# Synthesis and Characterization of Electrically Conducting Copolymer of Aniline and *o*-Bromoaniline Using Methane Sulfonic Acid as Dopant

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**ABSTRACT:** Polyaniline (PAN), poly(*o*-bromoaniline) (POBA), and poly(aniline-*co*-*o*-bromoaniline) (PABA) were synthesized by oxidative coupling. These polymers are protonated by 10–20% methane sulfonic acid (MSA) and $1M$ HCl. The new polymer bases have greater solubility than that of PAN in common polar organic solvents; PAN–MSA was observed to be the most thermally stable of these polymers. POBA is associated with residual quinoid diimine units as illustrated in the IR and UV-vis spectra, after reduction with hydrazine dihydrochloride. Both the doping agents cause a downward shift of the quinoid absorption in the IR spectra. MSA- and HCl-doped PAN and PABA polymers exhibit a coil-like conformation in DMSO, whereas only MSA-doped PAN and PABA show an "expanded coil-like" conformation in *m*-cresol with a "free carrier tail" above 800 nm in their electronic spectra. XPS spectra indicated the presence of covalent bromine in the POBA and PABA polymers. Bromine retention was greater in the homopolymer as evidenced by the IR studies after aging at 350°C. Compared to HCl, MSA is found to be a more effective dopant, enhancing the conductivity of the copolymers by $10^2$–$10^3$ times in magnitude. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2662–2669, 2002

## INTRODUCTION

Polyaniline (PAN), an important member of the class of conjugated conducting polymers, has attracted great attention because of its electronic, electrochemical, and optical properties.[1] Besides, it is easy to prepare and possesses good thermal as well as environmental stability.[2,3] Consequently, PAN and its derivatives have versatile applications including use as active electronic materials,[4,5] in secondary batteries,[6,7] and in microelectronic and electrochromic devices.[7–10] To improve the processibility and thermal and environmental stability and to induce novel electronic and electrochemical properties, substituted PANs are being developed.[11–19] Dopants also impart desired characteristics in conducting polymers. Thus, functionalized sulfonic acid dopants can improve the solubility and increase the conductivity substantially.[20]

Monohalo-substituted PANs prepared by oxidative polymerization in an aqueous acid medium were reported to have substantially lower oxidation states and doping levels.[15] Keeping this in view, we here report the synthesis of poly(*o*-bromoaniline) and poly(aniline-*co*-*o*-bromoaniline) and also their characterization, which includes the study of their thermal stability, oxidation, and protonation behavior. The effect of the novel methane sulfonic acid (MSA) dopant was also examined.

## EXPERIMENTAL

### Chemicals

Aniline was used after double-distillation. *o*-Bromoaniline, MSA (70%; Aldrich), and ammonium persulfate were used as purchased.

Homopolymers were prepared by ammonium persulfate oxidation in a manner similar to that of PAN.[21] The required amount of *o*-bromoaniline [3 g, (17.44 mmol)] was dissolved at 0–5°C in 250 mL of a $1M$ HCl solution and then a solution of $(NH_4)_2S_2O_8$ [3.57 g (15.66 mmol)] in 100 mL of $1M$ HCl was added dropwise. Stirring was continued for 2 h at that temperature. The resulting solution was further stirred for about 30 h at room temperature. The black precipitate was filtered and washed with $1M$ HCl and ethanol successively and dried in a vacuum for 48 h. A HCl-

**TABLE I**
**Experimental Details for the Polymerization of Aniline and *o*-Bromoaniline**

| Polymers | $f_1$ | Time (h) | Yield (%) | Conductivity (S/cm) | |
|---|---|---|---|---|---|
| Polyanilines | 0 | | 68 | 5.0 | 0.5 |
| Poly(aniline-*co*-*o*-bromoaniline) | 0.1308 | | 80 | $12.80 \times 10^{-2}$ | $6.40 \times 10^{-4}$ |
| Poly(aniline-*co*-*o*-bromoaniline) (PABA-19) | 0.1983 | | 78 | $10.50 \times 10^{-2}$ | $5.32 \times 10^{-4}$ |
| Poly(aniline-*co*-*o*-bromoaniline) (PABA-29) | 0.2944 | | 75 | $6.60 \times 10^{-2}$ | $4.68 \times 10^{-4}$ |
| Poly(aniline-*co*-*o*-bromoaniline) (PABA-39) | 0.3926 | | 70 | $4.58 \times 10^{-2}$ | $3.34 \times 10^{-4}$ |
| Poly(*o*-bromoaniline) (POBA) | 1.0 | | 30 | $1.28 \times 10^{-8}$ | $1.14 \times 10^{-8}$ |

