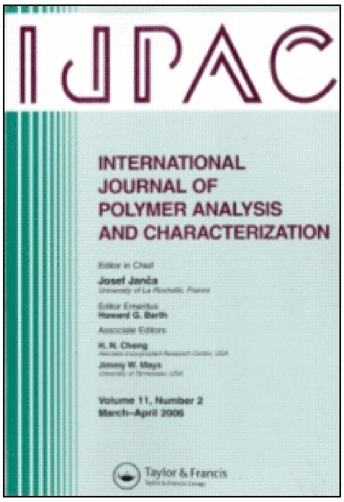

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Copolymerization of Benzidine with Substituted Anilines: A Comparative Study

Beena Bedekar[a]; H. S. Rama[a]
[a] Department of Chemistry, M.S. University of Baroda, Baroda, India

To cite this Article Bedekar, Beena and Rama, H. S.(2001) 'Copolymerization of Benzidine with Substituted Anilines: A Comparative Study', International Journal of Polymer Analysis and Characterization, 6: 6, 599 — 617
To link to this Article: DOI: 10.1080/10236660108030872
URL: http://dx.doi.org/10.1080/10236660108030872

International Journal of Polymer Anal. Charact., 6: 599–617, 2001

1023-666X/01 $12.00+.00

Copolymerization of Benzidine with Substituted Anilines: A Comparative Study

Beena Bedekar and H. S. Rama
Department of Chemistry, M.S. University of Baroda,
Baroda, India

Copolymers of benzidine and aniline derivatives were prepared chemically and electrochemically. A study of the effect of comonomer composition on the thermal and electrical properties of copolymers was carried out. Copolymers were found to have more electrical conductivity compared to polybenzidine. With increase in temperature, the copolymers show semiconducting behavior similar to polybenzidine. Homopolymers, as well as copolymers, show good thermal stability.

Keywords: Copolymer; Polybenzidine; Electrochemical synthesis; Electrical conductivity; Thermal stability

INTRODUCTION

Conducting polymers have been widely studied in last two decades, particularly with the aim of finding suitable applications. Use of polymers in rechargeable batteries[1–4], electrochromic devices[5–9], electrochromatography[10], etc. are a few examples; however, this class of compounds is nonprocessible. To overcome such limitations, copolymerization is often used. High added value of copolymers can be utilized in obtaining suitable applications. Polyanilines with high electrical conductivity[11] are used for suitable applications.

In this article, an attempt is made to copolymerize benzidine with ortho and meta toluidine and ortho and meta anisidine, and the effect of comonomer proportion on the thermal and electrical properties of the copolymers is reported.

Received 20 December 1999; In final form 29 November 2000.

Address correspondence to Dr. H. S. Rama, Department of Chemistry, Faculty of Science, The Maharaja Sayajirao, University of Baroda, Vadodara 390 002 (Guj.), India.

EXPERIMENTAL

Benzidine was obtained from National Chemicals (India) and purified by crystallization from alcohol:water (20:80); purity was checked by comparing the melting point of the products. Ortho and meta toluidine and anisidine were purchased from Fluka (Germany) and purified by distillation under vacuum. Hydrochloric acid, ammonium persulfate, and ferrous sulfate were obtained from Qualigens (India) and used without purification.

The copolymers with different monomer compositions (w/w) were synthesized chemically (C) and electrochemically (EC) as discussed in Rawat and Rama[12].

Comonomer compositions used were benzidine: (*o*/*m*)-toluidine (OT/MA)/anisidine (OA/MA) (1:1 and 1:5).

All the polymer samples were in the powder form, hence discs from polymer KBr mixture were prepared. IR spectra of the polymer were recorded on a Shimadzu IR408 spectrophotometer, and FTIR spectra were obtained on a JASCO FTIR analyzer. Microanalyses of polymers were performed on a Coleman automatic elemental analyzer.

The ESCA were obtained on a VG ESCA LAB MKII spectrometer with Mg K-X-ray source. The X-ray power supply was run at 12 KV and 10 mA. The pressure was kept below 10^{-8} mbar during measurements.

Thermal analysis of the polymers was carried out by TGA under nitrogen atmosphere from room temperature to 500°C/800°C using Shimadzu and Dupont analysers.

