

Synthesis and Characterization of Conducting Poly(aniline-*co*-diaminodiphenylsulfone) Copolymers

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ABSTRACT: Polyaniline, poly(aniline-*co*-4,4'-diaminodiphenylsulfone), and poly(4,4'-diaminodiphenylsulfone) were synthesized by ammonium peroxydisulfate oxidation and characterized by a number of techniques, including infrared spectroscopy, ultraviolet-visible absorption spectroscopy, ¹H-NMR, thermogravimetric analysis, and differential scanning calorimetry. These copolymers had enhanced solubility in common organic solvents in comparison with polyaniline. The conductivities of the HCl-doped polymers ranged from 1 S cm⁻¹ for polyaniline to 10⁻⁸ S cm⁻¹ for poly(4,4'-diaminodiphenylsulfone). The copoly-

mer compositions showed that block copolymers of 4,4'-diaminodiphenylsulfone ($r_1 > 1$) and aniline ($r_2 < 1$) formed and that the reactivity of 4,4'-diaminodiphenylsulfone was greater than that of aniline. The results were explained by the effect of the —SO₂— group present in the polymer structure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2337–2347, 2003

Key words: copolymerization; infrared spectroscopy; synthesis; thermogravimetric analysis (TGA)

INTRODUCTION

Polyaniline has attracted considerable attention because of its high electrical conductivity, environmental stability, and unique electrical and optical properties. However, the difficulty in processing it, due particularly to its instability at the melt-processing temperature and its insolubility in common organic solvents, has necessitated exploring other methods to minimize or eliminate these problems. Improved solubility has been achieved to some extent by suitable substitution on the polymer backbone structure, such as alkyl, aryl, or other groups in the benzene ring, but the electrical conductivity simultaneously decreases to a considerable extent.^{1–6} For example, poly(*o*-ethoxyaniline),^{5,7} poly(*o*-methoxyaniline),^{6,8} and poly(*o*-anthranilic acid)⁹ were reported to be water-soluble but to have reduced electrical conductivity (cf. 10⁻⁴ and 10⁻⁸ S cm⁻¹, respectively). Similarly, poly(*o*-toluidine), poly(*m*-toluidine), and poly(*o*-ethylaniline) showed improved solubility in common organic solvents in comparison with polyaniline, but the electrical conductivities were

10⁻¹ to 10⁻² S cm⁻¹ for polytoluidines and 10⁻⁵ S cm⁻¹ for poly(*o*-ethylaniline).^{10–12}

The fulfillment of the objective of higher conductivity and improved solubility characteristics has been achieved to an appreciable extent through copolymerization. Copolymers of aniline with *o*- or *m*-toluidine, *N*-butylaniline, *o*-anisidine, *o*-aminobenzyl alcohol, or *o*-anthranilic acid showed improved solubility and better electrical conductivity than ring-substituted polyaniline.^{8–11} Doped poly(aniline-*co*-toluidine) and poly(aniline-*co*-*o*-anthranilic acid) showed electrical conductivities of 10⁻¹ to 10 S cm⁻¹ and 10⁻⁸ to 10⁻² S cm⁻¹, respectively.^{9–11} However, in comparison with the homopolymer of aniline, these copolymers had somewhat lower molecular weights. The molecular weights of poly[aniline-*co*-*N*-(4-sulfophenyl)aniline] and poly(aniline-*co*-anthranilic acid) decreased with an increase in the *N*-(4-sulfophenyl)aniline and anthranilic acid contents in the copolymers.^{9,13}

Thermal stability is an important feature for the processability of polyaniline because it affects solubility at room temperature.¹² A study on the thermal stability of copolymers showed either a decrease or equal stability in comparison with polyaniline. The decomposition temperature of poly(aniline-*co*-*o*-ethylaniline) decreased with increasing *o*-ethylaniline content.¹² The thermal stability of poly(aniline-*co*-anthranilic acid) remained almost the same as that of polyaniline.⁹

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To overcome these difficulties in processing, solubility, and thermal stability, we attempted the chemical copolymerization of aniline and 4,4'-diaminodiphenylsulfone (DADPS), and we report the findings here.

EXPERIMENTAL

Materials and equipment

Aniline purchased from E. Merck and DADPS purchased from Ciba Geigy, Ltd., were used as monomers. Aniline was distilled twice under reduced pressure before polymerization, and DADPS was recrystallized from ethanol. Ammonium peroxydisulfate was purchased from S.D. Fine Chemicals, Ltd., and was used as an oxidant. Solvents such as *N*-methylpyrrolidone (NMP), tetrahydrofuran, dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) were reagent-grade chemicals and were obtained from S.D. Fine Chemicals. All the solvents were used as purchased. Concentrated HCl and aqueous NH₄OH solutions (25%) were analytical-reagent-grade and were obtained from S.D. Fine Chemicals.

The sulfur content of the polymer samples was analyzed by the oxygen flask method. The ultraviolet-visible (UV-vis) spectra of the polymers were recorded on a Hitachi UV-vis double-beam, double-monochromator spectrometer (model U3200) at the wavelengths of 250–800 nm with NMP as the solvent. The infrared (IR) spectra of the polymers were recorded on KBr pellets on a PerkinElmer Fourier transform infrared (FTIR) spectrometer (model 1600) with 16 scans at a resolution of 4 cm⁻¹. The ¹H-NMR spectra of the polymers in deuterated dimethyl sulfoxide (DMSO-*d*₆) were recorded on a JEOL JNM-100 spectrometer with tetramethylsilane as an internal standard. The polymers were subjected to thermal degradation studies on a PerkinElmer 7 series thermal ana-

lyzer system fitted with a data station. The analysis were carried out from 50 to 650°C at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. Finely divided samples of about 10 mg were used. Differential scanning calorimetry (DSC) studies of the polymer were performed on a PerkinElmer DSC-7. The analyses were carried out from room temperature to 300°C at a linear rate of 10°C min⁻¹ under a nitrogen atmosphere. Finely divided samples of about 5 mg were used. The electrical conductivity of the doped polymers was measured at room temperature by the collinear four-probe technique. A digital four-probe setup (DFP-2) was used for this measurement. The polymers tested were in the form of compacted disk pellets 12.7 mm in diameter and approximately 0.5 mm thick.