doped polymer was obtained by suspending the finely ground resultant polymer in 1*M* HCl and stirring for 4 h at room temperature followed by filtration. To prepare the base form, another portion of the finely ground polymer was suspended in a 0.1*M* NH$_4$OH solution, stirred for 6 h, and filtered.[11,19] The elemental analysis of the obtained polymer base gave C, 41.52%; H, 2.26%, N, 7.55%; Br, 45.07% (calcd for C$_{24}$H$_{14}$N$_4$Br$_4$: C, 42.47%; H, 2.06%; N, 8.25%; Br, 47.20%).[22]

MSA-doped polymers were prepared by adding 10–20% MSA to a finely ground emerldine base and stirring for 6 h at room temperature. The deep green resultant polymers were filtered, washed with methanol, and dried in a vacuum for 24 h.

### Synthesis of copolymer

Poly(aniline-*co*-*o*-bromoaniline) (PABA) copolymer feed ratios were synthesized chemically in an analogous manner to the homopolymers.[23,24] The reactions were carried out at 0–5°C. The experimental details are provided in Table I.

### Preparation of polymer film

Finely ground polymer emerldine base powder (PABA-19, 0.2 g) was added to 15 mL of NMP, stirred at room temperature for 2 h, and filtered.[25] The solution was then cast onto a clean glass plate and the solvent was allowed to evaporate at 50°C in a vacuum for 24 h. It was then placed in water and the film was
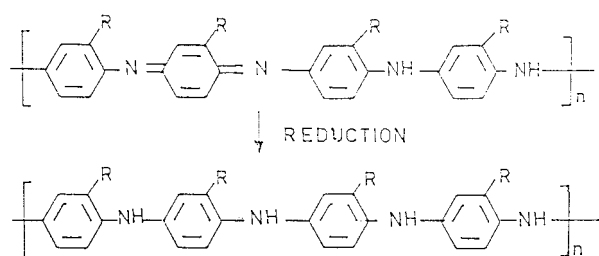


**Scheme 1** Reduction of poly(*o*-bromoaniline) with hydrazine dihydrochloride.

lifted off the glass. Finally, it was dried in a vacuum at room temperature for 48 h.

### Reduction

A leuco-base (POBA-R) of the homopolymer base powder was prepared by chemical reduction[26] (Scheme 1). A fine powder of POBA was suspended in an aqueous medium, hydrazine dihydrochloride (3.5 g) and sodium acetate (2.6 g) were added, and the mixture was refluxed for 24 h under nitrogen at 105°C. The reaction mixture was filtered and successively washed with methanol. A blackish polymer powder was obtained after drying at 50°C for 24 h, with an 82% yield.