Pellets of polymers of equal weight were prepared under nearly equal pressure using an IR pellet press. The electrical conductivities were measured by a two-probe technique in a temperature range from 30° to 360°C.

RESULTS AND DISCUSSION

Physical Properties

The copolymers synthesized were characterized by elemental analysis, IR/FTIR, ESCA, and electrical and thermal properties.

The chemically obtained copolymers varied in color depending on the comonomer composition. The homopolymer of benzidine is brown[13] and those of (*o*/*m*)-toluidine and (*o*/*m*)-anisidine are green. The electrochemically synthesized copolymers vary in color from dark brown to black with an increase in (*o*/*m*)-toluidine/anisidine content.

All the copolymers obtained from either method were amorphous in nature and slightly soluble in DMF, DMSO, and NMP. The electrochemically synthesized copolymers were qualitatively more soluble than the chemically synthesized copolymers.

Elemental Analysis

The elemental analyses of different copolymers are given in Tables I and II, and possible empirical formulae were derived for the copolymers. The homopolymers of (*o*/*m*)-toluidine/anisidine contain C, H, N, (O), and Cl in the doped state, but polybenzidine (PBS) contains sulfur as an additional element. The copolymer also shows the presence of S and O in addition to C, H, N, and Cl, indicating incorporation of benzidine units in the polymer chain. Sulfur could have originated from sulfate, the source of which is the initiator $(NH_4)_2S_2O_8$ and oxygen from sulfate or water. The copolymers synthesized electrochemically contain C, H, N, (O), and Cl in the doped state similar to their homopolymers.

IR Analysis

IR/FTIR spectral analysis of both the homopolymers and copolymers were carried out at room temperature. IR/FTIR can be discussed according to the frequency region.

3500–2500 cm^{-1}

This is the N–H stretching region. The absorption of homopolymers of (*o*&*m*)-toluidine/anisidine in this region is weak (Figure 1). In Figure 2, PBS also shows weak absorption in this region but broad peak is observed from 2500–3000 cm^{-1}. This is due to strongly hydrogen-bonded

TABLE I Elemental Analysis of Chemically Synthesized Copolymers of Benzidine (B) with *o*-Toluidine (OT), *m*-Toluidine (MT), and *o*-Anisidine (OA)

Copolymers	C	H	N	(O)	S	Cl	Empirical formula
B:OT (C)							
0:1	63.81	4.15	12.03	5.37	–	14.64	$C_{25}H_{20}N_4N_4O_{1.6}Cl_2$
1:5	53.47	3.54	8.24	9.59	4.79	20.34	$C_{12}H_7N_{0.7}O_{1.6}Cl_{1.4}S_{0.4}$
1:1	51.20	5.05	9.78	20.80	10.40	30.17	$C_{12}H_{14}N_4O_{3.5}ClS_{0.87}$
B:OA(C)							
0:1	63.21	5.32	10.50	10.15	–	10.82	$C_{24}H_{29}N_{3.4}O_3Cl_{1.4}$
1:5	54.31	5.78	8.34	12.03	6.01	13.49	$C_{24}H_{30}N_{3.6}O_4Cl_2S$
1:1	56.25	3.91	7.90	16.02	8.02	7.90	$C_{21}H_{18}N_{2.5}O_{4.5}ClS$
B:MT (C)							
0:1	61.30	6.50	9.43	5.20	–	17.57	$C_{24}H_{31}N_3O_{15}Cl_2$
1:5	53.92	5.73	9.67	10.79	5.39	14.50	$C_{26}H_{34}N_4OClS_{2.4}$
1:1	58.93	4.94	8.53	12.02	4.53	11.00	$C_{35}H_{35}N_4O_{5.4}ClS$

TABLE II Elemental Analysis of Electrochemically Synthesized Copolymers of Benzidine (B) with *o*-Toluidine (OT), *m*-Toluidine (MT), *o*-Anisidine (OA), and *m*-Anisidine (MA)