Synthesis

Polyaniline was synthesized in a dilute (1M) HCl medium at 0–2°C with (NH₄)₂S₂O₈ as the oxidant, as described in the literature.¹⁴ Copolymers of aniline and DADPS were synthesized by chemical oxidation with (NH₄)₂S₂O₈ as an oxidant in an HCl medium at approximately 2°C. The molar fraction of DADPS in the reaction mixture was varied from 0.25 to 0.75. The molar ratio of the monomer to the oxidant was kept at 1 in every case. A typical copolymerization procedure was as follows: 50 mL of a 1.2M HCl solution containing 4.88 g (0.0214 mol) of (NH₄)₂S₂O₈ was slowly added to a 100-mL 1.2M HCl solution containing 1 mL (0.0107 mol) of aniline and 2.69 g (0.0107 mol) of DADPS with constant stirring at approximately 2°C. The reaction mixture was stirred at approximately 2°C for 4 h. The polymer was collected by filtration, washed with 1.2M HCl until the filtrate was colorless, and then washed with methanol. The solid polymer was dried under a dynamic vacuum at 50°C. Poly(4,4'-

TABLE I
Variation of the Yield of the Copolymerization Reaction with the Reaction Time

Sample	[Aniline] (mol L ⁻¹ × 10 ²)	[DADPS] (mol L ⁻¹ × 10 ²)	<i>f</i> ₁	Reaction time (h)	Yield (%)
I	5.35	1.75	0.25	1	36
				4	62
				24	61
II	5.35	2.65	0.33	1	39
				4	60
				24	59
III	2.65	2.65	0.50	1	10
				4	52
				24	51
IV	2.65	5.35	0.66	1	8
				4	35
				24	33
V	2.65	8.00	0.75	4	4
				24	26

diaminodiphenylsulfone) [poly(DADPS)] was prepared in the same manner at approximately 2°C with a 24-h reaction time.

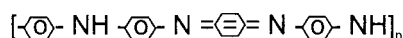
The base forms of the polymers were obtained by the stirring of 1 g of the as-synthesized polymer in 160 mL of a 3% aqueous NH₄OH solution for 4 h at room temperature. The solid was then filtered, washed with distilled water until free from NH₄OH, and dried at 50°C under a dynamic vacuum. The base forms of the polymers were equilibrated with constant stirring for 4 h in dilute HCl solutions (1M) to obtain the acid forms of the polymers.

The solubility of the copolymers (g/mL) was measured by the addition of 0.1 g of a polymer sample to 10 mL of a solvent and subsequent stirring for 24 h.

The dissolved amount of the sample was measured by a gravimetric method after filtration through a sintered bed crucible.

RESULTS AND DISCUSSION

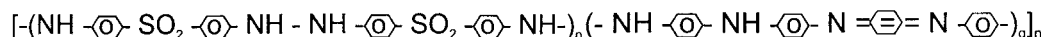
Copolymers of aniline and DADPS of various ratios were chemically synthesized to form poly(aniline-*co*-diaminodiphenylsulfone) [poly(aniline-*co*-DADPS)], in which the molar fraction of DADPS in the monomer feed mixture (f_1) was varied from 0.25 to 0.75. The copolymers were obtained as dark green powders, and the homopolymer of DADPS was obtained as a dark brown powder. The general structure for polyaniline is



The general structure for poly(DADPS) is

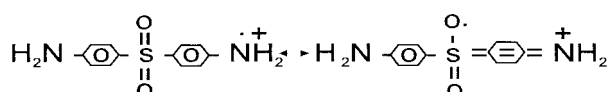


The general structure for poly(aniline-*co*-DADPS) is



The poly(aniline-*co*-DADPS) copolymers were recovered in 24–62% yields depending on the DADPS content, and the homopolymers polyaniline and poly(DADPS) were recovered in 75 and 24% yields, respectively. The results of the effect of the reaction time on the yield of the copolymerization reaction are presented in Table I.

The yield of the copolymerization reaction decreased with an increase in the DADPS content in the monomer feed mixture and attained a maximum value at a reaction time of 4 h, except when f_1 was 0.75. The results may be explained by the strong electron-withdrawing inductive effect of sulfone group —SO₂—, which attracted the lone pair of electrons on the —NH₂ group and, therefore, reduced the availability of these electrons in the polymerization reaction. The lower reactivity of the DADPS monomer could also arise because of resonance effects and steric effects. The radical cation formed by the oxidation of the DADPS monomer was resonance-stabilized by the electron-withdrawing mesomeric effect of the —SO₂— group:



The presence of the bulky —SO₂PhNH₂ group at the position para to the —NH₂ group imposed steric hindrance toward the addition of another radical cation of its own type at the position ortho to the —NH₂ group.

The copolymer composition was calculated by the estimation of the amount of sulfur present in the copolymer. As the rates of homopolymerization for the two monomers were quite different, there could have been a drift in the copolymer composition as the degree of conversion was increased. To avoid this problem, we always kept the degree of conversion below 10%. An analysis of the copolymer with various monomer feed compositions is given in Table II.