### RESULTS AND DISCUSSION

Figure 1 represents the general structure of the homo- and the copolymer, where R = H and Br, and the value of *y* exhibits the oxidation state of the polymers as it varies from 0 to 1.[21] Since the bromine atom withdraws electrons and is also associated with a substantial steric effect, therefore *o*-bromoaniline should be less reactive than is aniline in the polymerization.[11] In elemental analysis, some discrepancies observed may be due to the presence of water molecules, free and bound in the polymers and associated with a certain percentage of extra carbon and oxygen, as indicated by XPS analysis.[2,27,28] Homo- and copolymer bases (PABA-39) show improved solubility in polar solvents such as THF, DMF, DMSO, and NMP and also in concentrated H$_2$SO$_4$ (96%) compared to the PAN base. MSA-doped polymers are moderately soluble in DMSO and NMP and mostly soluble in *m*-
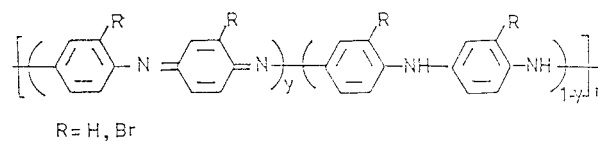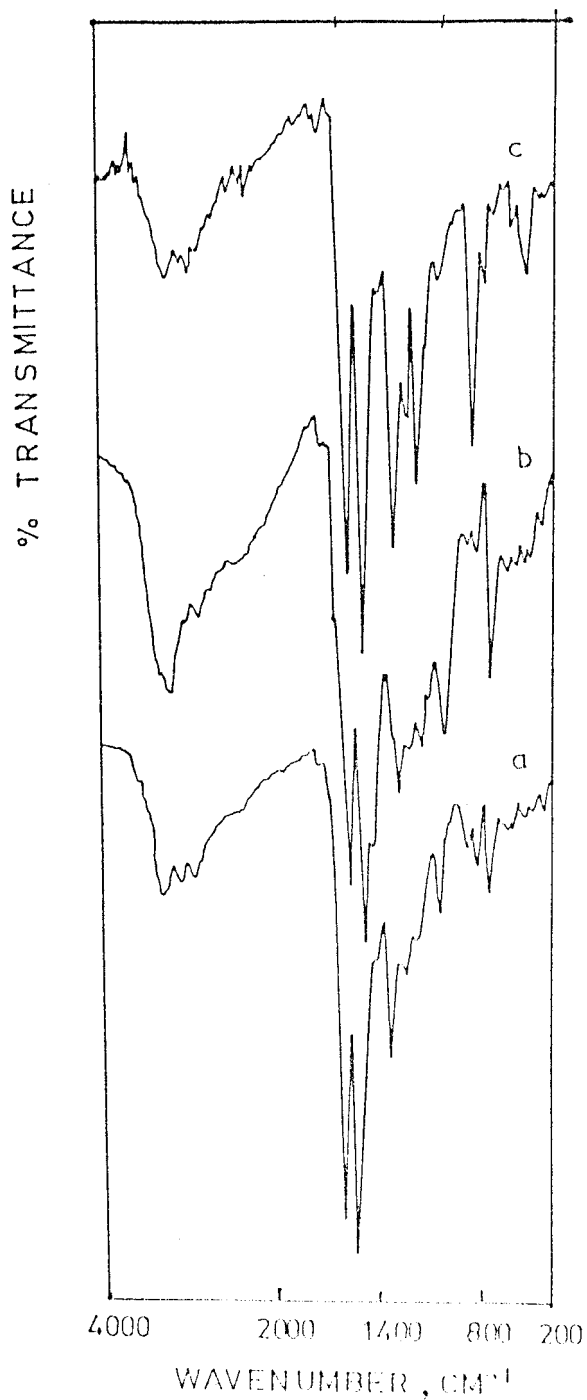


R = H, Br

**Figure 1** General structure of polymers.

**Figure 2** IR spectra of (a) POBA base, (b) reduced POBA base, and (c) PABA base-39.

cresol. The intrinsic viscosity values were measured in $H_2SO_4$ (96%) at 30°C. The data show that the intrinsic viscosity of POBA (0.080 dL/g) is too low compared to PABA-39 (0.39 dL/g), although the PAN base still exhibits a higher viscosity (0.57 dL/g). It can be concluded that the bulky and electron-withdrawing bromo substituent restricts the chain
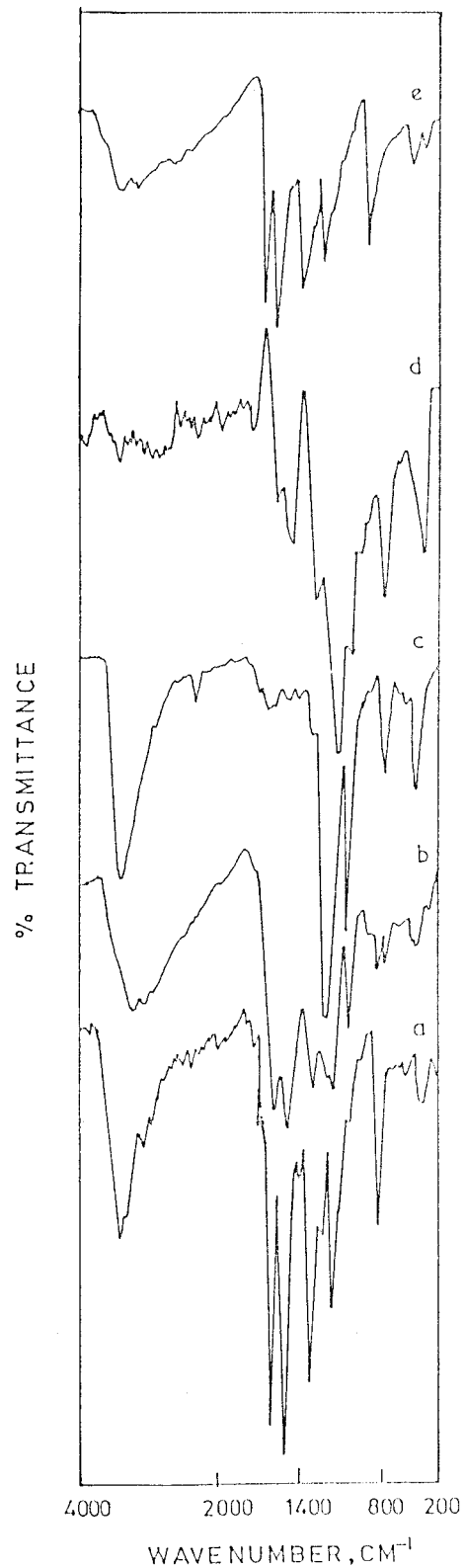


