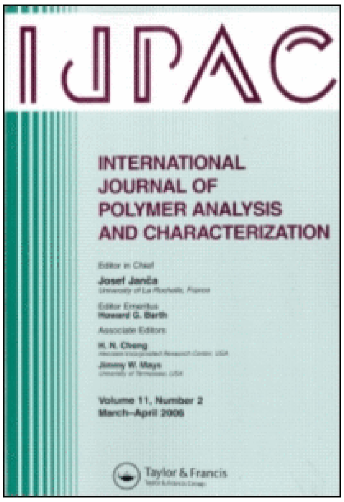


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Influence of Copolymer Composition on the Structure of Conducting Poly(aniline-co-o-phenylenediamine)

Suresh S. Umare[a]; Umesh S. Waware[a]; Sudeep Ingole[a]; S. G. Viswanath[b]
[a] Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur, India [b] Laxminarayan Institute of Technology Nagpur University, Nagpur, India

To cite this Article Umare, Suresh S. , Waware, Umesh S. , Ingole, Sudeep and Viswanath, S. G.(2005) 'Influence of Copolymer Composition on the Structure of Conducting Poly(aniline-co-o-phenylenediamine)', International Journal of Polymer Analysis and Characterization, 10: 1, 1 — 13

To link to this Article: DOI: 10.1080/10236660500345398

URL: http://dx.doi.org/10.1080/10236660500345398

International Journal of Polymer Anal. Charact., 10: 1–13, 2005
Copyright © Taylor & Francis, Inc.
ISSN: 1023-666X print
DOI: 10.1080/10236660500345398

Influence of Copolymer Composition on the Structure of Conducting Poly(aniline-*co*-*o*-phenylenediamine)

Suresh S. Umare, Umesh S. Waware, and Sudeep Ingole
Department of Chemistry, Visvesvaraya National Institute of Technology,
Nagpur, India

S. G. Viswanath
Laxminarayan Institute of Technology, Nagpur University,
Nagpur, India

Abstract: This study covers the synthesis of polymers of aniline, *o*-phenylenediamine, and their copolymers by chemical oxidation in HCl medium. The composition of the copolymers was changed by varying the monomer feed ratio. For examining the effect of composition on copolymer structure and properties, the copolymers were characterized by elemental analysis, FTIR, UV-visible spectra, and thermal analysis. The electrical conductivity of the compressed pellets was measured by the two-probe method. Magnetic studies shows that the polyaniline is paramagnetic in nature, which shows the presence of three unpaired electrons per chain unit, while the poly(*o*-phenylenediamine) and copolymers are diamagnetic and are found to contain no unpaired electrons. The copolymer exhibits excellent solubility in DMF. It was interesting to find that 20% *o*-phenylenediamine-containing copolymer exhibits good solubility by retaining a conductivity similar to polyaniline. The spectroscopic analysis, solubility test, and electrical

The authors are thankful to the Director of RSIC, Nagpur University, Nagpur for measuring FTIR spectra. SSU wishes to thanks the MHRD New Delhi for funding project No. F.26-1/98 TS1.

Address correspondence to Suresh S. Umare, Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur 440 011, India. E-mail: ssu@vrce.ernet.in

conductivity suggest that aniline and *o*-phenylenediamine units are distributed along the copolymer chain and the properties of copolymers can be modified by varying the monomer composition in copolymerization reactions. TG thermogram shows three-stage decomposition of the copolymer. Rapid decomposition starts after 400°C. The observed weight loss of samples was less than 17% at 225°C, showing good thermal stability of copolymers.

Keywords: Conducting copolymers; Polyaniline and derivatives; Conductivity and solubility; Thermal stability

INTRODUCTION

Polyaniline (PA) has attracted considerable interest because of its low density, high electrical conductivity,[1] electro-optical properties,[2] and good environmental and thermal stability.[3,4] However, PA in the oxidized state is insoluble in common organic solvents due to the stiffness of its backbone structure, which results from its delocalized electronic structure. It is necessary to modify the PA in order to make it as processible as conventional organic polymers. Several attempts have been made to improve the processibility of PA through the use of molecular design,[5] modification of monomer structure,[6] formation of blends or composite,[7,8] functionalized organic dopants,[9,10] and incorporation of a special type of dopant containing hydrophobic group and copolymerization.[11,12] Copolymerization is one of the simplest methods for improving the processibility of PA. In copolymerization two or more monomers are incorporated as integral segments of a polymer to produce copolymers with properties that are different from those of homopolymers. Copolymers possess physical properties intermediate between those of the two homopolymers. The magnitude of numerical values of their properties depends on the concentration of the monomer units incorporated into the copolymer chain. The advantage of copolymerization is that it leads to a homogeneous material, the properties of which can be regulated by adjusting the ratio of the concentration of monomers in the feed.

