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Synthesis, characterization and electrical properties of poly(dibromoaniline-co-aniline)s

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The chemical copolymerization of aniline and 2,5-dibromoaniline or 2,6-dibromoaniline by oxidation with $K_2Cr_2O_7$ in H_2SO_4/acetonitrile media has been carried out. Copolymer composition can be effectively controlled varying the monomer feed ratio. When substituted aniline fraction is increased in the copolymer, the electrical conductivity (σ) decreases; this effect is more important when 2,6-dibromoaniline is used. Thus, the conductivity can be controlled in a broad range, from 1.2 to 10^{-6}–10^{-11} S·cm^{-1} depending on the substituted aniline and the feed ratio. The relations between copolymer compositions and comonomer feed molar ratios shows that the aniline is slightly more reactive than dibromoanilines during the copolymerization process. All the copolymers were shown to be more processable than polyaniline.

1. Introduction

In the past few years, aromatic conducting polymers such as polypyrrole, polythiophene, or polyaniline (PANI) have received considerable attention owing to their good electrical, optical, and electrochemical properties [1, 2]. Among these polymers, a great deal of work was devoted to PANI which can be readily used in applications such as light-weigth batteries [3, 4] and electrochromic devices [5, 6]. However, due to the stiffness of its backbone, PANI is almost insoluble in common organic solvents [7]. Consequently, its post-synthesis processability is quite difficult. In most cases, the solubilization of a polymer can be achieved through functionalization of starting material with a suitable side chain prior to polymerization. On the one hand, PANI shows good conductivity (1.2 $\text{S}\cdot\text{cm}^{-1}$), but it is insoluble in common organic solvents. On the other hand, poly(halogensubstituted-aniline)s are soluble in some organic solvents like N-methylpyrrolidinone, dimethylformamide, tetrahydrofuran, dimethylsulfoxide and acetic acid 80% v/v, but their conductivity remain low ($\sigma < 10^{-11}\ \text{S}\cdot\text{cm}^{-1}$) [8].

Considering these data, the synthesis of a copolymer that combines the conductivity of PANI and the solubility of polyhalogenanilines would be of interest. Therefore the copolymerization of aniline with halogenanilines should lead, upon proper adjustment of the copolymer composition, to a soluble and conducting or semiconducting material. Until recently, this strategy was used only by a few workers for the synthesis of a new aromatic conducting polymer. The synthesis of a copolymer having a polyaniline backbone was performed with halogens such as chlorine and iodine, but not with bromine. In this paper, we report on the chemical synthesis of a series of poly(aniline-co-dibromoaniline) copolymers. The substituted aniline monomers selected for copolymerization with aniline were 2,5-dibromoaniline and 2,6-dibromoaniline. The resulting copolymers have been characterized by various experimental techniques. Furthermore, in this work the influence of bromine atoms on the extension of conjugation, and its consequences on the electrical properties, doping levels and solubility of the obtained copolymer was also explored.

2. Experimental

2.1. Reagents and instrumentation

The monomers 2,5-dibromoaniline and 2,6-dibromoaniline (Aldrich Chemical Co.) were recrystallized from aqueous methanol. Aniline was doubly distilled. Potassium dichromate was used as oxidant in chemical copolymerizations without further purification. All aqueous solutions were prepared by using freshly distilled water. Conductivity was measured by using the four-probe technique on polymer-powder pressed pellets with Elchema Electrometer as a source of constant current. Infrared spectra of polymers -KBr pellets were recorded on a Perking Elmer Model 1310 spectrophotometer. UV-Vis spectra were recorded on a Milton Roy 3000 spectrophotometer with diode arrangement, in 1 cm cells using N-methyl-pyrrolidone (NMP) as solvent in all cases. The elemental analysis of C, H, N, S was performed in a Fisons Elemental Analyser EA 1108. The halogen content in the copolymer was determined by the standard ASTM method E442 [9]. The copolymers and base form were doped with I_2 vapor. The determination of doping level by l_2 was measured as percentage of weight enhanced of products.

