\delta = 49.65$ ($^3\text{CH}_2$), $\delta = 136.939$ (C), $\delta = 139.199$ (CH).

Electrochemical synthesis of PPV

Prior to electrochemical polymerization, the oxidation-reduction behavior of p-xylene-bis(diethylsulphonium chloride), based on CV measurements, was studied. Measurements were carried out in an acetonitrile-TBAFB solvent-electrolyte couple versus SCE at room temperature under N_2 atmosphere. The cyclic voltammogram of the PXBDC monomer shows an irreversible peak at -2.50 V (Figure 1). The PXBDC monomer was polymerized by constant potential electrolysis (CPE) at -2.50 V versus SCE in an acetonitrile-TBAFB solvent-electrolyte pair. The insoluble polymer(II) was peeled off the electrode surface and was heated in a high vacuum oven at 180°C and 245°C for 6 h to obtain PPV(III) as represented in Figure 2.

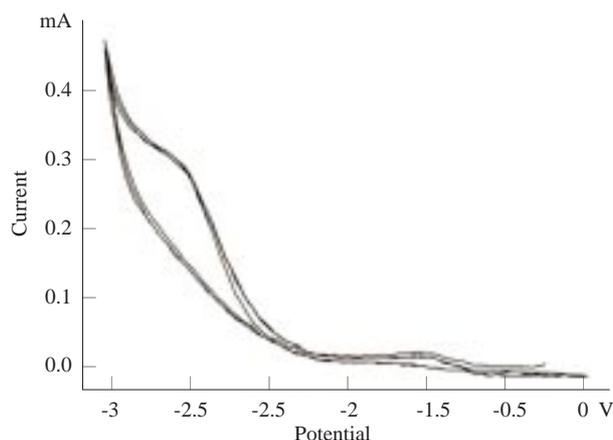


Figure 1. Cyclic voltammogram of PXBDC monomer in acetonitrile-TBAFB at 100 mV/sec at room temperature.

Chemical synthesis of PPV

The p-xylene-bis(diethylsulphonium chloride) monomer(I) was polymerized in an aqueous solution to obtain a poly(p-xylene- α -diethylsulphonium chloride) precursor polymer(II). The precursor polymer was subjected to stationary heat treatment at 180°C and 245°C for 6 h to obtain PPV(III) as represented in Figure 2.

Characterization

FTIR analysis

Figure 3 shows the FTIR spectra of electrochemically synthesized PPV (EPPV) (Figure 3a), electrochemically synthesized PPV heated under vacuum at 180°C for 6 h (EPPV-180) (Figure 3b) and electrochemically synthesized PPV heated under vacuum at 245°C for 6 h (EPPV-245) (Figure 3c). The chemical structure of PPV prepared from the sulfonium route and the electropolymerized PPV were examined by FTIR spectroscopy, as shown in Figures 3, 4. As shown by the FTIR spectrum, partial elimination of diethyl sulfide and HCl occur during the polymerization reaction. The presence of the absorption band near 960 cm^{-1} ,

resulting from C—H out-of-plane bending, is a characteristic of the trans configuration of the vinylene group Figures 3a-4b⁸. The absorption band around 3022 cm⁻¹ was due to the trans vinylene C—H stretching mode. The absorption band around 550 cm⁻¹ was attributed to the phenylene out-of-plane ring-bending. The bands at 830 cm⁻¹ and 1511 cm⁻¹ were assigned to para-phenylene ring C—H out-of-plane bending and C—C ring stretching, respectively. The bands at 2872 and 2960 cm⁻¹ were attributed to the CH₃ symmetric and CH₃ asymmetric deformation (Figures 3, 4). After the heat treatment under vacuum, the intensity of these two bands decreased. The intensity of the absorption band near 3022 cm⁻¹ increased due to the elimination of the diethyl sulfide and HCl. Figure 3 shows the FTIR spectra of the electrochemically produced PPV. The strong absorption band near 1057 cm⁻¹ (Figure 3a) was attributed to the dopant anion of the electrolyte. This band disappeared when the polymer was heated under vacuum at 180°C for 6 h. The substantial completion of the thermal conversion is clear from the absence of bands at 740 cm⁻¹, 1382 cm⁻¹, 1463 cm⁻¹, 2872 cm⁻¹ and 2960 cm⁻¹ that were present in the polymer obtained from the electrode surface. These bands are associated with the CH₃ asymmetric bending, CH₃ symmetric bending, CH₂ rocking, and CH₃ symmetric and CH₃ asymmetric deformation. When the electropolymerized polymer was further heated at 245°C for 6 h, their FTIR spectra were similar to those of the material prepared at 180°C for 6 h. This indicates that the ethyl sulfide and HCl elimination started before 180°C. However, complete conversion was not achieved even at 245°C. The absorption bands at 2872 cm⁻¹ and 2960 cm⁻¹ did not disappear completely (Figure 3c, Figure 4c).