The copolymerization of aniline with the solubilizing comonomers, *o*-phenylenediamine, gives new materials with high conductivity and solubility. In this study we report the chemical copolymerization of poly(aniline-*co*-*o*-phenylenediamine) (PA-*co*-PDA) from monomers, aniline, and *o*-phenylenediamine by varying the monomer feed ratio in the copolymerization reaction. The copolymers have been characterized by solubility, spectroscopic techniques, electrical conductivity, and magnetic properties.

EXPERIMENTAL

Polymer Synthesis

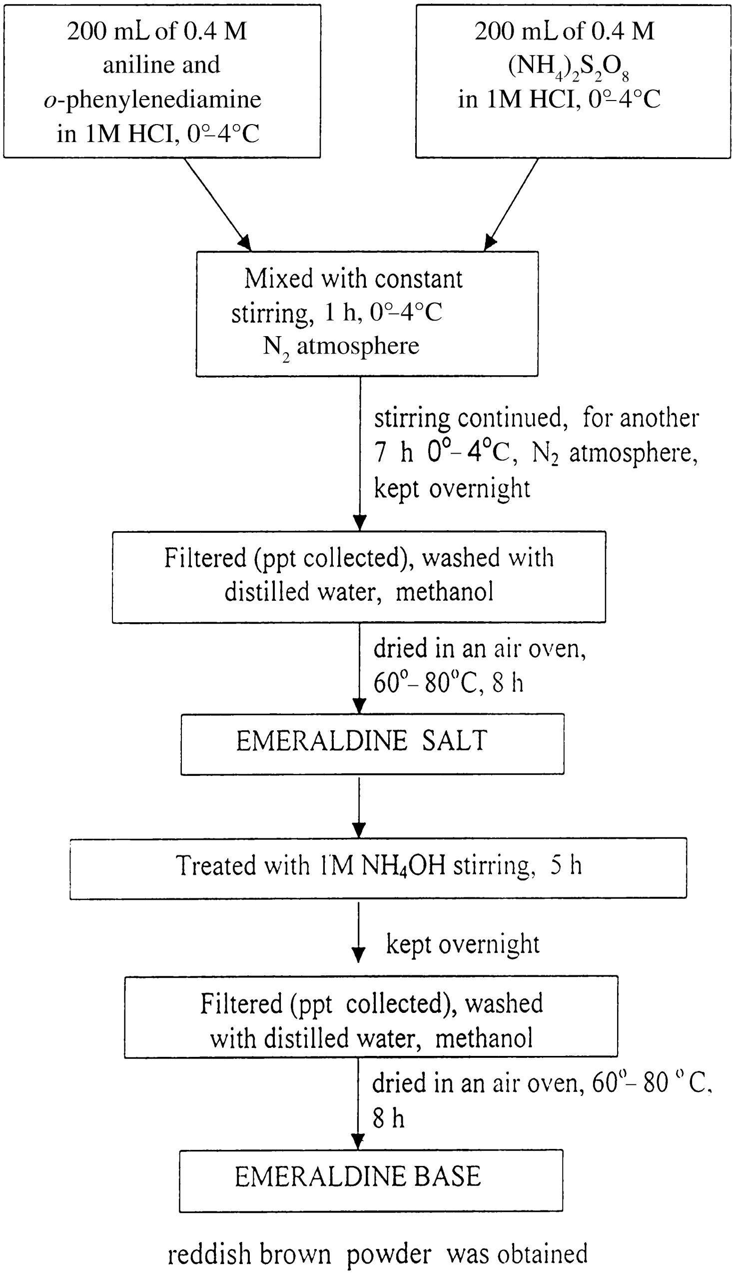
The homopolymers PA and P-*o*-PDA were chemically synthesized by oxidation of aniline and *o*-phenylenediamine individually with ammonium peroxidisulfate in hydrochloric acid.[13–15]

Synthesis of Copolymers

The PA-co-*o*-PDA copolymers were synthesized[13,15,16] by chemical oxidative coupling with varying molar fractions of aniline and *o*-phenylenediamine in aqueous solution of 1 M HCl using ammonium peroxidisulfate as an oxidant (molar ratio of monomers to oxidant = 1:1). The molar fraction of *o*-phenylenediamine in the reaction mixture was varied from 0.4 to 0.7. Various steps involved in the copolymerization process are shown in Scheme 1. Aniline (0.93 g) and *o*-phenylenediamine (1.08 g) were dissolved in 200 mL of 1 N HCl solution. The solution was cooled to 0°–4°C. A precooled solution of (4.56 g) ammonium peroxidisulfate dissolved in 200 mL of 1 N HCl was then added slowly to the monomer solution with constant stirring at 0°–4°C under a nitrogen atmosphere. The stirring was continued for an additional 5 h. The reaction mixture was than kept for 24 h at room temperature, after which the formed copolymer powder was filtered and washed with a small volume of 1 N HCl and dried in an air oven for 8 h at 70°C. A reddish-brown powder was obtained.