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TABLE I Conductivity at room temperature and doping level (within brackets) of poly(dibromoaniline-co-aniline) in base from and doped with H_2SO_4 and $I_{2(g)}$

			Conductivity (σ, $S \cdot cm^{-1}$)		
Copolymers	f_1	F_1	Base form 10^{-12}	Doped with H_2SO_4 1M (S/N)	Doped with $I_{2(g)}$
Poly(2,5-dibromaniline-co-aniline)	0.3	0.17	82.0	(0.35) 7.1×10^{-6}	(38) 1.1×10^{-6}
	0.4	0.24	61.0	(0.30) 1.2×10^{-8}	(35) 2.0×10^{-8}
	0.5	0.32	22.0	(0.22) 8.2×10^{-10}	(39) 1.3×10^{-10}
	0.6	0.40	8.3	(0.17) 6.3×10^{-10}	(33) 1.1×10^{-10}
	0.7	0.53	5.6	(0.14) 5.2×10^{-10}	(18) 8.4×10^{-11}
	0.8	0.67	4.1	(0.12) 4.1×10^{-10}	(12) 6.7×10^{-11}
Poly(2,6-dibromaniline-co-aniline)	0.3	0.24	56.0	(0.29) 2.3×10^{-6}	(35) 3.8×10^{-7}
	0.4	0.35	42.0	(0.22) 4.8×10^{-9}	(33) 6.8×10^{-9}
	0.5	0.45	12.0	(0.18) 2.8×10^{-10}	(28) 7.0×10^{-11}
	0.6	0.53	8.4	(0.10) 2.6×10^{-10}	(25) 5.5×10^{-11}
	0.7	0.66	4.2	(0.08) 1.7×10^{-10}	(23) 3.3×10^{-11}
	0.8	0.77	3.5	(0.07) 1.4×10^{-10}	(11) 3.1×10^{-12}

2.2. Chemical synthesis

Oxidative copolymerization of aniline with dibromoanilines was performed similarly to oxidative copolymerization of poly(aniline-co-dichloroaniline)s already reported [10], but using a 50% v/v mixture of 1 M H_2SO_4/acetonitrile. H_2SO_4 was used instead HCI, so that the fraction of dibromoaniline in the copolymers could be estimated from the bromine content.

All copolymerization reactions were carried out at 50°C, using potassium dichromate as oxydizing agent. Reagents were stirred for 6 h, and then filtered through a Büchner funnel, washed with 1 M H_2SO_4 and copious amount of methanol. The products were suspended in 1 M H_2SO_4 and stirred during 24 h at room temperature. Then the products were filtered, washed with water and methanol and later dried at 60°C under vacuum. All copolymers were undoped at room temperature, suspended in an aqueous NH_4OH (50% v/v) solution and stirred for 24 h, then were filtered and washed with water and methanol and again were dried at 60°C at reduced pressure. The various comonomer feed compositions f_1 (in mole fraction of substituted anilines) are shown in Table I.

3. Results and discussion

3.1. Synthesis and spectroscopy

Poly(2,5-dibomoaniline-co-aniline) and poly-(2,6-dibromoaniline-co-aniline) were synthesized by chemical copolymerization from the respective dihaloaniline and aniline at various molar fractions of dihaloaniline (f_1) in the feed, according to the reaction:

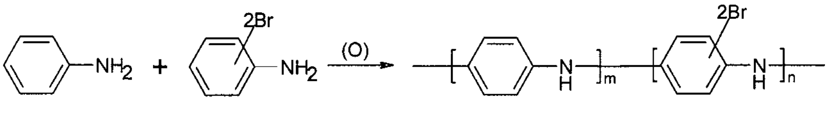

Fig. 1 depicts as and example, the FT-IR spectra of poly(2,5-dibromoaniline-co-aniline) in the lowest ($F_1 = 0.17$) and highest ($F_1 = 0.67$) compositions. Also, the FT-IR spectrum of PANI is shown. FT-IR spectra of poly(2,5-dibromoaniline-co-aniline)s are similar to that of poly(2,6-dibromoaniline-co-aniline). It can be seen that the spectra present similarity with polyaniline. The FT-IR bands of copolymers can be assigned as follows: 3383–3235 cm^{-1} (N—H stretching); 3060–3086 cm^{-1} (aromatic C—H stretching); 1483–1569 cm^{-1} (quinoid C=N and C=C stretching); 1568–1601 cm^{-1} (aromatic C—H stretching); 803–832 cm^{-1} (aromatic C—H bending). The band at 829 cm^{-1} in PANI was attributed to the C—H disubstitution pattern and its intensity decreases as the value of F_1 is increased.