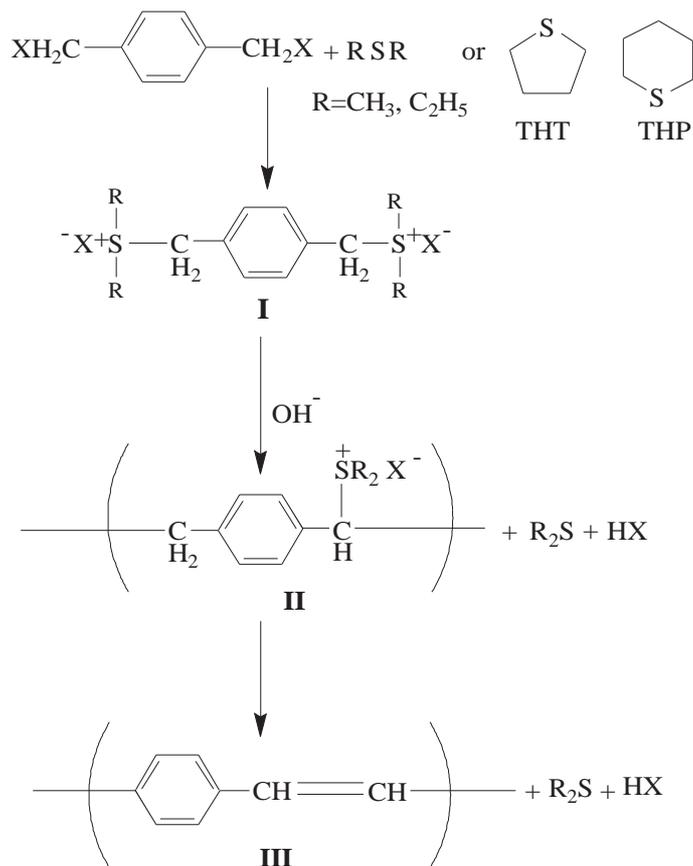


Figure 2. Synthesis and processing scheme of PPV.

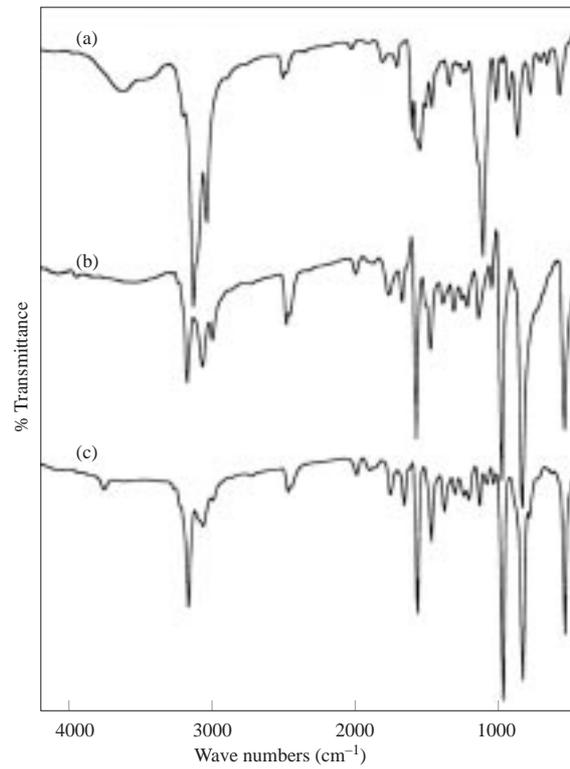


Figure 3. FTIR spectra of (a) the EPPV (b) the EPPV-180 and (c) the EPPV-245 (by using KBr pellet at room temperature).