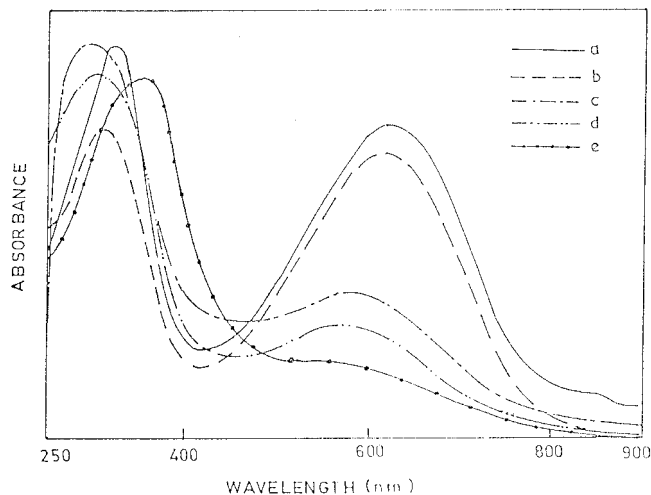**Figure 3** IR spectra of (a) PABA-19 film, (b) POBA–MSA, (c) PAN–MSA, (d) PABA–MSA-29, and (e) PABA–HCl-29.

**Figure 4** UV-v is spectra of (a) PABA base-19 film in NMP, (b) PABA base-39 in DMSO, (c) POBA–MSA in NMP, (d) POBA base in DMSO, and (e) reduced POBA in DMSO.

growth and results in a low molecular weight polymer.

The IR spectra of the polymers show (Figs. 2 and 3) the quinoid and benzoid stretchings at 1573–1590 and 1481–1499 cm$^{-1}$, respectively. The quinoid/benznoid intensity ratio, which may be taken as a measure of the oxidation level in the polymers,[17] decreases as expected [Fig. 2(b)], after POBA is reduced by hydrazine dihydrochloride (Scheme 1). Upon doping with sulfonic acid, the quinoid absorption band at 1590 cm$^{-1}$ and the N=Q=N stretch[29,30] at 1165 cm$^{-1}$ shift down-

ward by 20–30 cm$^{-1}$ [Fig. 3(C)] in the case of the PABA copolymers[31] and are absent in PAN–MSA [Fig. 3(d)], indicating a certain degree of conversion of quinoid to benzoid rings. Besides, quionoid and benzoid band intensities are almost equal (Fig. 3), indicating that protonation has been achieved. The expected symmetric S=O stretching band[32] of the sulfonic acid group at 1027–1058 cm$^{-1}$ is masked by the C—Br aromatic stretch at the same region. IR absorption at 820–1120 cm$^{-1}$ due to C—H in-plane and out-of-plane bending vibrations, corresponding to the 1,4- and 1,2,4-substituted benzene rings,[33] indicates that the polymers have head-to-tail coupling. The expected C—Br aromatic benzoid and quinoid stretch at 1027–1032 and 980 cm$^{-1}$ are exhibited by both POBA and PABA,[16] respectively, but are affected by heat treatment, as observed in the thermal analysis. In polymer film, the peak appearing in the IR at 1666 cm$^{-1}$ shifts by 16 cm$^{-1}$ from 1682 cm$^{-1}$ for the C=O group in NMP and the C—N stretching vibration shifts by 4 cm$^{-1}$. This may be due to a hydrogen-bonding interaction of the C=O group in NMP with the NH group of the polymer.[34]