The above results are similar in all copolymer families. On the other hand, it should be pointed out that in the copolymers it was not possible to clearly observe the pattern corresponding to the tetra-substitution in the rings. We think that this band is overlapped with the analogue band of disubstitution of the aniline portion, and perhaps with bands corresponding to the C-Br vibrations.

Fig. 2 shows the UV-Vis spectra of the series of copolymers between aniline and 2,5-dibromoaniline in its base form. The spectra of polyaniline are dominated by two absorption bands at 320 and 610 nm. The 320 nm band is often assigned to π-π^* transition in the benzenoid structure [11]. The absorption in the visible range, at 610 nm, is ascribed to exiton formation in the quinoid rings [12]. This absorption gives rise to a blue coloration on the PANI-NMP solution.

It is observed that the shape of the UV-Vis spectra of the copolymers is a function of the F_1 composition. In general, at low values of F_1, they present the same bands as polyaniline, but shifted towards lower wavelengths (hypsochromic shift). As the fraction of dihaloaniline increases in the copolymers, the band corresponding to the benzenoid transition remains unchanged, undergoing only a hypsochromic shift, while the band corresponding to the exiton formation in the quinoid structure, in addition to the hypsochromic shift, becomes less intense tending to dissapear for the copolymer with the highest fraction of dihaloaniline. This behavior is related to steric factors of the bromine atoms in the polymeric chain, which a decrease in the extension of conjugation along the macromolecule, in comparison with polyaniline, and this is very much related to the decrease in conductivity as the dihaloaniline fraction