Copolymers	C	H	N	(O)	Cl	Empirical formula
B:OT (EC)						
0:1	63.20	4.10	8.50	8.30	15.90	$C_{23}H_{18}N_{2.5}O_2Cl_2$
1:5	58.73	6.70	9.34	9.09	16.14	$C_{27}H_{37}N_4O_3Cl_{2.5}$
1:1	60.90	6.10	8.90	10.12	13.98	$C_{25}H_{30}N_3O_3Cl_2$
B:OA (EC)						
0:1	65.21	5.32	9.50	8.15	11.82	$C_{16}H_{16}N_2O_{1.5}Cl$
1:5	56.21	5.78	8.34	12.03	17.54	$C_{20}H_{25}N_{2.5}O_3Cl_2$
1:1	62.25	3.91	7.92	10.02	15.90	$C_{23}H_{17}N_{25}O_3Cl$
B:MT (EC)						
0:1	60.21	3.52	3.50	9.27	18.50	$C_{28}H_{20}N_{3.1}O_3Cl_3$
1:5	58.57	4.16	9.10	6.43	27.74	$C_{25}H_{21}N_{3.3}O_2Cl_2$
1:1	54.22	4.07	8.18	8.44	25.09	$C_{25}H_{21}N_3O_3Cl_4$
B:MA (EC)						
1:5	54.41	2.89	8.89	5.05	28.66	$C_{27}H_{18}N_4O_2Cl_5$
1:1	52.53	3.74	7.50	14.33	20.90	$C_{24}H_{21}N_3O_{1.5}Cl_3$

O–H stretching vibration. C–H stretching at 2800–3100 cm^{-1} can also contribute in this region. Overall the three factors contribute to give a broad peak from 2200–3000 cm^{-1} (Figure 2). Copolymers show this broad peak (Figures 3 and 4). No shift of absorption peaks are observed for the copolymers with respect to the ratios of either of the monomers.

2000–1450 cm^{-1}

The homopolymers as well as copolymers showed three prominent peaks at 1510, 1590, and 1610 cm^{-1}. The peak at 1505 cm^{-1} is assigned to benzenoid ring stretching and 1600 cm^{-1} band as characteristic band of nitrogen quinone. A 1,4-substituted benzene ring or C=N stretching also contributed to absorption in this region. In PBS, as well as for the copolymers obtained chemically, the intensity of the latter two bands is much less than the former bands. In the electrochemically obtained copolymers, the bands were almost the same. No shift in the bands was observed with varying comonomer ratios.

1400–1200 cm^{-1}

This is a C–N stretching region for aromatic amines. It shows a broad band at 1310 cm^{-1} that includes a weak peak at 1250 cm^{-1}. The C–N