The UV absorption spectrum of the POBA base [Fig. 4(d)] shows the $\pi$–$\pi$ and the "exciton" transitions at 311 and 584 nm, respectively, exhibiting significant blue shifts. These hypsochromic shifts in the copolymers increase with the proportion of *o*-bromoaniline (Fig. 4), indicating a substantial decrease in the degree of conjugation.
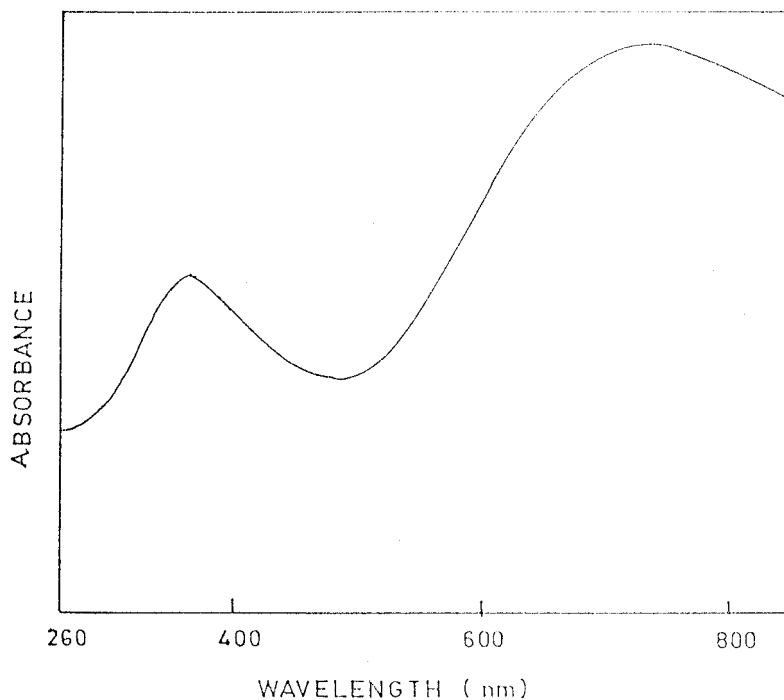


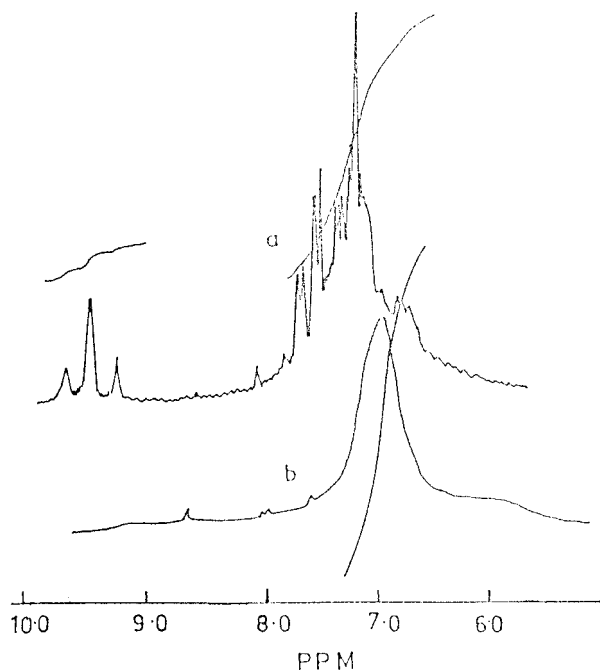**Figure 5** Reflectance spectra of PABA-19 film.

**Figure 6** ¹H-NMR spectra of (a) POBA base and (b) PABA base-39 in DMSO-$d_6$

In the reduced POBA base [Fig. 4(e)], considerable bathochromic shifts of $\pi-\pi^*$ absorption are also observed. The reflectance spectrum of PABA-19 film (Fig. 5) has a band at 361 nm due to the interband $\pi-\pi^*$ transition.[16] The strong absorption or reflection at 724 nm is associated with the conductivity in the oxidized polymer.[35] Upon doping PAN and PABA by MSA, four distinctive peaks appear at 310–323, 443–448, 573–628, and 856 nm in DMSO, indicating a more "coil-like" conformation and a localized polaron structure,[36,37] with DMSO acting as a poor solvent as far as the solute/solvent interaction is concerned. In $m$-cresol, the absorption at 430 nm and the free carrier tail above 800 nm in the IR region, consistent with an expanded coil-like conformation and a consequent delocalized polaronic structure, gradually decreased with an increasing fraction of the $o$-bromoaniline unit
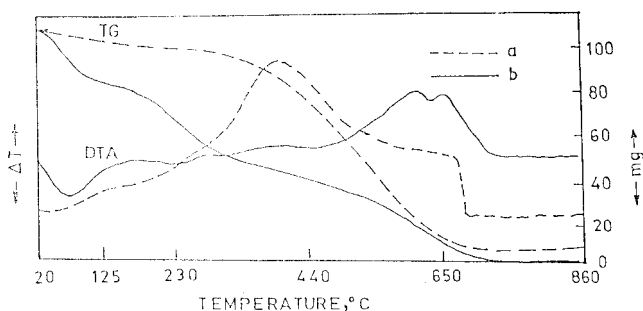