For each of the copolymers made, the molar composition of DADPS in the copolymer (F_1) was plotted

TABLE II
Effect of the Monomer Feed Composition on the Copolymer Composition

f_1	F_1
0.80	0.93
0.66	0.68
0.50	0.67
0.33	0.57
0.25	0.48
0.20	0.47

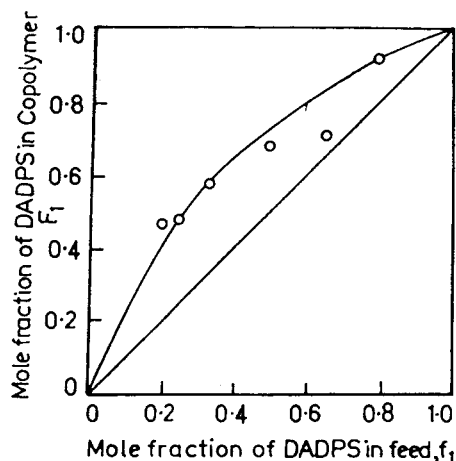


Figure 1 F_1 versus f_1 .

against that of DADPS in the monomer feed mixture (f_1), as shown in Figure 1. The diagonal line represents the identical reactivities of the two monomers, which yielded a copolymer with a composition equivalent to the feed mixture. All the data points are above this diagonal line, and this indicates that DADPS had a higher reactivity ratio than aniline. The monomer reactivity ratios, r_1 and r_2 (where monomer 1 is DADPS and monomer 2 is aniline), were calculated with the simplified Fineman-Ross equation:¹⁴

$$\frac{F(f-1)}{f} = \frac{r_1 F^2}{f} - r_2 \quad (1)$$

where F and f are the molar ratios of monomers 1 and 2 in the initial monomer feed and copolymer, respectively. The plot of $F(f-1)/f$ versus F^2/f , as shown in Figure 2, is linear. The r_1 and r_2 values, determined from the slope and intercept of the straight line produced by eq 1, were 3.5 for DADPS and 0.5 for aniline.

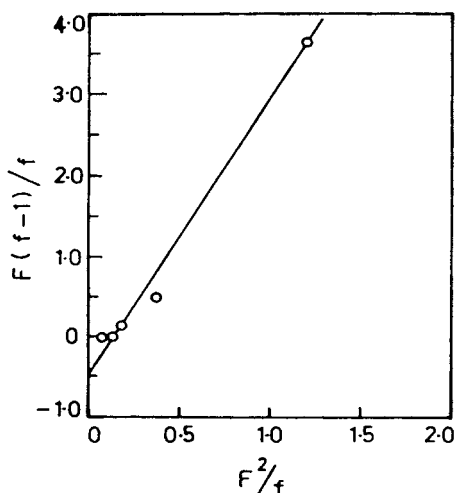


Figure 2 Determination of r_1 and r_2 by the slope intersection method (with the simplified Fineman-Ross equation).

TABLE III
Solubility of the Homopolymers and Copolymers
in Different Solvents

F_1	Solubility (g/10 mL)		
	DMF	DMSO	NMP
0.00	0.0088	0.0060	0.0350
0.48	0.0204	0.0240	0.0368
0.57	0.0280	0.0380	0.0560
0.67	0.0560	0.0602	0.0700
0.93	0.0812	0.0978	0.0920
1.00	0.1000	0.1000	0.1000

These values indicated that the DADPS monomer was more reactive in the copolymerization than aniline. However, the rate of homopolymerization of aniline was much higher than that of DADPS.

Reactivity ratios are related to the ability of a monomer to react in a copolymerization, which, in turn, is dependent on the steric factor, resonance stabilization, and polarity of the monomer. This study revealed that for a copolymer of aniline and DADPS, the steric factor played an important role. The steric hindrance between *p*-substituted $-\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$ groups on the attacking DADPS radical cation and on the DADPS monomer was responsible for its lower reactivity in the homopolymerization. The higher reactivity of the DADPS monomer toward copolymerization with aniline might have been due to a lack of the *p*-substituent on the attacking anilinium radical cation. As the value of the product of r_1 and r_2 was greater than 1, it is likely that the formation of the block copolymer occurred with long blocks of DADPS and short blocks of aniline. Earlier findings also showed the formation of block copolymers when aniline was copolymerized with *o*-toluidine, *m*-toluidine, *N*-butylaniline, or *o*-ethylaniline in HCl solutions.¹⁰⁻¹²

The improved solubility of the copolymers was observed by the direct comparison of the copolymers in various organic solvents. Equal amounts of the copolymers (0.10 g) were added to 10 mL of each of the following solvents: DMF, DMSO, and NMP. Table III summarizes the solubility behavior of the homopolymers and copolymers in these solvents. The improved solubility of the copolymers in organic solvents appeared to be related to the incorporation of polar sulfone group in the copolymer backbone. The soluble fraction in NMP formed films on evaporation.

The homopolymerization of the DADPS monomer into a polymer was indicated by the variation of the N—H stretching pattern at $3500\text{--}3300\text{ cm}^{-1}$ and the N—H in-plane bending and C=C stretching pattern at $1700\text{--}1500\text{ cm}^{-1}$ (Fig. 3). On polymerization, the sharp absorption peaks at 3454 and 3335 cm^{-1} for aromatic asymmetric and symmetric N—H stretching of the primary $-\text{NH}_2$ group, respectively, in IR spectra of the DADPS monomer (Fig. 3) were replaced by