Characterization

The solubility of the polymers in the salt form was tested by dissolving each material in *N*-methyl-2-pyrrodinone (NMP). The mixture was kept for 24 h at room temperature, the solution was filtered through a sintered-glass crucible (porosity 2 μm), and the room temperature solubility was determined. Elemental analysis was carried out by a microanalytical technique using a Carlo-Erbastrum DP-2000 instrument at Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute, Lucknow. UV-visible absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Fourier transform infrared (FTIR) spectra were obtained by KBr pellet technique using a Nicolet-Magna FTIR-550 series II spectrometer. ^{1}H NMR (nuclear magnetic resonance) spectra were obtained in dimethylsulfoxide (DMSO) using a Varian EM-360 L spectrometer. Magnetic susceptibility of polymer



Scheme 1. Synthesis of copolymers.

samples were determined by Guoy's method[17] at room temperature using mercury tetrakis(thiocyanato)cobaltate(II), Hg[Co(CNS)$_4$] as a reference material. The polymer powder was pressed under a pressure of 5000 kg/cm^2 to form a pellet, and resistivity was measured by the two-probe method. Thermal analyzer 4000 Mettler TC II, TA processor was used for thermogravimetric analysis. The samples were heated up to 700°C with a heating rate of 10°C/min, in a nitrogen atmosphere.

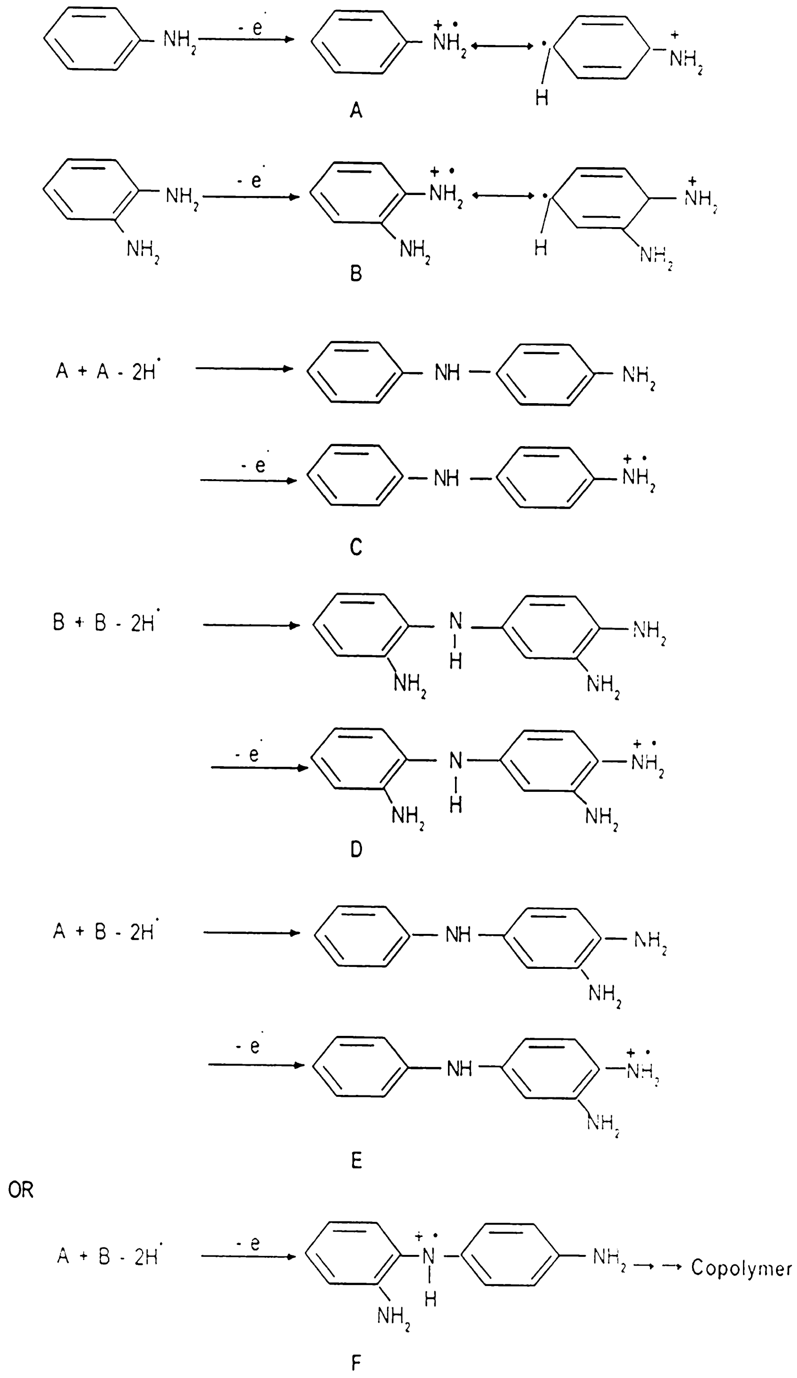
The solution viscosity was measured by a Tuan-Fouss viscometer at 30°C, by preparing a solution of homopolymer and copolymer in dimethylformamide (DMF). From the time flow of solution and solvent the intrinsic viscosity $[\eta_{\text{ints}}]$ was determined.