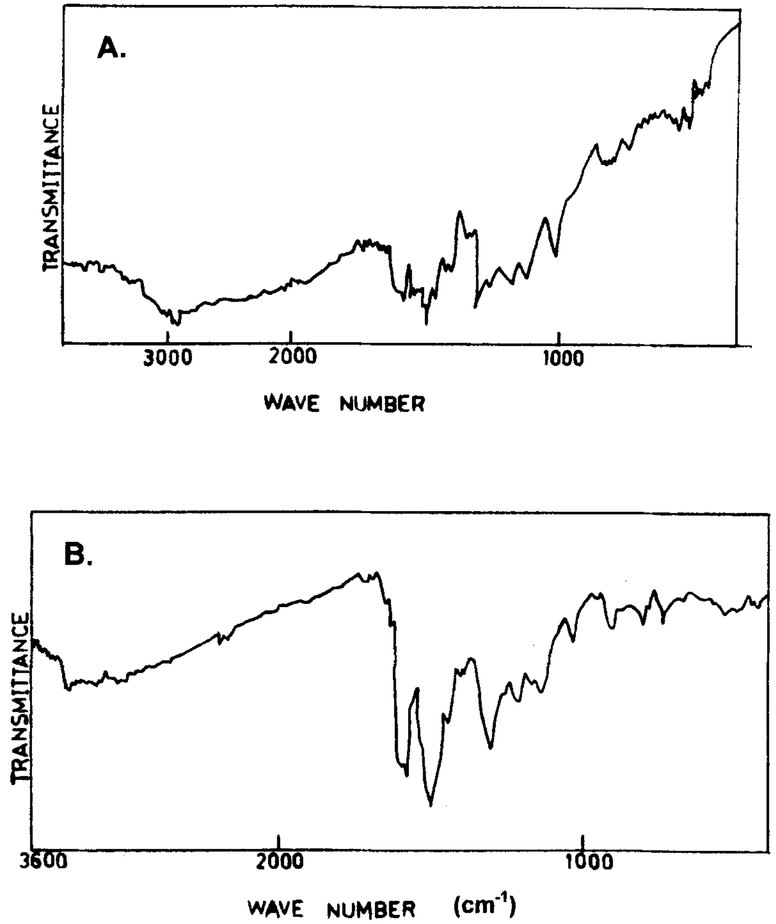

FIGURE 1 IR spectra of chemically synthesized (a) poly (*o*-toluidine) and (b) poly (*o*-anisidine).

stretching of most of the aromatic amines couples partly with N–H bonding, so it is possible that C–N stretching might show a peak at a lower frequency. PBS showed a sharp peak at 1320 cm^{-1}, which could be due to asymmetric stretching of –N=N– in the polymer. The copolymers show a very weak band at 1320 cm^{-1} irrespective of different ratios of either monomers. The electrochemically synthesized homopolymers, as well as copolymers, show peaks near 1390 cm^{-1} and 1290 cm^{-1} for all the comonomer ratios.

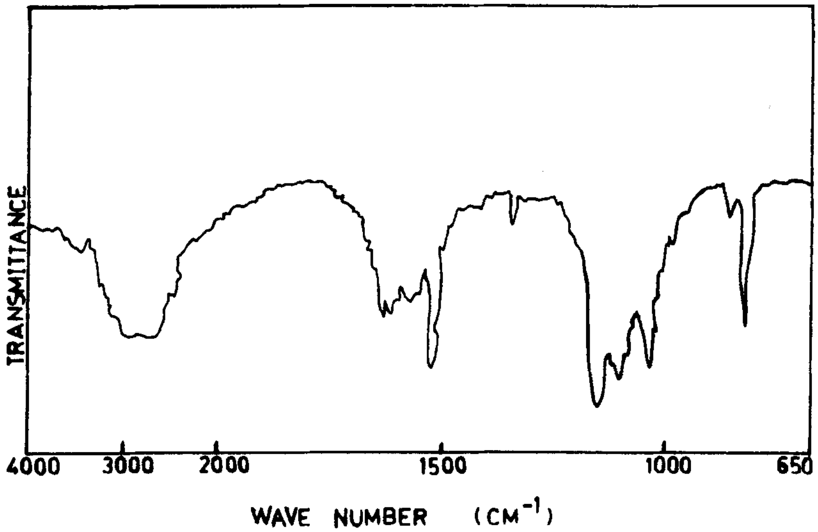

FIGURE 2 IR spectra of chemically synthesized polybenzidine.

1220–500 cm^{-1}

This is the region of in-plane and out-of-plane bending of C—H bonds on aromatic rings. According to MacDiarmid[14], the band at 1160 cm^{-1} was considered as a measure of the degree of delocalization of electrons. Peaks at 810 cm^{-1} indicate the presence of a C—Cl bond. For PBS the major peaks in this region occur at 810, 1020, 1090, and 1130 cm^{-1}. The peak at 810 cm^{-1} shows the presence of C—Cl bonding indicating chlorination of the benzene ring. The peaks at 840 and 1020 cm^{-1} indicate 1,4 substitution in the polymer chain. The peaks at 1120, 1140, and 1160 cm^{-1} in homopolymers of toluidine and anisidine represent a mode of N=Q=N, Q=NH=Q, or B—NH—B type of structures (Q = quinoid and B = benzenoid). Strong bands at 1130–1080 cm^{-1} in PBS suggest the presence of inorganic sulfate, which was detected also in elemental and chemical analysis. All the copolymers obtained chemically show peaks of inorganic sulfate. These characteristic peaks were absent in homopolymers of toluidine (Figure 5), anisidine, and in copolymers synthesized electrochemically (Figure 6).