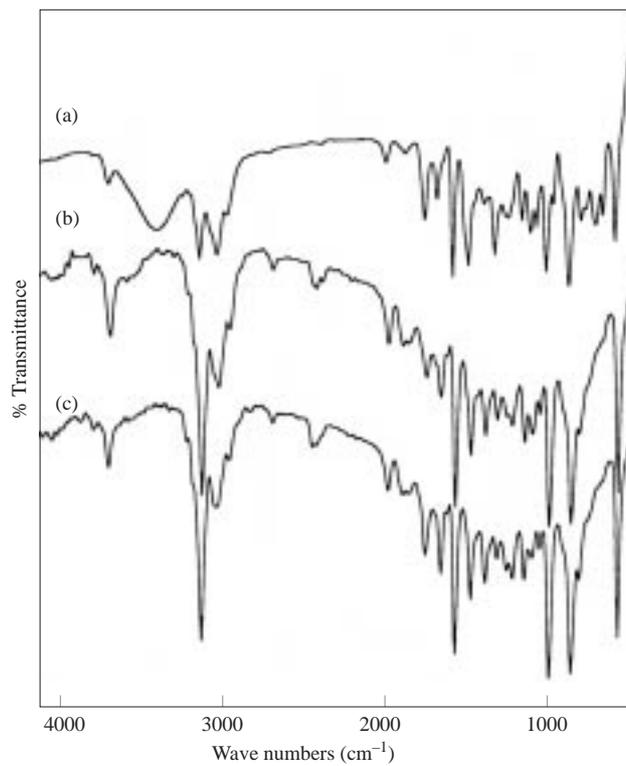


Figure 4. FTIR spectra of (a) the CPPV (b) the CPPV-180 and (c) the CPPV-245 (by using KBr pellet at room temperature).

Thermal analysis

The thermal behavior of the polymers was investigated by using the DSC and TGA techniques. Figures 5-8 show the results for the samples that were electrochemically synthesized PPV (EPPV), electrochemically synthesized PPV heated under vacuum at 245°C for 6 h (EPPV-245), chemically prepared PPV (CPPV) and chemically prepared PPV heated under vacuum at 245°C for 6 h (CPPV-245). There are three transitions for the EPPV at 99°C, 237°C and 315°C (Figure 5). The first one is due to the removal of the solvent from the polymer. The second transition, at 237°C, is related to the elimination reaction, yielding diethyl sulfide and HCl which converts the PPV precursor to PPV⁹. The third transition is attributed to the degradation reaction of the PPV. When the EPPV was heated at 245°C under vacuum for 6 h, it had one transition at 93°C (Figure 6) which is due to the removal of the physically absorbed water. Similarly, the DSC thermogram of CPPV exhibits three transitions at 80°C, 199°C and 383°C (Figure 7). The first is the result of the removal of the solvent or impurities from the polymer. The transition seen at 199°C is related to the elimination of diethyl sulfide and HCl and the final transition is due to the decomposition of the polymer. When the CPPV was subjected to the heat treatment at 245°C, it showed only one transition at 97°C (Figure 8) that was due to the removal of the physically absorbed water. The onset temperature of endothermic transitions fits well with the TGA data. The DSC results show that when the electrochemically and chemically prepared polymers were subjected to stationary heat treatment under vacuum at 245°C for 6 h, they were almost completely converted to PPV. The endothermic transitions which were responsible for the elimination reaction disappeared after the heat treatment.