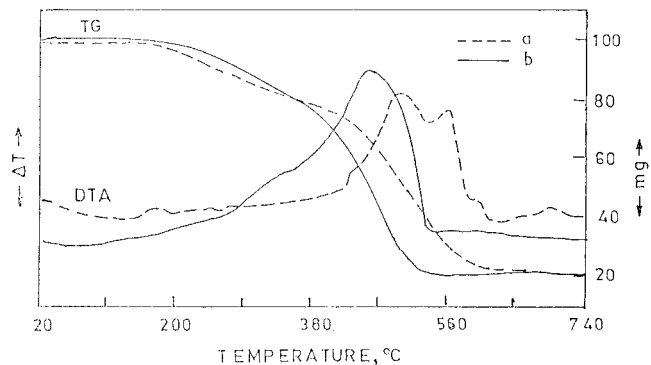**Figure 7** TG–DTA thermogram of (a) PAN–HCl and (b) PAN–MSA.



**Figure 8** TG–DTA thermogram of (a) POBA–HCl and (b) POBA–MSA.

in the copolymer backbone. There is, however, no change in the absorption pattern of the corresponding POBA–MSA homopolymer. It is possible that a high positive charge density and the resultant electrostatic repulsion induced by simultaneous protonation of imine and amine nitrogen sites of the polymer in $m$-cresol (acidic, highly hydrogen-bonding solvents) would promote an expanded coil conformation using MSA as the dopant. DMSO and NMP (only two peaks), however, being weak bases, would induce deprotonation of relatively weaker basic amine states.[38] POBA, on the other hand, has heavy pendent bromine atoms at closer intervals which could squeeze the polymer chain to a "compact coil-like" structure, irrespective of the solvent type and dopants.

## Spectral studies

The ¹H-NMR spectra are shown in Figure 6. The polymer has multiple and broad peaks at 7.00–7.56 ppm which have been assigned to aromatic protons of the homopolymer (POBA) and copolymer (PABA-39), respectively. A small hump appeared at the 6.78–6.98-ppm range for the $NH_4^+$ cation[32] and the signals in the
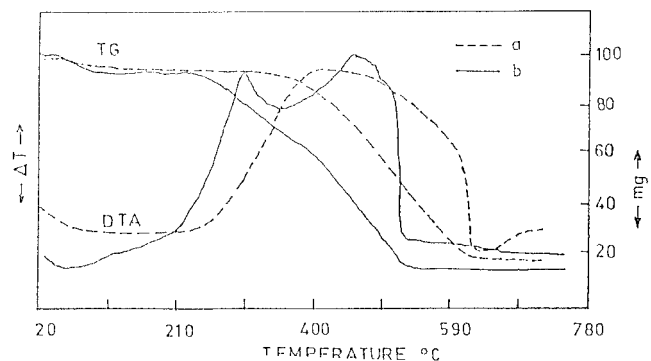


**Figure 9** TG–DTA thermogram of (a) PABA–HCl 19 and (b) PABA–MSD

**TABLE II**
**Thermal Degradation Parameters of Doped Polymers**

| Samples | Weight loss | | | Range of decomposition temperature (°C) | Maximum decomposition temperature (°C) |
|---|---|---|---|---|---|
| | 25–100°C | 150–300°C | 350–550°C | | |
| PAN–HCl | 6–7 | 6–7 | 58–60 | 100–560 | 430, 545 |
| PAN–MSA | 21–22 | 21–22 | 21–22 | 492–734 | 609, 654 |
| POBA–HCl | 0 | 18–20 | 40–45 | 430–620 | 500, 563 |
| POBA–MSA | 0–1 | 13–14 | 60–70 | 300–550 | 461 |

region of 8.82–8.88 ppm are assigned to the amine and imine protons.[38]