The salt form of the copolymer sample was dissolved in DMF, and the mixture was stirred for 1 h. Then the solution was filtered and the filtrate solution was used as an acid/base indicator. Ten mL aliquats of 0.1 N HCl, H_2SO_4, and HNO_3 were individually transferred to a 100 mL conical flask, four drops of the above copolymer solution were added, and a reddish brown color was obtained. The individual mixture was titrated with NaOH solution, and the color changed to yellow. At the end point the values obtained from the volumetric titration are in full agreement with the potentiometric end point. At the end point the indicator changes structure from the emeraldine salt form in the acid medium to the emeraldine base form in the basic medium.

RESULTS AND DISCUSSIONS

The copolymerization is believed to proceed via the cation radical. The oxidation of the comonomers, aniline and *o*-phenylenediamine, gives cation radicals A and B, respectively. The radical cation A and B couples together to form C, D, E, and F as shown in Scheme 2. The formation of F terminates continuous growth of the chain because of strong steric hinderance. The growth of the copolymer is mainly through the reaction of C (or D) with A (or B) and or monomers. The copolymerization mechanism is similar to that of homopolymerization with minor modification.

The solubility of homopolymers and copolymers in NMP is presented in Table I. PA and P-*o*-PDA homopolymers show low and high solubility in NMP, respectively, as compared to copolymers, which indicates that the incorporation of *o*-phenylenediamine units in the copolymer gives solubility intermediate between the corresponding homopolymers. The $-NH_2$ substituents introduces flexibility in the rigid PA backbone structure. As a result, copolymers show higher solubility than PA, and the copolymer containing 80 mol % *o*-phenylenediamine shows solubility similar to that of P-*o*-PDA.



Scheme 2. Reaction mechanism of copolymer growth.

Table I. Solubility of homopolymers and copolymers in NMP

Polymers	Solubility (W/v %), g/dL
PA	8.20×10^{-2}
PA-*co*-*o*-PDA20	23.19×10^{-2}
PA-*co*-*o*-PDA40	26.13×10^{-2}
PA-*co*-*o*-PDA50	30.90×10^{-2}
PA-*co*-*o*-PDA60	40.25×10^{-2}
PA-*co*-*o*-PDA80	47.96×10^{-2}
P-*o*-PDA	49.16×10^{-2}

The elemental analysis data for parental homopolymers and copolymers together with the theoretical values are recorded in Table II. The theoretical values (in parentheses) were calculated using four-ring monomer units for homopolymers and eight-ring monomer units (four units of each monomer) for copolymers and were found to fit the empirical repeat unit of the oxidized and protonated form,[18] as shown in Figures 1(a) and 1(b). Elemental analysis indicates that the polymer consist of monomer with a counterion and water. (The presence of water was estimated by thermogravimetric analysis of a dried sample.) The discrepancy in the calculated and experimental values is due to the different levels of counterions, protonation, and reactivity of monomers in the copolymerization process. While calculating the theoretical values, the complete protonation and equal reactivity of monomer units that have been assumed which may not be the same in all the cases. Only few counterions may be substituted and linked to nitrogen.[19]

The salt forms of PA, P-*o*-PDA homopolymers, and copolymers were dissolved in DMF, and the absorption spectra were recorded. The absorption maxima are listed in Table III. The absorption band at

Table II. Elemental analysis data of polymers

Polymers	C	Experimental (Theoretical) % H	N
PA	52.40 (66.20)	4.61 (4.60)	10.41 (12.80)
PA-*co*-*o*-PDA20	46.82 (55.59)	4.83 (4.02)	16.52 (14.03)
PA-*co*-*o*-PDA60	47.75 (56.67)	4.98 (4.51)	16.47 (15.76)
P-*o*-PDA	51.67 (58.18)	4.62 (4.84)	14.25 (12.67)