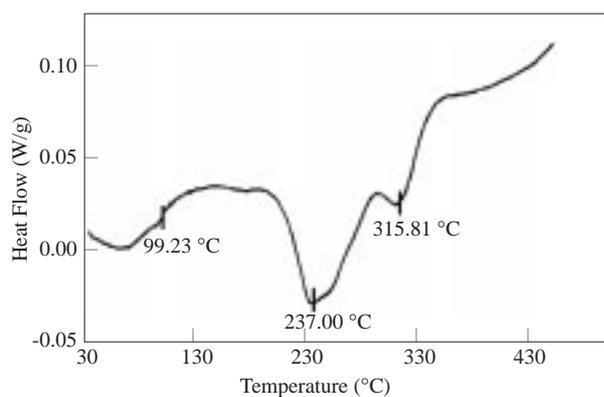


Figure 5. DSC thermogram of the EPPV.

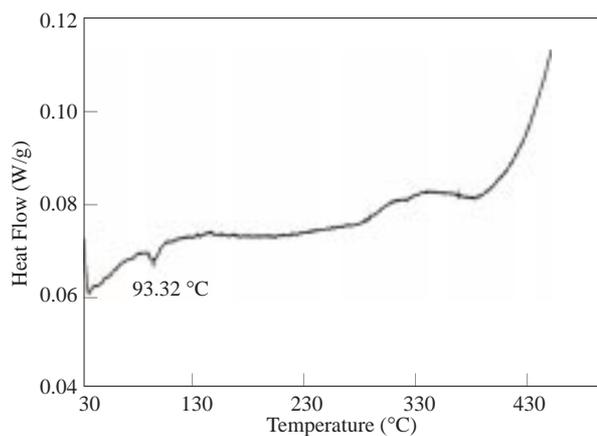


Figure 6. DSC thermogram of the EPPV-245.

The thermal conversion of chemically prepared poly(p-xylene- α -diethylsulphonium chloride) into PPV can occur through two successive reactions¹⁰. The principle reaction is the elimination of diethyl sulfide and HCl, while the second, an undesirable reaction that involves the nucleophilic attack of the halide counter ion on the ethyl group to form ethyl chloride and ethyl sulfide. Figure 9 shows the TGA of the PPV obtained from the electrode surface, and the thermogram for the PPV, exhibits three transitions at 263°C, 388°C and 554°C. The first transition, at 263°C, is related to the thermal elimination of diethyl sulfide and HCl and the second is due to the elimination of ethyl sulfide. The third thermal transition, seen at 554°C, is the result of the degradation reaction of PPV². The same thermal behavior was observed for the polymer film obtained by the chemical method (Figure 11). When the EPPV and CPPV were heated at 245°C

under vacuum for 6 h, only one weight loss was observed (Figures 10, 12). This transition is related to the degradation of the polymer. The TGA results confirmed that organic sulfides and HCl were approximately eliminated and both electrochemically and chemically prepared polymers were almost completely converted to the PPV. The TGA results also showed that chemically synthesized polymer has higher thermal stability, because after the thermal treatment the amount of residue for chemically prepared polymers is higher than that of electrochemically prepared polymers.

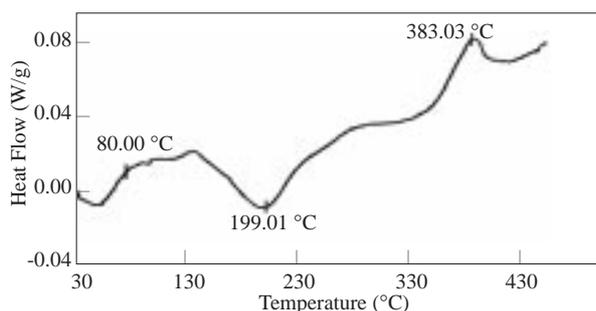


Figure 7. DSC thermogram of the CPPV.

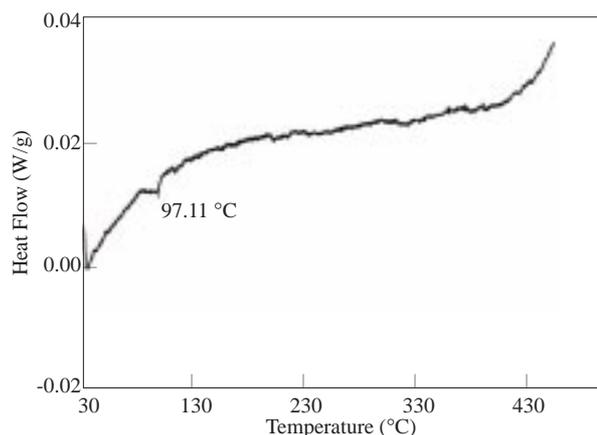


Figure 8. DSC thermogram of the CPPV-245.