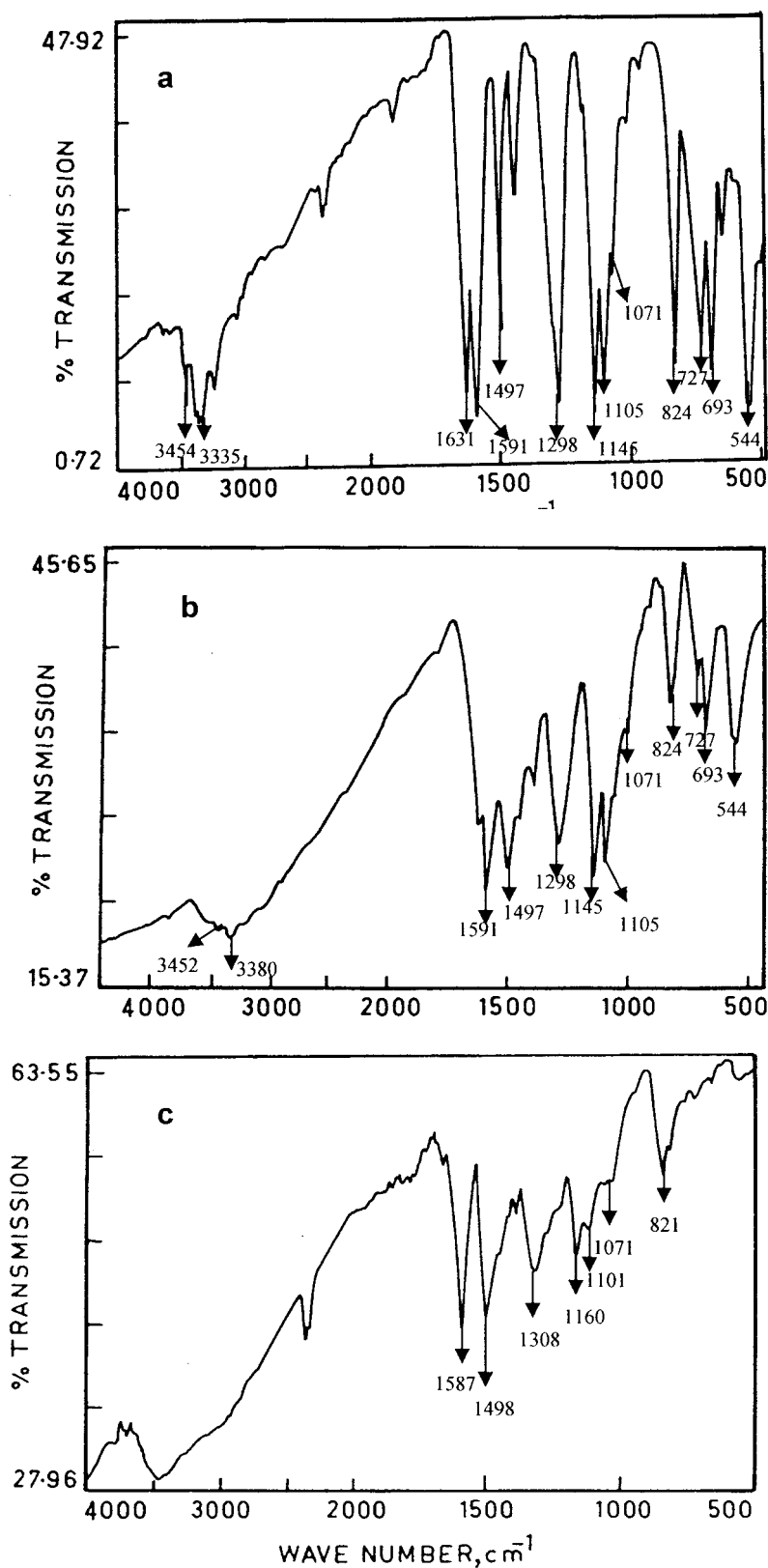


Figure 3 FTIR spectra of (a) the DADPS monomer, (b) poly(DADPS), and (c) polyaniline.

peaks for secondary aromatic N—H stretching at 3380 cm^{-1} along with primary aromatic N—H stretching at 3452 cm^{-1} . The intensity of the peak at 1631 cm^{-1} ,

attributed to N—H in-plane bending of the primary —NH₂ group, decreased to a considerable extent on polymerization as the intensity of the peak for N—H

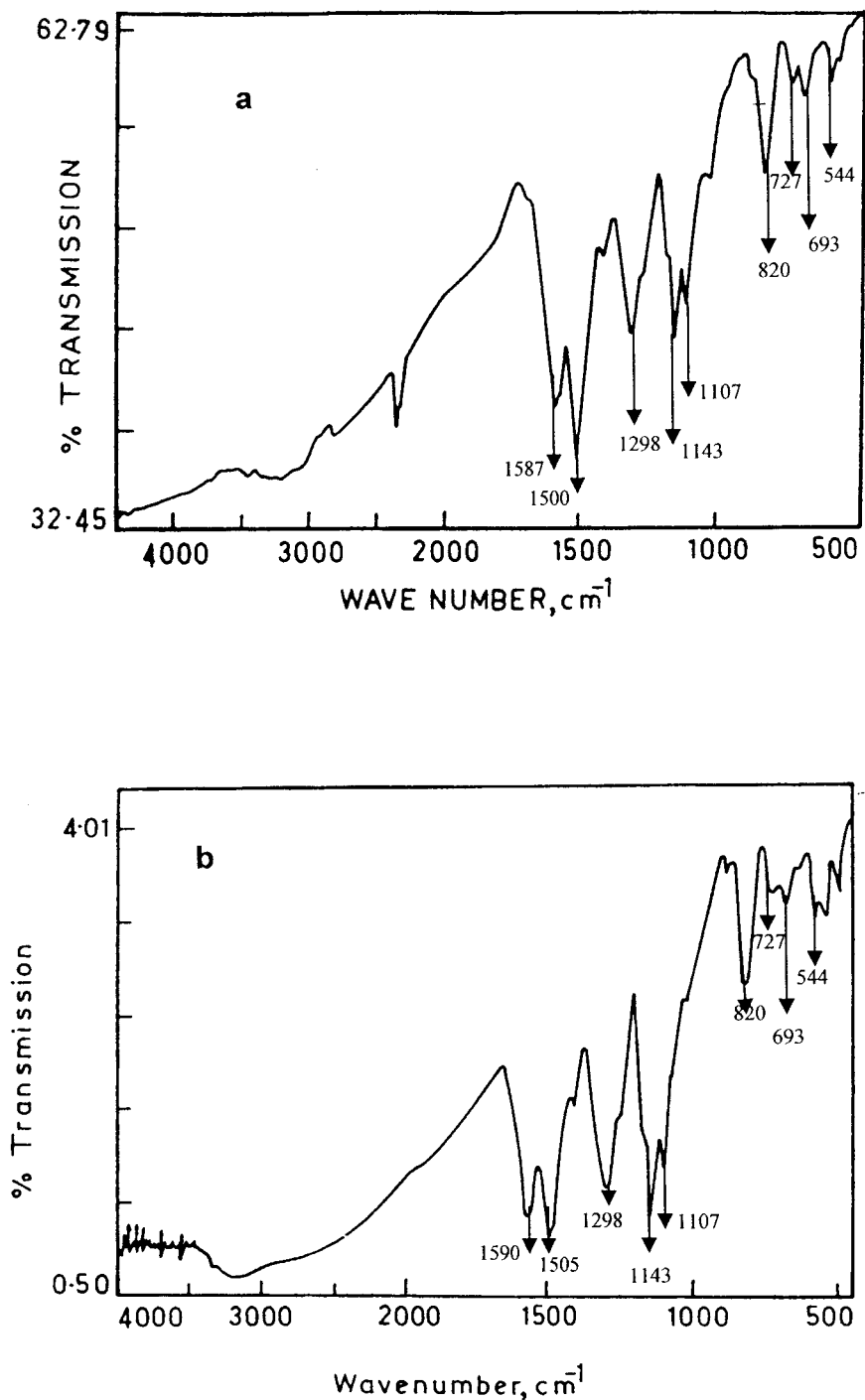


Figure 4 FTIR spectra of poly(aniline-co-DADPS): (a) base form and (b) acid form.