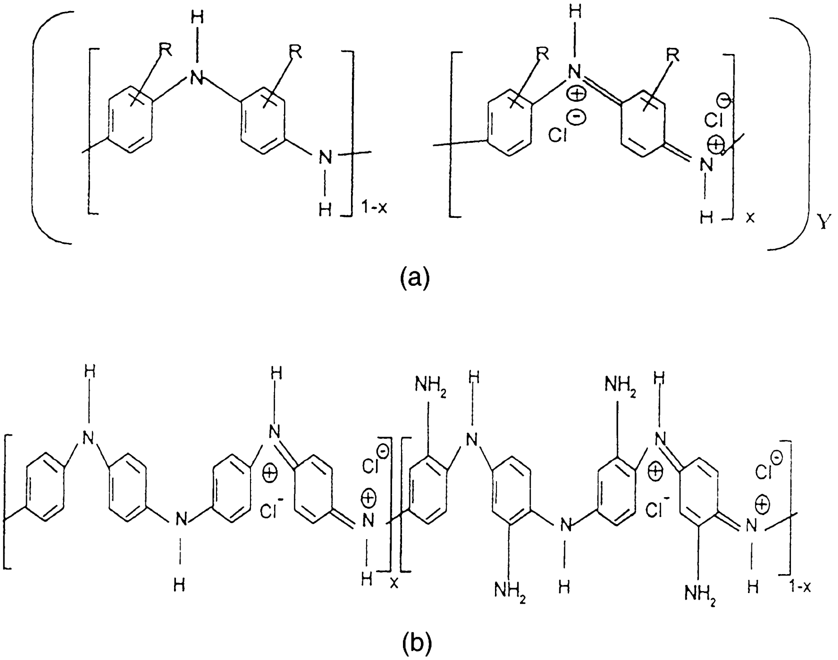


Figure 1. (a) Repeat unit for homopolymers (R = H for PA, R = NH_2 for P-o-PDA). (b) Repeat unit for copolymers.

328 nm is assigned to the electronic transition of the phenyl rings in the polymer backbone. The transition bands show a hypsochromic shift from 328 nm for PA to 300 nm for the P-*o*-PD, implying a decrease in the extent of conjugation and an increase in the band gap. The absorption band at 425 nm corresponds to the exciton transition of the quinonoid

Table III. UV-visible absorption band of polymers

	UV-visible absorption band, nm (eV)	
Polymers	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
PA	328 (3.78)	425 (2.91)
PA-*co*-*o*-PDA20	321 (3.86)	428 (2.89)
PA-*co*-*o*-PDA40	319 (3.88)	427 (2.90)
PA-*co*-*o*-PDA50	318 (3.89)	600 (2.06)
PA-*co*-*o*-PDA60	309 (4.01)	—
PA-*co*-*o*-PDA80	305 (4.06)	406 (3.05)
P-*o*-PDA	300 (4.13) (sh)330	435 (2.85)

rings.[20] This absorption band shifts from 425 to 435 nm when the *o*-phenylenediamine in the copolymer is increased. This blue shift with increasing *o*-phenylenediamine in the copolymer is due to the steric effect of substituents, which produces torsional twists and shortens the conjugation lengths in the polymer.

The FTIR spectra of PA salt (Figure 2, spectrum a) exhibits a band at 1558 and 1472 cm^{-1}, corresponding to the C–C ring stretching vibration of the quinonoid and benzenoid forms. The sharp intense peak of 1384 cm^{-1}