ESCA

The X-ray photoelectron spectroscopic analysis gives the characteristic binding energies of the photoelectrons and thus the elements involved can be identified. The shift in the binding energy is accompanied with the

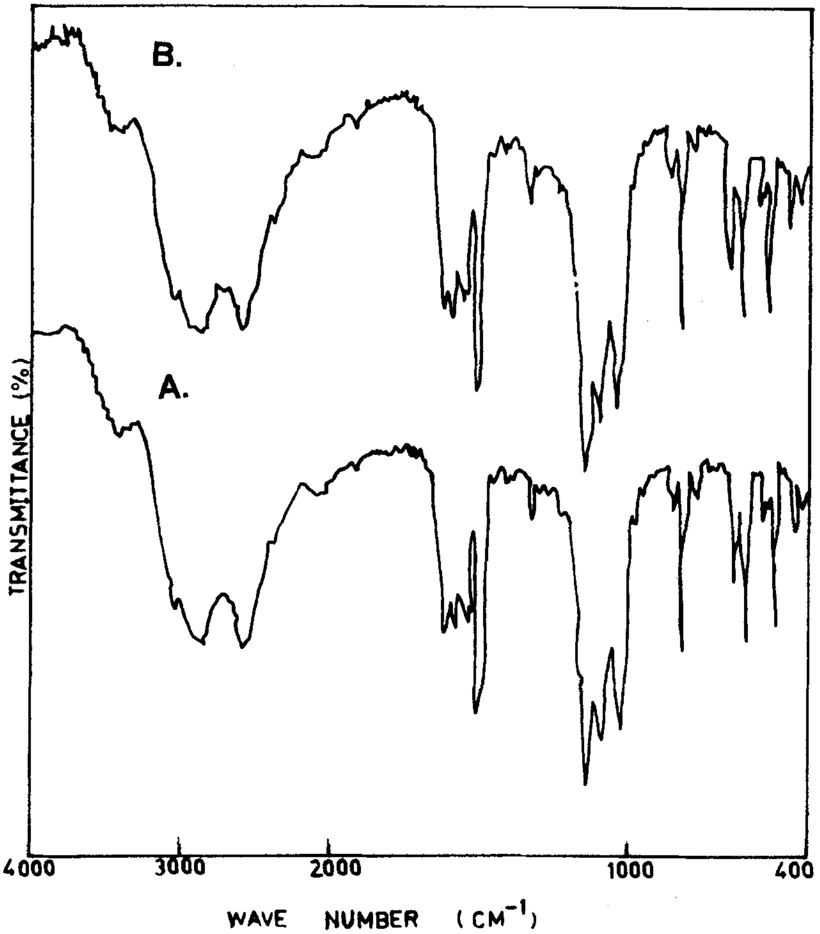

FIGURE 3 IR spectra of chemically synthesized copolymers of benzidine with *o*-toluidine (a) 1:1, (b) 1:5.

change in the chemical environment. All the core level spectra were referenced to the Cls neutral carbon peak at 284.6 e.v. The quinoid imine (=N−), benzenoid amine (−NH−) structure, and the positively charged nitrogen ($-\overset{+}{N}-$) corresponding to binding energies at about 398.2, 399.4 and > 400 e.v. respectively. The copolymer of B:OT(1:1)C contains only ($-\overset{+}{N}-$) structural form whereas in addition to this, PBS contain −NH− and −N=[12]. The C12P core level spectra for copolymer reveals the presence of ionic and covalent species. The proportion of covalent species