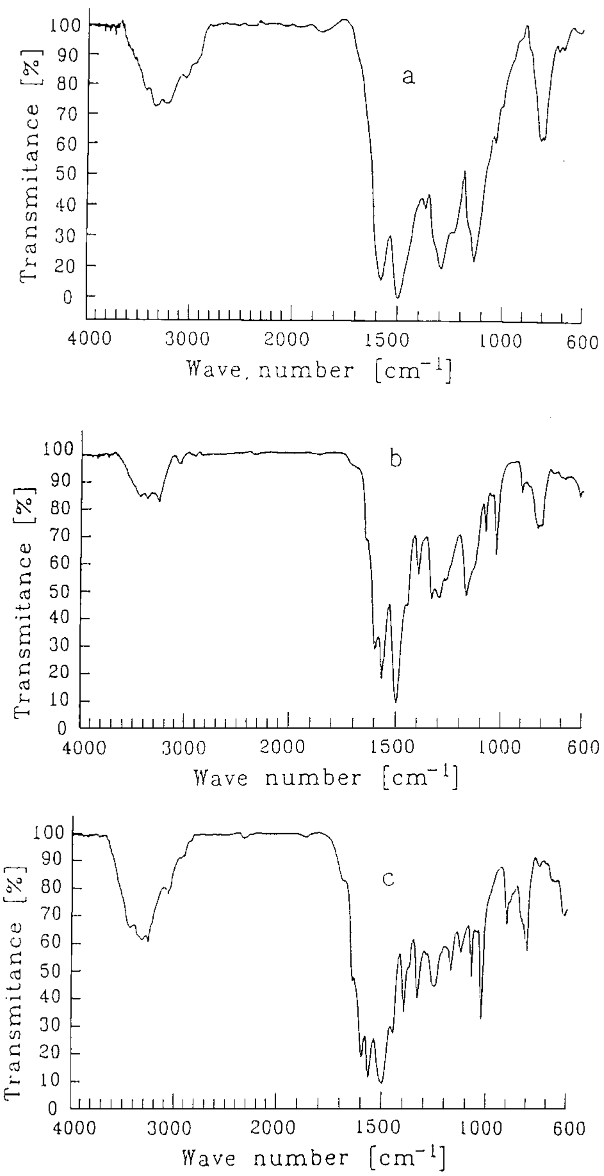

Figure 1 FT-IR spectra of (a) polyaniline and poly(2,5-dibromoaniline-co-aniline) in doped form: (b) $F_1 = 0.17$; (c) $F_1 = 0.67$.

increases in the copolymer. The disappearance of the exiton when the fraction of substituted aniline is the highest, has been reported before, and has been attributed to the interference of the substituents in the levels of doping. The poorer polaron formation of the copolymers with the higher degree of dibromoaniline is consistent with the conductivity decrease of copolymers. Watanabe *et al.* [13] and Moon *et al.* [14] reported similar results for poly(N-alkylaniline)s, where the poorer polaron formation was observed with the bulkier alkyl group substitution. In this case, the same behaviour was observed for both series of copolymers.

Figs 3 and 4 show the behavior of the copolymers composition (F_1, defined as molar fraction of the dibromoaniline units in the copolymer) versus the molar fraction of dibromoaniline in the feed (f_1). The diagonal line represents the case in which both monomers have identical reactivity. In both cases, the values of F_1 for the copolymers are under the diagonal line, indicating that the copolymers contain in their structures higher fractions of aniline than dihaloaniline, this effect being stronger when the bromine atoms are found in the 2 and 5 positions of the benzenoid ring. In both cases, aniline as a monomer, shows a greater reactivity than 2,5-dibromoaniline and 2,6-dibromoaniline.

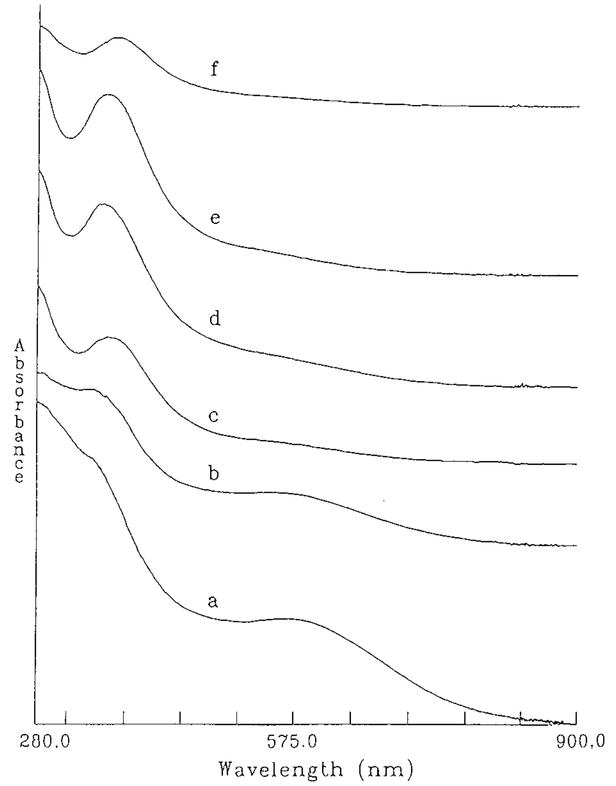

Figure 2 UV-Vis spectra of undoped poly(2,5-dibromoaniline-co-aniline) in doped form: (a) $F_1 = 0.67$; (b) $F_1 = 0.53$; (c) $F_1 = 0.40$; (d) $F_1 = 0.32$; (e) $F_1 = 0.24$; (f) $F_1 = 0.17$.