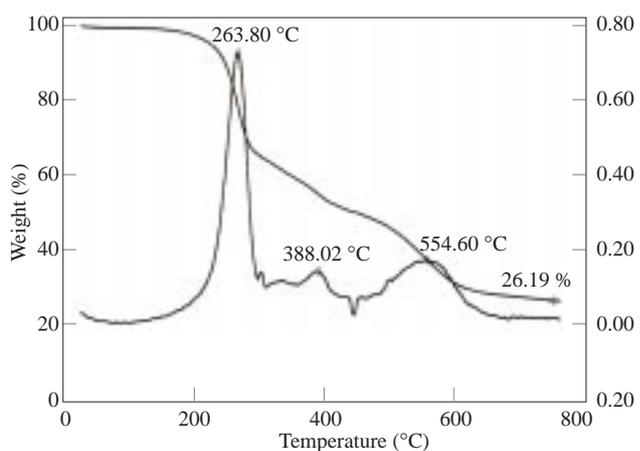


Figure 9. TGA of the EPPV.

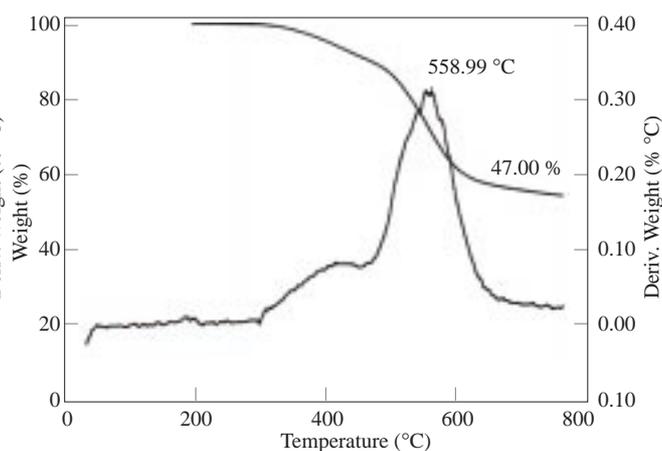


Figure 10. TGA of the EPPV-245.

Electrical conductivity of PPV

PPV belongs to a class of conjugated polymers, that become electrically conductive upon the addition of electron donors and acceptors. The electrical conductivity of EPPV and CPPV was investigated by using a number of doping agents. These H_2SO_4 , I_2 and metallic sodium. The conductivities obtained for each sample are given in Table 1. When the EPPV-245 was doped with H_2SO_4 , I_2 and metallic Na, the increasing conductivity of the polymer was in the same order. On the other hand, the same results were not observed for CPPV-245. Polymer doped with sodium has the highest conductivity, whereas the polymer doped with H_2SO_4 has the lowest. With vapor phase doping, higher conductivity was obtained, which may be due to

the easier diffusion of the dopant into the polymer matrix. The samples showed the maximum conductivity of 10^{-3} S/cm.

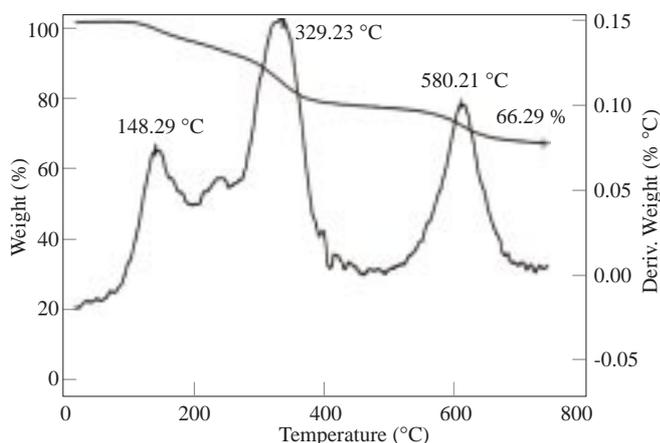


Figure 11. TGA of the CPPV.