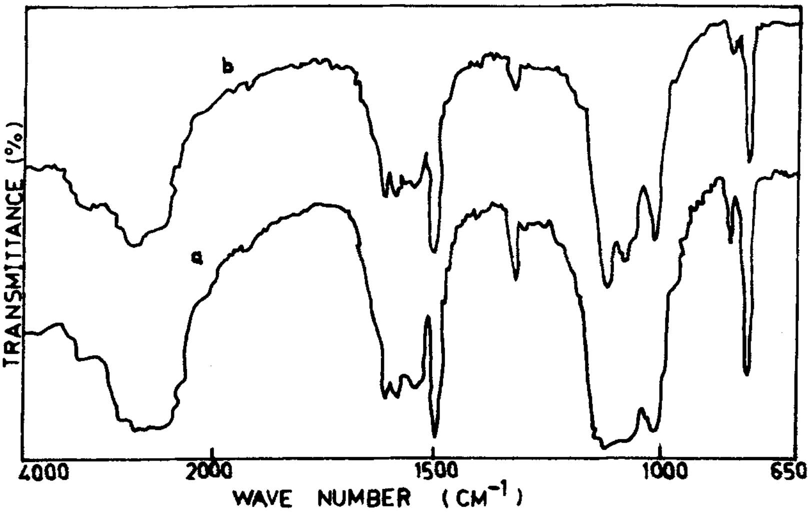

FIGURE 4 IR spectra of chemically synthesized copolymers of benzidine with *o*-anisidine (a) 1:1, (b) 1:5.

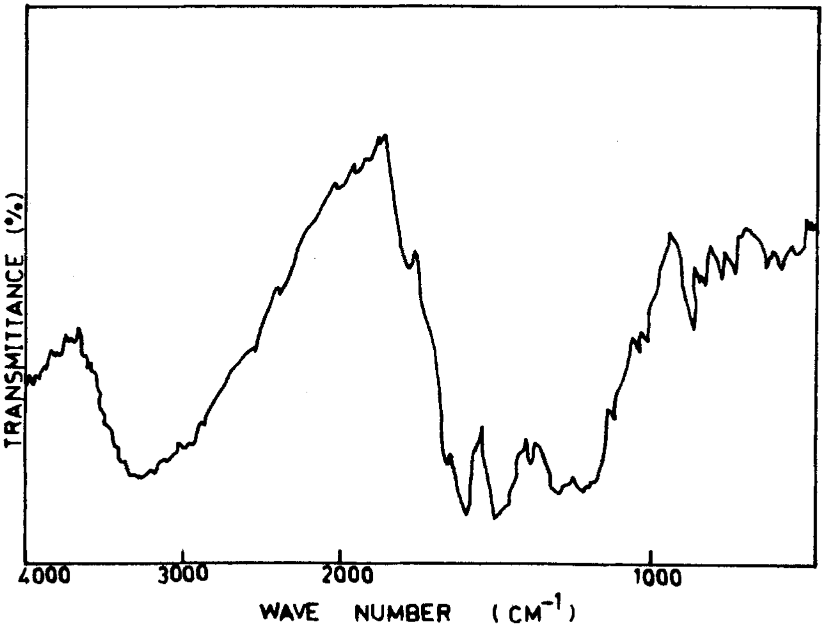

FIGURE 5 FTIR spectra of electrochemically synthesized poly (*o*-toluidine).