## Thermal studies

Thermal analysis patterns of the polymers show the relative thermal stability of the doped PAN, poly(*o*-bromoaniline), and the copolymer, respectively, in Figures 7–9. First, two stages of weight loss (Table II) can be attributed to the expulsion of the free and bonded water and dopant[3,26,39] and the final weight loss is due to the thermal degradation of the HCl-doped polymers and the homopolymer POBA–HCl shows maximum thermal stability. Bromine retention is large compared to the copolymer, indicated by the presence of the C—Br band in the IR spectra of the polymer after heat treatment 350°C, before the onset of final degradation. In the copolymer PABA–HCl, a significant decrease in the intensity ratio of quinoid-to-benzoid IR stretching peaks and the disappearance of the N=Q=N stretch indicate crosslinking through conversion of the quinoid rings to the benzoid rings.[40–42]

Among all the doped polymers studied here, the MSA-doped (PAN–MSA) shows a maximum decomposition temperature (609, 654°C) and a minimum weight loss, prior to the final degradation [Fig. 8(b)]. This significant thermal stability of PAN–MSA may be rationalized by the proposed structure in Figure 10. Sulfonic acid units may interact with amine/imine hydrogens, whose electropositivity are enhanced in the doped polymers. The impairing of such interactions by shielding, due to intervening large bromine atoms, may be the reason for the lower stability of POBA–MSA and PABA–MSA. It is significant that POBA–MSA shows single-stage degradation, unlike its copolymer, PABA–MSA. POBA–HCl, however, undergoes two competing degradation steps as shown by the overlapping peaks of the derivatograph [Fig. 9(b)]. This could be due to the loss of bromine in stages in POBA–HCl, which was seen to be more stable toward bromine loss, compared to its copolymer. It is thus apparent, that doping by MSA profoundly affects the thermal stability-related characteristics of PANs, without causing significant changes in the

primary structural pattern, as is evident from the results of the IR and electronic spectral analyses in this work.
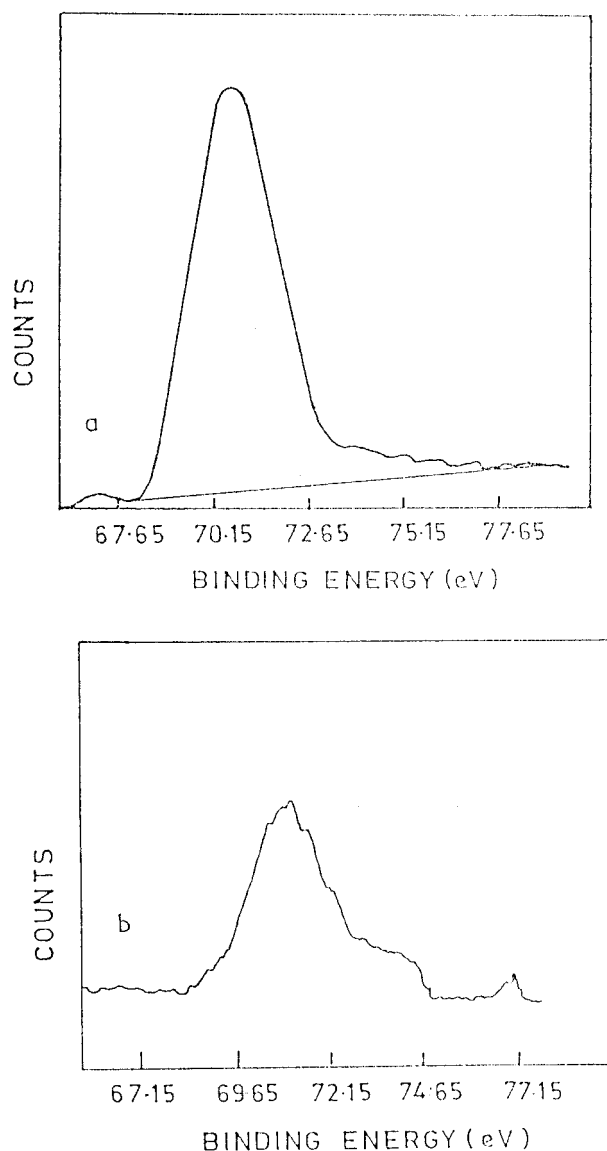


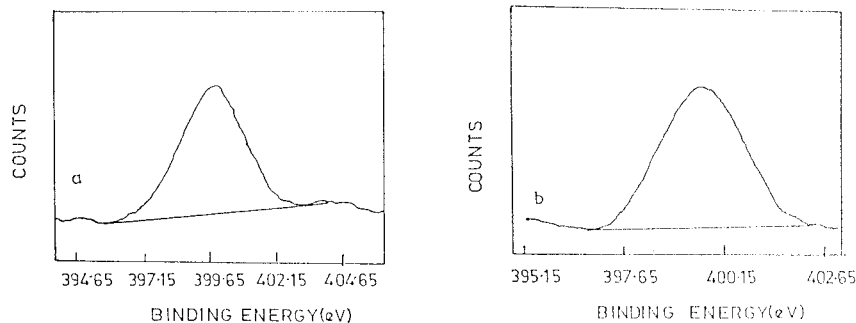**Figure 10** Cl*s* XPS spectra of (a) POBA base and (b) PABA base-19.