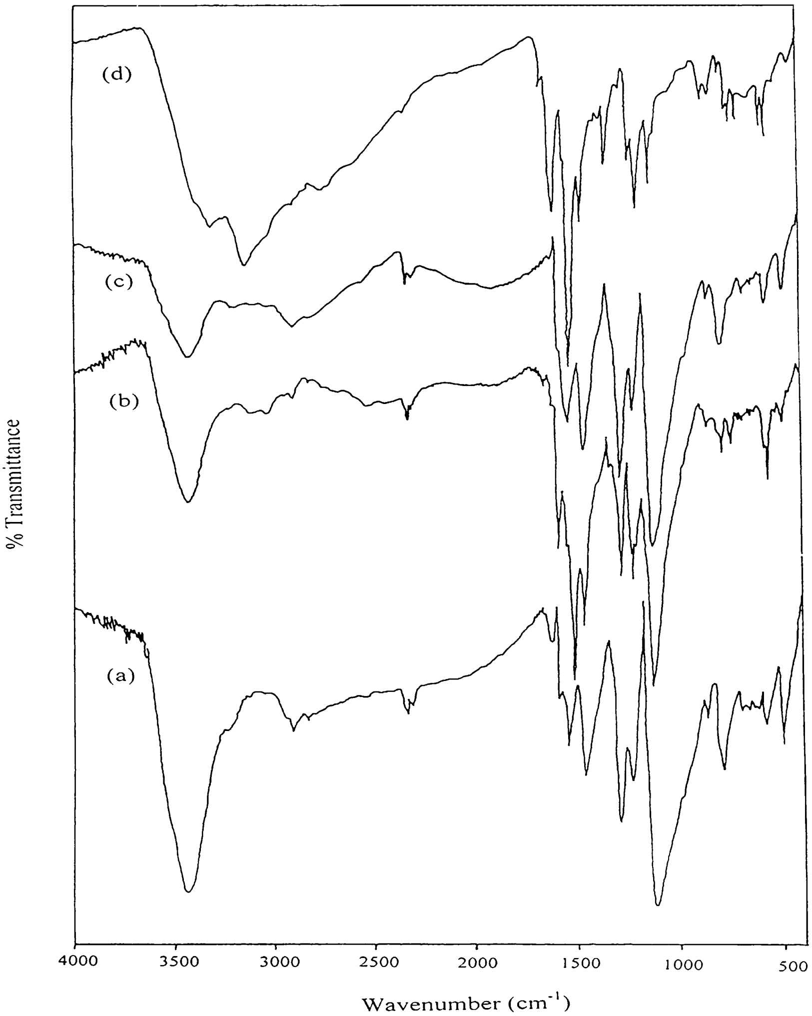


Figure 2. FT-IR spectra of (a) PA, (b) PA-co-o-PDA 50:50, (c) PA-co-o-PDA 80:20, (d) P-o-PDA.

Table IV. Electrical and magnetic data of polymers

Polymers	(χ_m), emu/2 ring unit mol.	μ_{eff}, B. M.	σ, S/cm
PA	6.23×10^{-3}	4.103	3.65×10^{-2}
PA-*co*-*o*-PDA20	-2.49×10^{-3}	D[a]	9.78×10^{-4}
PA-*co*-*o*-PDA40	-2.57×10^{-3}	D[a]	9.18×10^{-4}
PA-*co*-*o*-PDA50	-1.78×10^{-3}	D[a]	8.24×10^{-4}
PA-*co*-*o*-PDA60	-2.24×10^{-3}	D[a]	5.45×10^{-4}
PA-*co*-*o*-PDA80	-2.21×10^{-3}	D[a]	2.70×10^{-4}
P-*o*-PDA	-1.13×10^{-3}	D[a]	2.23×10^{-7}

[a] Diamagnetic.

is assigned to C—H bending mode. Absorption at 1296 cm^{-1} is ascribed to C—N stretching, 1122 cm^{-1} corresponds to in-plane C—H bending mode, and 3433 cm^{-1} N—H stretching. The FTIR spectrum (Figure 2, spectrum d) of P-*o*-PDA shows a weak band at 3309–3140 cm^{-1}, characteristic of $-NH_2$ and N—H stretching, and 1618–1534 cm^{-1}, assigned to the quinonoid and benzenoid phenyl ring. Other bands are similar to the case of PA. The spectral characteristics of copolymers are similar to those of the corresponding PA and P-*o*-PDA homopolymers. The IR spectrum of the copolymer PA-*co*-*o*-PDA (Figure 2, spectra b and c) has been analyzed by monitoring the relative intensity of the peak at 3153 cm^{-1}. The IR spectrum of PA-*co*-*o*-PDA 80 resembles that of P-*o*-PDA, and with the increase in amount of *o*-PDA in copolymer chain, the intensity of the $-NH_2$ band increases.

Magnetic susceptibility (χ_m) data of the polymers are given in Table IV. The susceptibility values obtained from Guoy's method shows that PA is paramagnetic, whereas P-*o*-PDA and copolymers are diamagnetic, i.e., they contained no unpaired electron. Based on these results, it can be assumed that synthesized P-*o*-PDA and the copolymer show a bipolaron structure, in which all the electrons are paired; such a structure is known to be more stable in terms of energy. In the spin dynamics study of PA, Mizoguchi[21] has proposed that polaron-polaron reaction or polaron ionization to bipolaron (spinless charge defects) could change the spin concentration in the sample and hence the magnetic susceptibility.