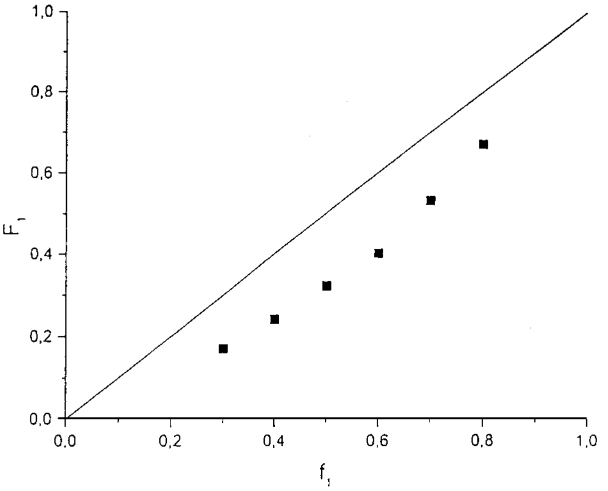

Figure 3 Plot of F_1 against f_1: poly(2,5-dibromoaniline-co-aniline).

Using the mole fraction of substituted aniline in the monomer feed (f_1) and F_1, the monomer reactivity ratios, r_1 (for substituted aniline) and r_2 (for aniline) can be estimated from the plot shown in Fig. 5, according to the following equation:

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1} \qquad (1)$$

The intercept gives r_2 while the slope gives r_1 [14]. For poly(2,5-dibromoaniline-co-aniline), r_1 is 2.2 and r_2 0.5, while for poly(2,6-dibromoaniline-co-aniline)

TABLE II Protonation levels of polyaniline, poly(2,5-dibromoaniline) and poly(2,6-dibromoaniline)

Polymer	S/N
Polyaniline	0.51
Poly(2,5-dibromoaniline)	0.04
Poly(2,6-dibromoaniline)	0.05

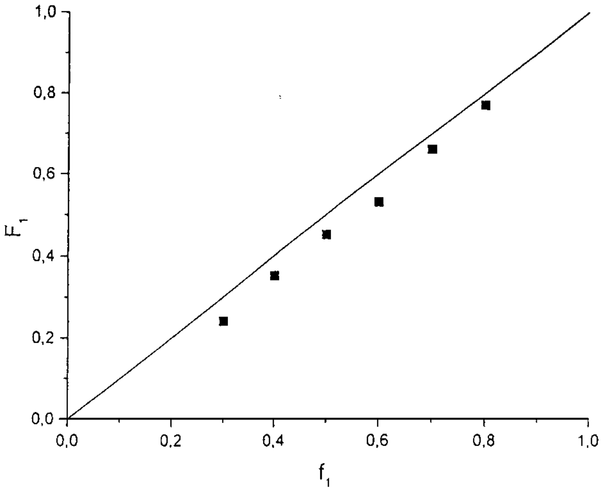

Figure 4 Plot of F_1 against f_1: poly(2,6-dibromoaniline-co-aniline).

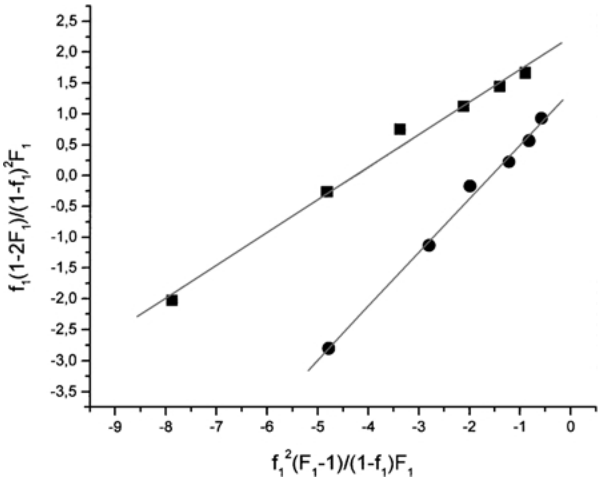

Figure 5 Plot to evaluate reactivity ratios, r_1 and r_2: (●) poly(2,5-dibromoaniline-co-aniline) and (■) poly(2,6-dibromoaniline-co-aniline).

r_1 is 1.3 and r_2 is 0.8. In both cases, $r = r_1 \cdot r_2$ is very close to unity. A value of unity indicates that a given monomer shows the same preference for adding to its own type of units as for it to add to the other type.