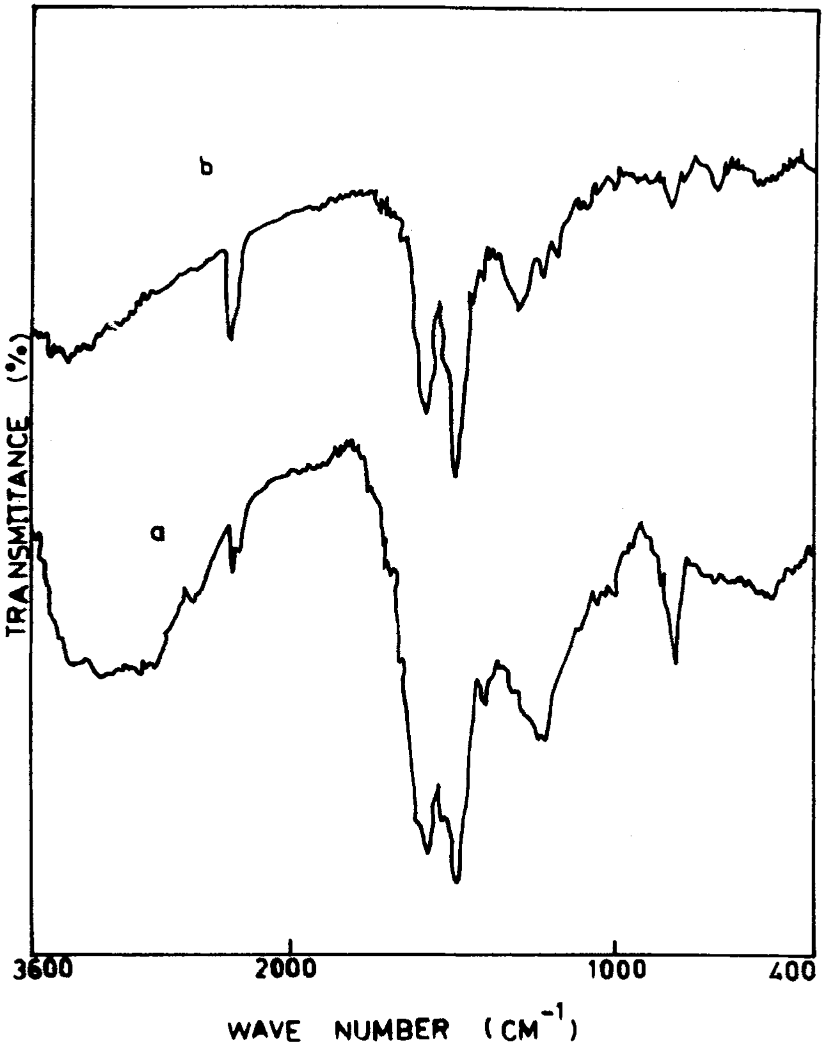

FIGURE 6 FTIR spectra of electrochemically synthesized copolymers of benzidine with *m*-anisidine (a) 1:1, (b) 1:5.

is much higher than the ionic species (Table III) indicating a high extent of chlorination reaction taking place during synthesis as reported for polyanilines[15]. B:OT(1:1)C also shows the presence of S in the form of sulfate at a binding energy of 168.2 e.v. Also the O1s core level spectra peak component at binding energy level of 533.7 and 532 e.v. can be due to –N–O and SO_4^{2-} environments.

TABLE III XPS Stoichiometries for Chemically Synthesized Copolymers of Benzidine (B) with *o*-Toluidine (OT) and Electrochemically Synthesized Copolymers of Benzidine with *m*-Toluidine (MT) and *m*-Anisidine (MA)

	XPS Stoichiometries			Proportion of			Elemental
Copolymers	−Cl/N	Cl^-/N	S/N	=N−	−NH−	−N−	Cl/N
B:OT (C) 1:1	0.33	0.07	0.44	–	–	1.11	–
B:MT (EC) 1:1	10.03	–	–	–	0.41	0.59	1.2
B:MA (EC) 1:1	1.00	–	–	–	–	1.0	1.03

In electrochemically synthesized copolymer, e.g., B:MT(1:1)EC, two nitrogen peak components corresponding to amine and imine structures were obtained, but a single peak component was obtained for B:MA(1:1)EC. In both the copolymers, the $(-\overset{+}{N}-)$ structure is more predominant. The Cl 2p core-level spectra for B:MA(1:1)EC show the presence of Cl $2p3/2$ and Cl $2p1/2$ components at binding energies of 200.4 and 201.4 e.v., and at 199.7 e.v. for B:MT(1:1)EC corresponding to covalently bonded chlorine only. This covalently bonded chlorine could be attributed to ring-substituted chlorines or molecular HCl. The oxygen envelope in the spectra demonstrates the presence of OCH_3 (533.7 e.v.) and C=O (532.2 e.v.) in B:MA(1:1)EC. The O1s core level for B:MT(1:1)EC also could be resolved into components C=O and −N−O at 532.6 and 533.0 e.v.

Electrical Conductivity

The specific electrical conductivities of the copolymers measured in air at room and higher temperatures (30°–360°C) are given in Tables IV and V. Polybenzidine has a specific conductivity in the semiconducting range, and homopolymers of toluidine and anisidine have comparatively higher conductivity values. With an increase in the ratio of anisidine/toluidine, the specific conductivity of the copolymer increases. At room temperature the specific conductivities of chemically synthesized homopolymers varied in the order POA $<$ POT $\approx$ PMT. The electrical conductivity is affected by the type of the substitution in the benzene ring. It is possible that due to increase in the electron density of the ring, because of the electron donating ability of the substituent, electron delocalization on the polymer backbone is favored leading to lowering of transition energy and an increase in the electrical conductivity of the polymers. Thus the higher specific