in-plane bending of the secondary aromatic amine was very weak. All the other absorption peaks for aromatic C=C stretching at 1591 and 1497 cm^{-1} , for asymmetric and symmetric S=O stretching at 1298 and 1145 cm^{-1} , respectively, for C—H in-plane bending at 1105 and 1071 cm^{-1} , for C—H out-of-plane bending at 824, 727, and 693 cm^{-1} , and for S=O bending at 544 cm^{-1} were common in both cases. The absence of any peak in the 885–870- cm^{-1} region for

poly(DADPS) indicated that 1,2,4-trisubstitution did not occur. FTIR spectra of both the homopolymers (Fig. 3) and the copolymer in its base form (Fig. 4) showed a broad absorption band centered between 3300 and 3400 cm^{-1} that was due to N—H stretching vibrations. The relative intensity of the quinoid ring ($=\text{E}=\text{E}$) stretching at 1587 cm^{-1} to the benzenoid ring ($\text{$\text{C}=\text{C}$$) stretching at 1498 cm^{-1} ^{8,14,16} was equal in the polyaniline base, whereas poly(DADPS) showed rela-

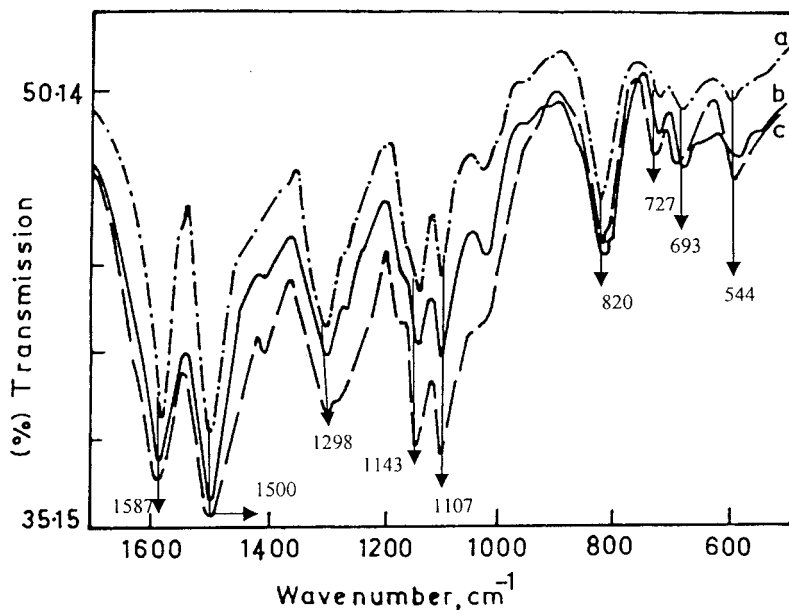


Figure 5 FTIR spectra of the base forms of the copolymers with (a) $F_1 = 0.48$, (b) $F_1 = 0.57$, and (c) $F_1 = 0.67$.

tively greater intensity for quinoid ring stretching at 1587 cm^{-1} in comparison with benzenoid ring stretching at 1500 cm^{-1} . The relative intensity of quinoid ring stretching compared with that of benzenoid ring stretching increased as the DADPS content decreased in the copolymer (Fig. 5), and this indicated that the amount of the quinoid moiety increased as the aniline content in the copolymer increased. For each copolymer, the absorption peaks for both C—N stretching and S=O asymmetric stretching appeared at the same wave-number region (ca. 1298 cm^{-1}). The incorporation of the DADPS moiety in the copolymer was indicated by the appearance of the characteristic absorption peak for symmetric S=O stretching at 1143 cm^{-1} as the absorption peak for asymmetric S=O stretching was masked by C—N stretching. As the DADPS content in the copolymer increased the relative intensity

of the peak for S=O stretching increases (Fig. 5). The spectra of the copolymers did not show any peak at 1160 cm^{-1} , the characteristic mode of N=Q=N vibrational stretching^{17,18} (where Q denotes a quinoid ring) in polyaniline, which may be masked by the strong absorption peak for S=O stretching. With the HCl doping of the copolymer, the intensity of the peaks at $1150\text{--}1100\text{ cm}^{-1}$ increased to a considerable extent in comparison with its base form, that is, its dedoped form (Fig. 4). Polyaniline showed similar behavior^{19,20} on doping, and this indicated the presence of an aniline moiety in the copolymer. The copolymer spectra also showed a peak around 820 cm^{-1} ascribed to C—H out-of-plane bending, which indicated a para-substitution pattern of the benzene ring. The intensity

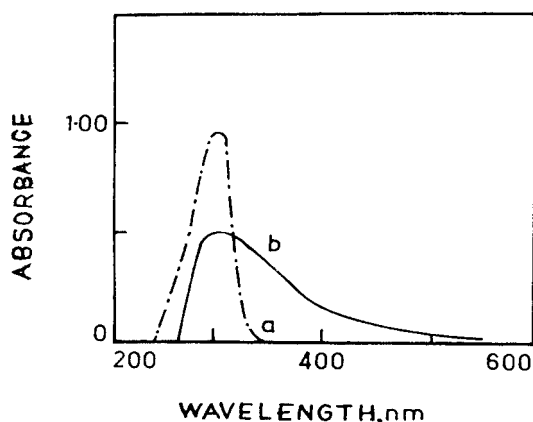


Figure 6 UV-vis spectra of (a) the DADPS monomer and (b) poly(DADPS) in NMP.