Comparing the S/N ratios of the homopolymers (Table II) and those of the copolymer it can be seen that, as the fraction of substituted aniline in the copolymer increases beyond 0.4, the S/N ratio decreases from 0.35 to 0.12–0.07 for the substituted aniline copolymers. Thus, it appears that the "dopping" of the polymer chain by protonating acid is inhibited by the substituent group.

3.2. Electrical conductivity

The conductivities for both series of copolymers are also listed in Table I. Very sharp variations of up to 6 orders of magnitude can be seen when the comonomer feed composition varies. However, according to others workers [15], it is more appropriate to consider the variation of the logarithm of the conductivity with the copolymer composition F_1 as shown in Fig. 6. It can be observed that the electrical conductivity (σ) of the copolymers is strongly dependent on the amount of substituted aniline incorporated, decreasing as the dihaloaniline fraction in the copolymer increases. Initially, the value of σ decreases sharply, but from a certain composition, there is little variation in conductivity, becoming almost independent of the copolymer composition. The reduction in conductivity observed when the fraction of dihaloaniline in the copolymer increases, can be explained by two types of steric effect. The first possible explanation is the conformational steric effect of the substituted bromine groups, since the substituent may restrict the ring conformation of aniline. Substituent groups in positions 2,5 or 2,6 of aniline in the copolymer may induce ring twisting, i.e., nonplanar conformations, which decreases the π conjugation length along the polyaniline backbone and thus destabilizes the polysemiquinone radical cation and gives higher redox potentials. This type of explanation for the reduction of conductivity of substituted polyaniline has been reported in the literature for various polyanilines derivatives [16]. The other possible explanation for the reduction of the copolymer conductivities is the intermolecular steric effect. The substituted groups may also reduce the intermolecular contacts between the neighboring polyaniline backbones through their steric effect, and hence induce a disorder in chain separations within the metallic conduction region of the copolymer. Considering the conduction mechanism of polyaniline, the reduction of interchain contact is indicative of the shortening of coherence length between the neighboring polyaniline backbones. Thus the electrons in the polaronic lattice in polyaniline are confined to segments of a chain and become localized. This localization of electrons may reduce the interchain diffusion rate of electrons and therefore lead to the decrease of conductivity. Similar arguments have been reported for the polymeric acid-doped polyaniline systems [17, 18].

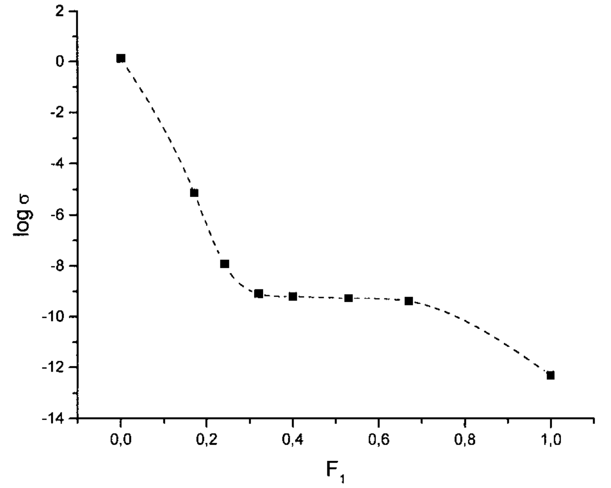

Figure 6 Room-temperature dc conductivities of the H_2SO_4-doped poly(2,5-dibromoaniline-co-aniline) against F_1.

For polyaniline, it has been shown that the conductivity is strongly dependent on the protonation (doping) level (S/N), which also decreases as the dihaloaniline fraction in the copolymer increases. Table I shows also that doping with iodine is easier than with H_2SO_4. However, as can be seen in the graph, the doping with H_2SO_4 is more effective. We believe that the dihalogenation hinders the delocalization structure. We have reported that dihalogenated homopolymers present conductivities in the order of 10^{-12} S·cm^{-1} [8], therefore, the conductivities of copolymer are between those of polyaniline (1.2 S·cm^{-1}) and dihalogenated homopolymers.