The electrical conductvity (σ) of the copolymers is strongly dependent on the amount of *o*-phenylenediamine incorporated in the copolymer chain (Table IV). The value of σ for PA is 3.65×10^{-2} S/cm, and that of P-*o*-PDA is 2.23×10^{-7} S/cm. The electrical conductivity of copolymers is lower than that of PA, and increased of *o*-phenylenediamine content in the copolymer chain decreases electrical conductivity. The lower conductivity of the copolymer is due to the steric effect of the $-NH_2$ group. This could induce additional deformation along the polymer backbone and reduce the mobility of the charge carriers along

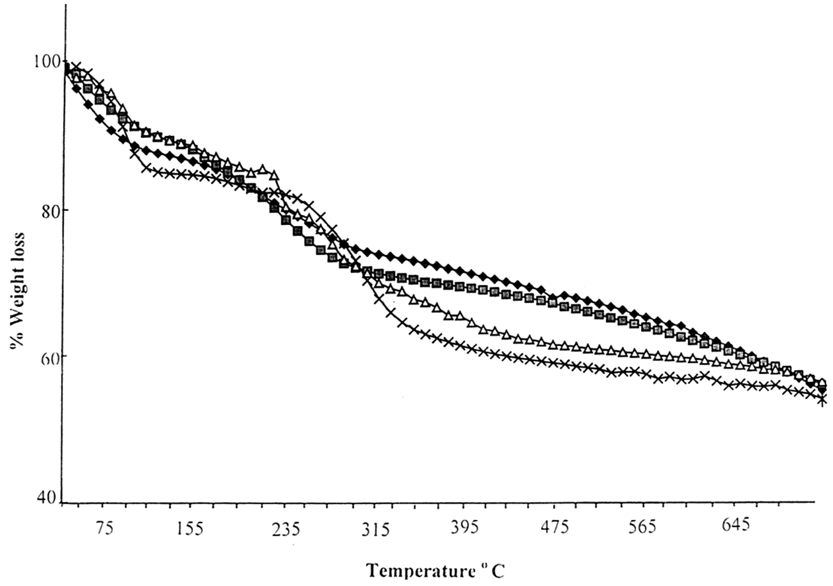


Figure 3. TG thermogram of copolymers; –◆– PA, –□– P-o-PDA, –△– PA-co-o-PDA, 40:60, –✕– PA-co-o-PDA 40:60.

the main chain. Also, on copolymerization, the substituent group lowers the structural regularity that results in reduced interchain interaction, which lowers conductivity.

The thermal stability of the homopolymers and copolymers were studied using thermogravimetric analysis (Figure 3). The nature of the thermograms of copolymers is similar to that of homopolymers. The thermogram shows three stages of mass loss. The initial mass loss is due to the loss of moisture. The second stage loss occurs around 200°C and is very gradual afterwards, more rapid decomposition starts at 400°C; even at 225°C the fractional weight loss of the sample was less than 20%. In order to compare the relative thermal stability of PA,

Table V. Percentage mass loss data for copolymers at different temperatures

Polymers	% mass loss at 110°C	% mass loss at 290°C	% mass loss at 450°C	% mass loss at 600°C
PA	11	25	31	37
PA-*co*-*o*-PDA40	10	28	32	41
PA-*co*-*o*-PDA50	7	34	41	47
PA-*co*-*o*-PDA60	14	23	41	44
P-*o*-PDA	9	27	39	42

P-*o*-PDA, and their copolymers, percent mass loss at 450°C is given in Table V. The PA is more stable as compared to P-*o*-PDA and copolymers. On increasing the percentage of *o*-phenylenediamine in the copolymer, the stability increases slightly.

The solution viscosity measurement data from the Tuan-Fouss viscometer is 1.62 dL/g for PA, 1.65 dL/g for PA-*co*-*o*-PDA40, 1.67 dL/g for PA-*co*-*o*-PDA 50/60, and 1.76 dL/g for P-*o*-PDA. The solution viscosity of P-*o*-PDA is more than that of PA. It may be due to the presence of $-NH_2$ group in the P-*o*-PDA molecules, so that the copolymer chain may be in coiled form and might be showing high viscosity. The viscosity of copolymers increases by increasing the content of P-*o*-PDA monomer in the copolymer chain.

CONCLUSIONS

A series of aniline and *o*-phenylenediamine copolymers were chemically synthesized by varying the molar feed ratio of monomers in copolymerization reaction. The ratio of the two monomers influences the copolymerization process due to the different reactivity of monomers. Copolymers have lower conductivity and better solubility due to the existence of $-NH_2$ groups in the main chain. The conductivity of copolymer also follows a similar order. PA shows paramagnetic behavior, whereas poly-*o*-phenylenediamine and copolymers show diamagnetic behavior, which may due to a change in unpaired spin concentration in the chain. The magnetic susceptibility of the copolymer may be explained on the basis of polaron-bipolaron interaction.