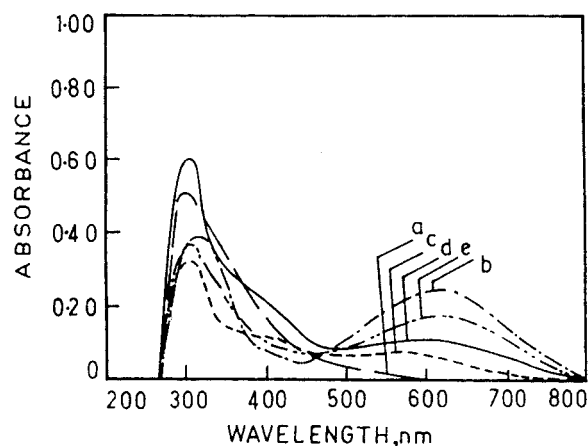


Figure 7 UV-vis spectra of the base forms of (a) poly(DADPS), (b) polyaniline, (c) the copolymer with $F_1 = 0.67$, and (d) the copolymer with $F_1 = 0.57$.

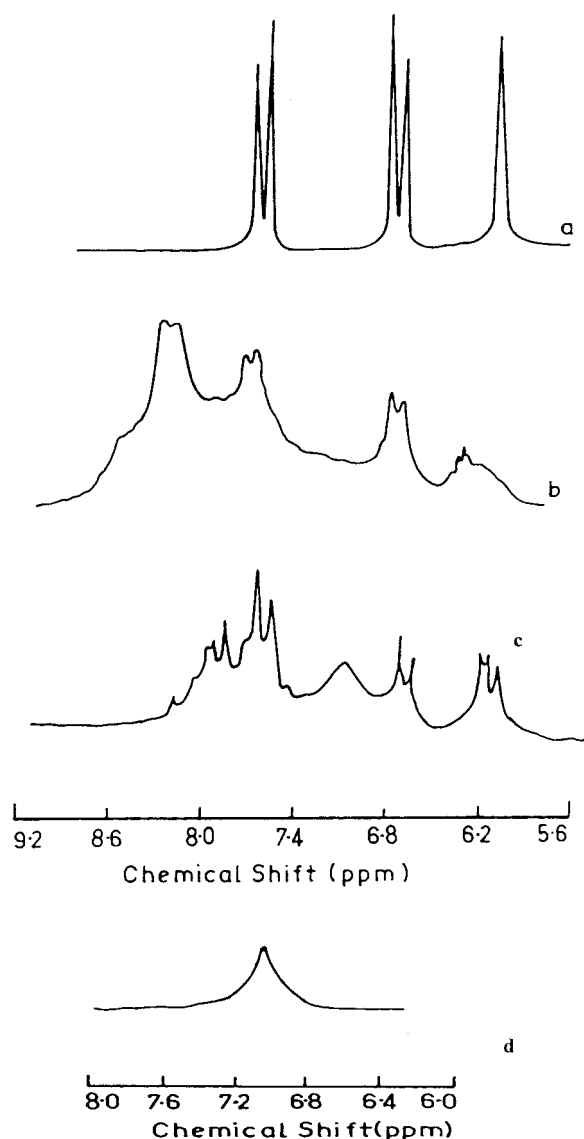


Figure 8 $^1\text{H-NMR}$ spectra of (a) the DADPS monomer, (b) poly(DADPS), (c) poly(aniline-co-DADPS), and (d) polyaniline in $\text{DMSO-}d_6$.

of the peaks for C—H out-of-plane bending at 727 and 693 cm^{-1} and S=O bending at 544 cm^{-1} , which were characteristic for poly(DADPS), decreased with an increase in the number of aniline units in the copolymer.

The UV-vis spectra of the DADPS monomer in Figure 6 show an absorption peak at 303 nm assigned to the $\pi-\pi^*$ transition of the benzenoid ring. The UV-vis spectra of the poly(DADPS) base form do not show any shift in the position of the peak for the $\pi-\pi^*$ transition, as shown in Figure 6. This indicates that the level of conjugation did not increase to any substantial extent with polymerization. The absence of any absorption band at the 600-nm region indicates that there was no intrachain or interchain charge transfer taking place along the polymer backbone. The UV-vis spectra of the polyaniline base form in Figure 7 show

both major absorption peaks at 324 and 625 nm, as reported earlier.^{8,14,16,21,22} The 324-nm peak, assigned to the $\pi-\pi^*$ transition, was related to the extent of conjugation between adjacent phenyl rings in the polymer chain,²³ whereas the band at 625 nm was a measure of extended conjugation, corresponding to the exciton transition caused by interchain or intrachain charge transfer.²⁴⁻²⁶ The UV-vis spectra of the copolymers in their base forms (Fig. 7) show the $\pi-\pi^*$ transition for the benzenoid rings in the copolymer backbone around 307 nm. The exciton band for these copolymers shifted hypsochromically from 619 to 544 nm as the percentage of the DADPS content in the copolymer increased from 48 to 67. For a copolymer with 57% DADPS content, the absorption band for exciton transition appeared at 597 nm. However, the exciton band disappeared for a copolymer with 93% DADPS content. As the position of the exciton band was dependent on the distribution of benzenoid and quinoid rings,²⁷ the blueshift of this band with increasing DADPS content in the copolymer implied a decrease in the conjugation length along the copolymer backbone.^{13,23,28}

The $^1\text{H-NMR}$ spectra of the DADPS monomer, poly(DADPS), polyaniline, and poly(aniline-co-DADPS) ($F_1 = 0.67$) in the base form are shown in Figure 8. The DADPS monomer showed two sharp doublets at 6.5–6.7 and 7.4–7.8 ppm, which were assigned to aromatic protons ortho to $-\text{NH}_2$ and $-\text{SO}_2-$ groups, respectively, and one singlet at 6 ppm assigned to the aromatic amine protons. Poly(DADPS) showed two multiplets at 7.8–8.4 and 5.8–6.4 ppm, which were assigned to aromatic protons and amine protons, respectively, present in the polymer backbone. In addition, there were two doublets at 6.5–6.7 and 7.4–7.8 ppm, which were assigned to aromatic protons on the terminal $-\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$ group. These resonances were broader because of the higher molecular weight of poly(DADPS) compared with that of the DADPS monomer. The $^1\text{H-NMR}$ spectra of the polyaniline base form show a multiplet at 6.8–7.4 ppm, which was assigned to aromatic²⁹ and amine protons.³⁰ The base form of poly(aniline-co-DADPS)