Finally, it is important to mention that the copolymers are soluble in solvents such as N-methylpyrrolidone, dimethylformamide, tetrahydrofuran, dimethylsulfoxide and 80% v/v acetic acid. The fact that these copolymers are soluble in the above solvents, and show conductivities values between those of polyaniline and the corresponding polydihaloanilines, is a strong proof that they are true copolymers, instead of a mixture of homopolymers. Thus, in a control experiment, a mixture of equal parts of polyaniline and poly(2,5-dibromoaniline) was prepared and its conductivity and solubility in dimethylsulfoxide was determined. The conductivity value was intermediate between that of polyaniline and poly(2,5-dibromoaniline), but the polyaniline fraction was completely insoluble.

4. Conclusions

In this paper, we have examined the effect of the actual composition (in mole fractions of dibromoanilines, F_1) of chemically synthesized poly(dibromoaniline-co-aniline) copolymers on the electrical and physical properties. The aniline resulted to be slightly more reactive than 2,5- or 2,6- dibromoanilines. The electrical conductivity of the copolymer can be effectively modified by varying its composition, decreasing as the amount of dibrominated aniline increases in the copolymer. The synthesized copolymers present conductivity values between those of the corresponding homopolymers (10^{-6}–10^{-12} S·cm^{-1}), and show solubility in some common solvents, which may be important in order to improve the processability of PANI.

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References

1. T. A. SKOTHEIM (Ed.), "Handbook of Conducting Polymers" Vol. 1. (Marcel Dekker, New York, 1987).
2. M. ALDISSI, Proceedings of the International Conference on the Science and Technology of Synthetic Metals, Synth. Met. (1988/1989) p. 27.
3. T. NAKAJIMA and T. KAWAGOE, *ibid.* **28** (1989) C629.
4. M. MIZUMOTO, M. NAMBA, S. NISHIMURA, H. MIYADERA, M. KOSEHI and Y. KOBAYASHI, *ibid.* **28** (1989) C639.
5. M. T. NGUYEN and L.-H. DAO, *J. Electrochem. Soc.* **136** (1989) 2131.
6. L. H. DAO and T. M. NGUYEN, Proc. 24th Intersoc. Energy Conversion Eng. Conf. (IECEC-89) Vol. 4 (1989) p. 1737.
7. J. H. LAI (Ed.) "Polymers for Electronic Applications" (CRS Press, Boca Raton, FL, 1989) ch. 4.
8. F. R. DÍAZ, C. O. SÁNCHEZ and M. A. DEL VALLE, *Synth. Met.* **92** (1998) 99.
9. ASTM Method. **30** (1981) 103.
10. F. R. DÍAZ, C. O. SÁNCHEZ, M. A. DEL VALLE, J. L. TORRES and L. H. TAGLE, *Synth. Met.* **118** (2001) 2531.
11. L. H. DAO, M. LECLERC, J. GUAY and J. W. CHEVALIER, *ibid.* **29** (1989) E377.
12. S. STAFSTROM, J. L. BREDAS, A. J. EPSTEIN, H. S. WOO, D. B. TANNER, W. S. HUANG and A. G. MACDIARMID, *Phys. Rev. Lett.* **59** (1987) 1464.
13. A. WATANABE, K. MORI, A. IWABUCHI, Y. IWASAKI and Y. NAKAURA, *Macromol.* **22** (1989) 3521.
14. H. S. MOON and J. PARK, *ibid.* **31** (1998) 6461.
15. K. G. NEOH and E. T. KANG, *Eur. Polym. J.* **26** (1990) 403.
16. M. LECLERC, G. DAPRANO and G. ZOTTI, *Synth. Met.* **55–57** (1993) 1527.
17. H. S. MOON and J. K. PARK, *J. Polym. Sci., Polym. Chem. Ed.* **36** (1998) 1431.
18. *Idem.*, *Synth. Met.* **92** (1998) 223.

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