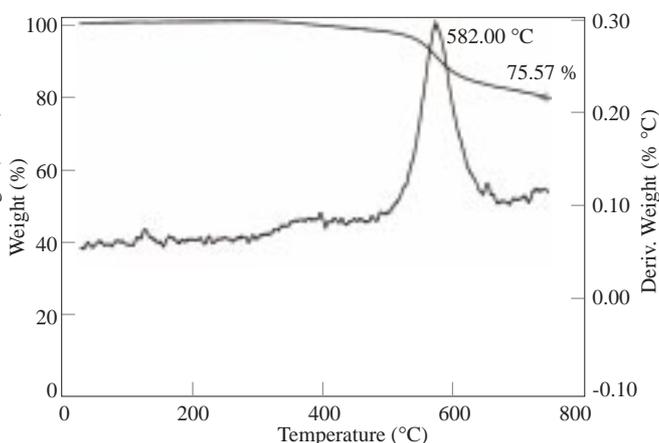


Figure 12. TGA of the CPPV-245.

Table 1. Electrical Conductivity of PPV doped by H_2SO_4 , I_2 and metallic Na.

Samples	Conductivity (S/cm)		
	I_2	H_2SO_4	Na
EPPV-245	9.09×10^{-4}	9.52×10^{-4}	8.33×10^{-4}
CPPV-245	2.30×10^{-4}	7.32×10^{-5}	1.00×10^{-3}

Conclusion

In this study PPV was successfully synthesized from PXBDC by electrochemical polymerization. PPV was also synthesized by chemical polymerization method. In both methods, insoluble and insulator polymer films were obtained.

The characterization of these products was performed by means of FTIR, and their thermal behavior was investigated by the DSC and TGA techniques. Thermal analysis and FTIR data confirmed that polymers prepared by electrochemical and chemical methods were almost completely converted to poly(p-phenylene vinylene) upon heating. The TGA results showed that polymers, obtained by chemical polymerization have higher thermal stability. FTIR spectra indicated that the intensity of the absorption band near 960 cm^{-1} increases as the heat treatment temperature rises, which is due to the formation of the trans-vinylene unit on the polymer backbone. This trend was observed for both chemically and electrochemically synthesized polymers.

To impart electrical conductivity to the insulating PPV, two types of doping techniques, solution and vapor, were used. The samples showed the maximum conductivity of 10^{-3} S/cm.

References

1. I. Murase, T. Ohnishi, T. Naguchi and T. Hirooka, **Polym. Commun.** **25**, 1327 (1984).
2. D.R. Gagnon, J.D. Capistran, F.E. Karasz, R.W. Lenz and S. Antoun, **Polymer** **28**, 567 (1987).

3. K.D. Gourley, C.D. Lillya, J.R. Reynolds and J.C.W. Chien, **Macromolecules** **17**, 1025 (1984).
4. R.A. Wessling, **J. Polym. Sci. Polym. Symp.** **72**, 55 (1986).
5. R.W. Lenz, C.C. Han and F.E. Karasz, **J. Polym. Sci., Part A: Polym. Chem.** **26**, 3241 (1988).
6. W.P. Chang, W.T. Whang and P.W. Lin, **Polymer** **37**, 1513 (1996).
7. P. Damlin, C. Kvarnström and A. Ivaska, **Electrochim. Acta** **44**, 1919 (1999).
8. D.D.C. Bradley, R.H. Friend, H. Lindenberger and S. Roth, **Polymer** **27**, 1709 (1986).
9. C.J. Wung, Y. Pang, P.N. Prasad and F.E. Karasz, **Polymer** **32**, 605 (1991).
10. G. Montaudo, D. Vitalini and R.W. Lenz, **Polymer** **28**, 837 (1987).
11. T. Granier, E.L. Thomas and F.E. Karasz, **J. Polym. Sci. Polym. Phys. Edn.** **27**, 469 (1989).