TABLE IV
Electrical Conductivity and Onset Temperature of the Thermal Degradation of the Homopolymers and Copolymers

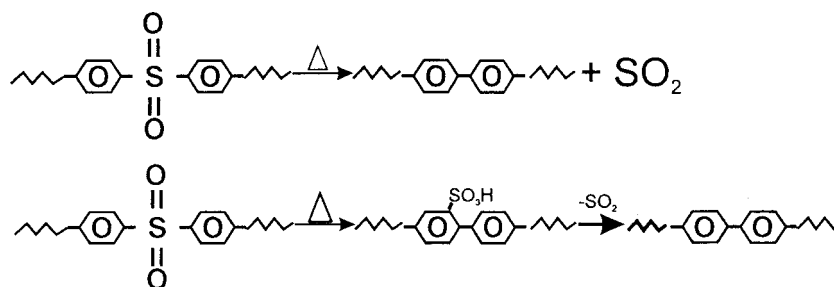
F_1	Electrical conductivity (S cm^{-1})	Onset temperature of thermal degradation ($^{\circ}\text{C}$)
0.00	1.0	480
0.48	6.1×10^{-2}	415
0.57	1.3×10^{-2}	414
0.67	1.6×10^{-4}	405
0.93	3.7×10^{-7}	385
1.00	3.8×10^{-8}	410

showed two doublets at 6.5–6.8 and 7.4–7.7 ppm for aromatic protons on the terminal $-\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$ group, and two multiplets at 5.8–6.4 and 7.8–8.0 ppm may be assigned to amine protons and aromatic protons, respectively, for the DADPS block present in the copolymer. The appearance of a broad multiplet at 6.8–7.3 ppm may be assigned to aromatic protons and amine protons of aniline blocks present in the copolymer.

The room-temperature electrical conductivities of the copolymers decreased from 1.0 S cm^{-1} for polyaniline to $3.8 \times 10^{-8} \text{ S cm}^{-1}$ as the DADPS content in the copolymer increased. The room-temperature electrical conductivities of the homopolymers and copolymers are listed in Table IV. The gradual decrease in the conductivity probably reflects the decrease in the conjugation lengths along the polymer backbone as the presence of sulfone groups in the DADPS moiety restricted π -electron conjugation along the polymer chain. The decrease in the extent of conjugation is also

supported by the UV-vis spectroscopic results for the copolymers.

Thermogravimetric analysis (TGA)/dynamic thermal analysis (DTA) patterns of poly(DADPS), polyaniline, and poly(aniline-*co*-DADPS) ($F_1 = 0.57$) bases are shown in Figure 9. The TGA thermogram of poly(DADPS) shows thermal degradation behavior of the polymer taking place through a number of steps. The initial weight loss from 60 to 100°C was due to loss of moisture. The polymer was stable up to approximately 300°C , above which temperature the polymer began to decompose. The onset temperature of thermal degradation was around 410°C . The thermal degradation might have occurred by a process involving the extrusion of SO_2 from the backbone in addition to main-chain breakdown. Radical cleavage and a radical-radical recombination process might be involved in this process.³¹ Thermal degradation may also involve rearrangement leading to the formation of sulfonic acid groups:



The TGA thermogram of the polyaniline base shows that the polymer was stable up to approximately 400°C and that the onset temperature of thermal degradation was around 480°C . Extensive π -electron conjugation along the backbone of polyaniline presumably made the polymer more stable than poly(DADPS), in which the π -electron conjugation was hindered by the presence of the $-\text{SO}_2-$ group. The TGA thermogram of poly(aniline-*co*-DADPS) containing 57% DADPS and 43% aniline shows an initial weight loss (ca. 5–7%) up to 100°C due to the loss of moisture. The second-step weight loss (ca. 5–7%) that took place at 100 – 200°C may be attributed to the evolution of residual acid present in the copolymer even after an alkali treatment. The polymer was stable up to approximately 300°C , above which temperature decomposition started. The onset temperature for the thermal degradation of the copolymer decreased with an increase in the DADPS content in the copolymer, as shown in Table IV.

DSC curves of poly(DADPS), polyaniline, and poly(aniline-*co*-DADPS) in the base form are shown in Figure 10. The DSC study of polyaniline indicated an endothermic transition starting at approximately 50°C and centered at approximately 100°C that was fol-

lowed by an exothermic peak at approximately 260°C . This endothermic peak was attributed to the evaporation of water.³² DSC thermograms of poly(DADPS) and the copolymer also showed this endothermic peak. However, in all these cases, no sharp glass-transition temperature (T_g) was obtained. The exothermic transition at approximately 260°C was not T_g . When the polymer powder was heated above 260°C , cooled, and reheated, no exotherm was observed upon reheating. In the case of T_g , it should have been observed repeatedly upon heating and cooling. The exotherm observed in the DSC thermogram may be attributed to a series of chemical reactions involving bond scission.¹²

CONCLUSIONS

Conducting homopolymers and copolymers based on aniline and DADPS were synthesized chemically. The copolymers showed improved solubility in organic solvents in comparison with their parent polyaniline. The soluble fraction in NMP formed films. The characterization of the polymers by a host of techniques supported their proposed structures. The monomer reactivity ratios indicated that the DADPS monomer