REFERENCES

[1] Anand, J., S. Palaniappan, and D. N. Sathyanarayana. (1998). Spectral, thermal and electrical properties of poly(*o*- and *m*-toludine)–polystyrene blends prepared by emulsion pathway. *J. Polym. Sci. Polym. Chem.* **36**, 2291–2299.

[2] MacDiarmid, A. G. and A. J. Epstein. (1991). The polyaniline: A novel class of conducting polymers. *Am. Chem. Soc. Poly. Chem.* **32**, 709–710.

[3] Oh, S. Y., K. Akagi, H. Shirakawa, and K. Araya. (1993). Synthesis and properties of liquid-crystalline polyacetylenes with a phenycyclohexyl mesogenic moiety in the side group. *Macromolecules* **26**, 6203–6206.

[4] Genies, E. M., A. Boyle, M. Lapkowski, and C. Tsintavis. (1990). Polyaniline: A historical survey. *Synth. Met.* **36**, 139–182.

[5] Kaneko, M. and H. Nakamura. (1985). Photoresponse of the liquid junction polyaniline film. *J. Chem. Soc. Chem. Commun.* **6**, 346–347.

[6] Sato, M., S. Tanaka, and K. Kaeriyama. (1986). Soluble conducting polythiophenes. *J. Chem. Soc. Chem. Commun.* **2**, 873–874.

[7] Li, S., Y. Cao, and Z. Xue. (1987). Soluble polyaniline. *Synth. Met.* **2**, 141–149.

[8] Mattoso, L. H. C. and L. F. Malmonge. (1999). Morphology variation as a function of composition for blends of PVDP and a polyaniline derivative. *Polymer* **40**, 513–518.

[9] Fan, J., M. Wan, and D. Zhu. (1998). Synthesis and characterization of water-soluble conductivity copolymer poly(aniline-*co*-*o*-aminobenzenesulfonic acid). *J. Polym. Sci. Polym. Chem.* **36**, 3013–3019.

[10] Gupta, M. C. and S. S. Umare. (1992). Studies on poly(*o*-methoxyaniline). *Macromolecules* **25**, 138–142.

[11] Umare, S. S., M. M. Huque, M. C. Gupta, and S. G. Visvanath. (1996). Studies on substituted derivatives of polyaniline: Effect of polymerization conditions on electrical conductivity. *Macromol. Rep.* **A33**, 381–389.

[12] Cao, Y., P. Smith, and A. J. Heeger. (1992). Counter-ion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers. *Synth. Met.* **48**, 91–97.

[13] Borkar, A. D., M. C. Gupta, and S. S. Umare. (2001). Electrical and optical properties of conducting copolymer: Poly(aniline-*co*-*N*-ethylaniline). *Polym. Plast. Technol. Eng.* **40**, 225–234.

[14] Dao, L. H., M. Leclerc, J. Guoy, and J. W. Chevalier. (1989). Synthesis and characterization of substituted polyanilines. *Synth. Met.* **29**, E377–E382.

[15] Ye, S., N. T. Do, L. H. Dao, and A. K. Vijh. (1997). Electrochemical preparation and characterization of conducting copolymers: Poly(aniline-*co*-*N*-butylaniline). *Synth. Met.* **88**, 65–72.

[16] Chen, S. A. and G. W. Hwang. (1995). Water soluble self-acid doped conducting polyaniline: Structure and properties. *J. Am. Chem. Soc.* **117**, 10055–10062.

[17] Inoue, H., Y. Morioka, and S. Yanagisawa. (1973). Bonding nature of coordination polymers. $M(II)_3[Rh\text{-}(CN)_6]_2X \cdot H_2O$. *J. Inorg. Nucl. Chem.* **35**, 3455–3461.

[18] Huang, W. S., B. D. Humphrey, and A. G. MacDiarmid. (1986). Polyaniline: A novel conducting polymer. Morphology & chemistry of its oxidation-reduction in aqueous electrolytes. *J. Chem. Soc. Faraday Trans.* **82**, 2385–2400.

[19] Chiang, J. C. and A. G. MacDiarmid. (1986). Polyaniline: Protonic acid doping of the emeraline form to the metallic regime. *Synth. Met.* **13**, 193–205.

[20] Ray, A., A. G. MacDiarmid, J. M. Ginder, and A. J. Epstein. (1990). Optical studies of polyanilines: Effect of alkyl ring substitution and solvent environment. *Mater. Res. Soc. Symp. Proc.* **173**, 353–357.

[21] Mizoguchi, K. (1990). Spin dynamics in conducting polymers. *Makromol. Chem., Macromol. Symp.* **37**, 53–66.