**Figure 11** Br3*d* XPS spectra of (a) POBA-base and (b) PABA-base-19.

## XPS studies

The binding energy values of the XPS core-level spectra of the POBA and PABA polymer bases for C1*s*, Br3*d*, and NI*s* (Figs. 10–12) are given in Table III. The absence of a residual low binding energy tail corresponding to the anionic bromine[15] in Figure 12 shows that the bromine is mainly covalently bonded. In addition to the elements of polybromoaniline, oxygens (O1*s* peak) were incorporated during oxidative binding energy in the range of 531–541 ev.[28] The Nl*s* spectra of the polymer bases consist of a symmetric peak in range 396–402 eV.

The conductivity of poly(*o*-bromoaniline) (Table I) is about as low as that of poly-(*o*-chloroaniline),[42,43] even with the use of MSA as the dopant. This is expected, because the large size of the bromine atom causes a significant torsional imbalance, hampering the $\pi-\pi^*$ congregation. MSA doping increases the conductivity of the copolymer $10^2-10^3$ times, which increases with the increase in the proportion of aniline.

## CONCLUSIONS

A homopolymer and a copolymer based on *o*-bromoaniline and aniline were synthesized by oxidative coupling using persulfate as the oxidant. The resultant polymers of *o*-bromoaniline have better solubility in common organic solvents and are easily processible. The ESCA studies indicated that the carbon–bromine bond in the polymer has a covalent character. IR data of the homopolymer (POBA) and the copolymer (PABA) after heal treatment indicated increased stability and bromine retention in the homopolymer, in spite of the deactivating influence induced by the large bromine atom. The electronic spectra of the doped polymer showed nonhomogeneous doping, with the electronic absorptions corresponding to the protonated and unprotonated segments. The oxidation level is lower in the homopolymer compared to the copolymers and is still lower for the reduced POBA polymer. The presence of residual quinoid diimine units in the reduced homopolymer indicate an intrinsic level of oxidation.[26] MSA doping enhances the thermal stability of the polymers, with PAN–MSA being most stable of all the polymers studied. The conductivity of PAN and its copolymers with bromoaniline shows marked enhancement after doping by MSA. Doping by MSA evidently influences the thermal stability and conductivity patterns without inducing significant changes in the primary structural character of these polymers.
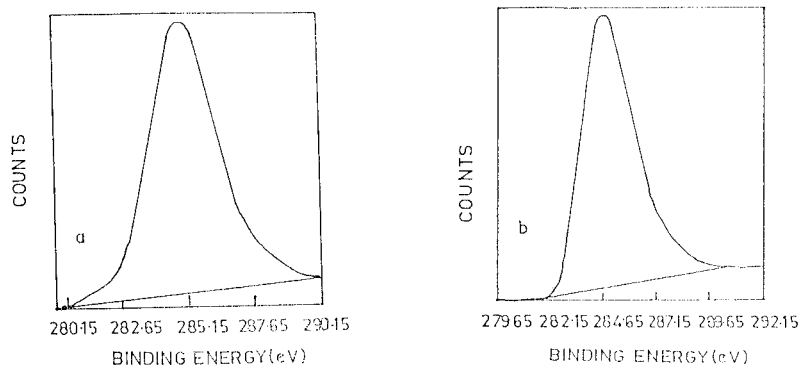
**Figure 12** Nl*s* XPS spectra of (a) POBA-base and (b) PABA-base-19.

**TABLE III**
**XPS Binding Energies for Cl*s*, Nl*s*, and Br3*d* Core Levels of Polymers**

| Sample | Cl*s* (eV) | | | Nl*s* (eV) | | | Br3*d* (eV) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Range | Center | fwhm | Range | Center | fwhm | Range | Center | fwhm |
| POBA | 280.65–289.40 | 285.00 | 2.91 | 397.40–402.20 | 399.45 | 2.30 | 67.15–76.40 | 70.80 | 2.55 |
| PABA-19 | 282.15–289.65 | 285.00 | 2.90 | 396.41–402.65 | 399.85 | 2.57 | 67.15–74.65 | 70.80 | 2.40 |

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