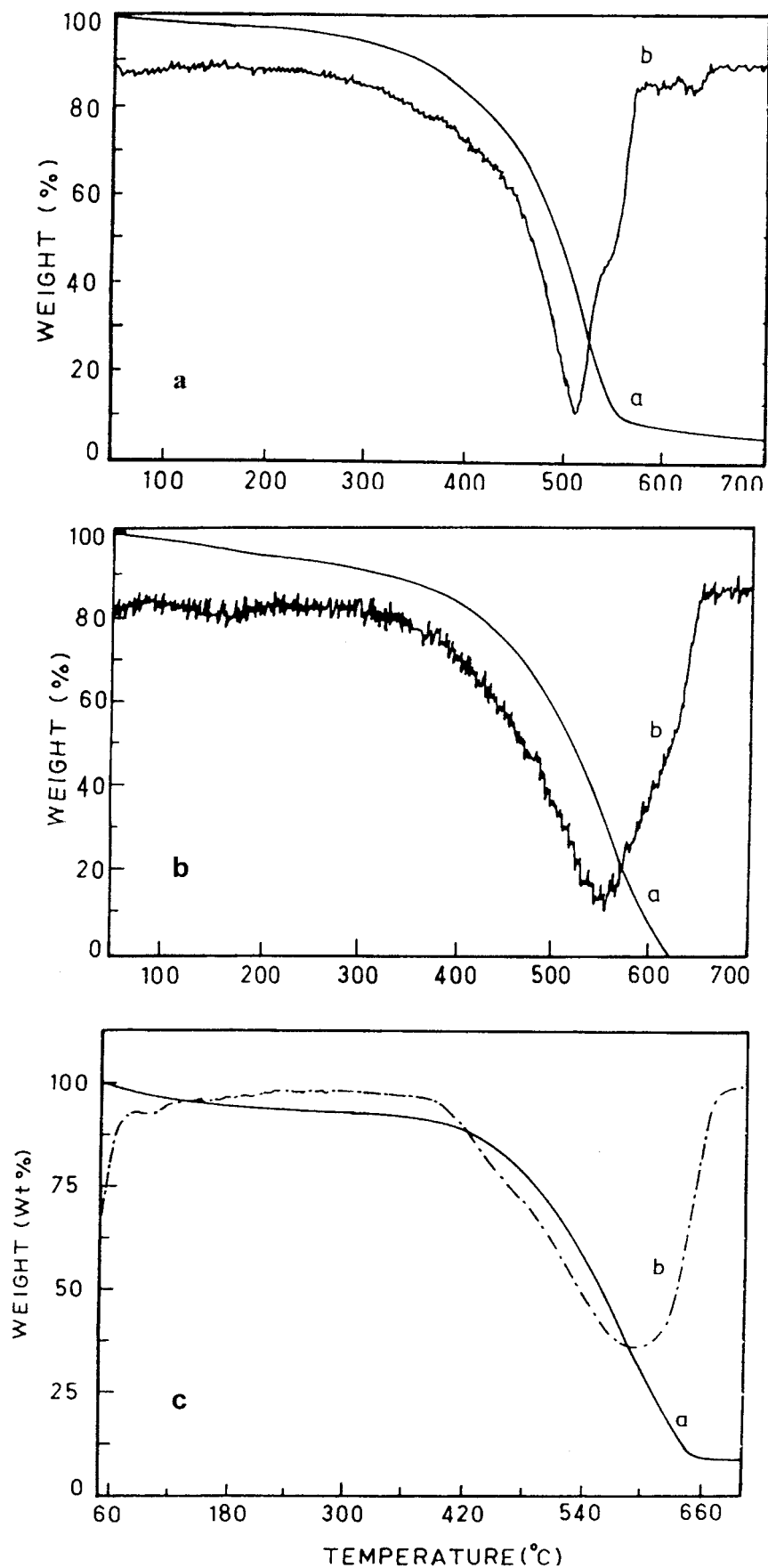


Figure 9 TGA/DTA thermograms of the base forms of (a) poly(DADPS) and (b) poly(aniline-co-DADPS).

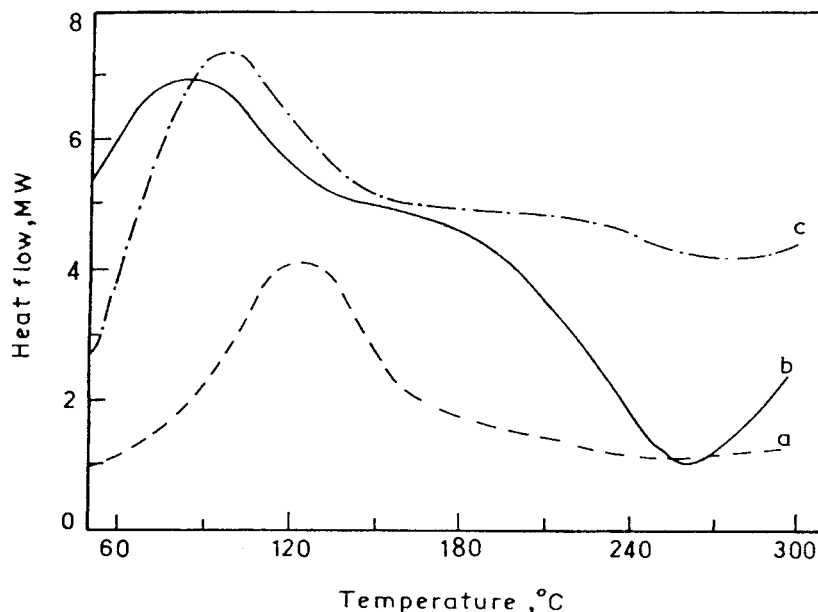


Figure 10 DSC curves of (a) poly(DADPS), (b) polyaniline, and (c) poly(aniline-co-DADPS) in its base form.

was more reactive in copolymerization than aniline and led to the formation of a block copolymer. The FTIR, UV-vis, and $^1\text{H-NMR}$ spectra indicated the incorporation of the DADPS moiety into the copolymers that did not have a conjugated structure. The reduced conjugation lengths in the copolymers strongly affected the electrical conductivity: the logarithm of the electrical conductivity for the copolymers decreased linearly with the molar fraction of DADPS in the copolymers. The decrease in the conductivities was due mainly to the presence of the $-\text{SO}_2-$ group, which lowered the conjugation, as indicated by the hypsochromic shifts in the exciton transition in the UV-vis spectra. The copolymers did not show improved thermal stability in comparison with polyaniline.

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