TABLE IV Specific Conductivities of Chemically Synthesized Copolymers of Benzidine with *o*-Toluidine (OT), *o*-Anisidine (OA), *m*-Anisidine (MA) in the First- and Second-Cycle Conductivity Measurements

	First cycle		Second cycle	
Copolymer	S/cm (°C) $\sigma \times 10^7$	S/cm (°C) $\sigma_m \times 10^5$	S/cm (°C) $\sigma' \times 10^8$	S/cm (°C) $\sigma'_m \times 10^6$
B:OT (C)				
0:1	98000.0 (40)	149000.0 (110)	23200.0 (50)	74800.0 (150)
1:5	57.0 (40)	25.0 (150)	–	–
1:1	4.58 (40)	0.86 (140)	1.2 (260)	–
B:OA (C)				
0:1	116.0 (40)	163.00 (170)	1.95 (160)	–
1:5	0.11 (40)	9.9 (130)	0.16 (30)	0.003 (110)
1:1	0.07 (35)	1.98 (140)	0.01 (50)	–
Copolymer	$\sigma \times 10^7$	$\sigma_m \times 10^5$	$\sigma' \times 10^7$	$\sigma'_m \times 10^5$
B:MT (C)				
0:1	90000.0 (40)	125000.0 (130)	–	–
1:5	5.50 (40)	1.20 (130)	–	–
1:1	0.18 (40)	0.03 (105)	–	–
B:MA (C)				
1:5	0.148 (40)	0.047 (140)	0.015 (240)	–
1:1	0.02 (40)	–	–	–

σ and σ' are conductivity in the first and second cycle at starting temperature.

σ_m and σ'_m are maximum conductivity in the first and second cycle at starting temperature.

TABLE V Specific Conductivities of Electrochemically Synthesized Copolymers of Benzidine (B) with *o*-Toluidine (OT), *m*-Toluidine, *o*-Anisidine (OA), and *m*-Anisidine (MA) in the First- and Second-Cycle Conductivity Measurement

	First cycle		Second cycle	
Copolymer composition	S/cm (°C) $\sigma \times 10^7$	S/cm (°C) $\sigma_m \times 10^5$	S/cm (°C) $\sigma' \times 10^9$	S/cm (°C) $\sigma'_m \times 10^5$
B:OT (EC)				
0:1	1460.0 (40)	10700.0 (110)	18200.0 (50)	–
1:5	1.31 (40)	5.10 (150)	–	–
1:1	0.30 (40)	0.33 (170)	0.18 (130)	–
B:OA (EC)				
0:1	8500.0 (40)	2100.00 (130)	–	–
1:5	0.04 (40)	0.10 (150)	–	–
1:1	0.03 (40)	0.01 (130)	0.05 (120)	–
Copolymer composition	$\sigma \times 10^7$	$\sigma_m \times 10^5$	$\sigma' \times 10^7$	
B:TM (EC)				
0:1	907.0 (40)	152000.0 (130)	–	
1:5	0.45 (40)	3.50 (120)	–	
1:1	0.006 (40)	74.0 (110)	–	

σ and σ' are conductivity in the first and second cycle at starting temperature.

σ_m and σ'_m are maximum conductivity in the first and second cycle in whole range of temperature used.

conductivity of toluidine as compared to anisidine may be due to the higher ability of the CH_3 group to donate an electron than OCH_3 group. The same explanation may be given to the fact that copolymers of (*o*/*m*) toluidine with benzidine have higher electrical conductivity as compared to copolymer of (*o*/*m*) anisidine with benzidine. Plots of specific conductivity (σ) versus temperature of copolymers B:OT(C) and B:OT(EC) are given in Figures 7 and 8. The plots show an increase and then a decrease in conductivity values with an increase in temperature.

The maximum conductivity (σ_m) obtained at higher temperature generally lies in the temperature range of 100°–150°C. This shows that the presence of water or volatile species like ionic chloride can be one of the responsible factors. Above 100°C, water and ionic chloride are removed from the polymer leading to a decrease in conductivity values with temperature. Reaction with oxygen in air can also accelerate or retard the conductivity values obtained. The homopolymers of toluidine and

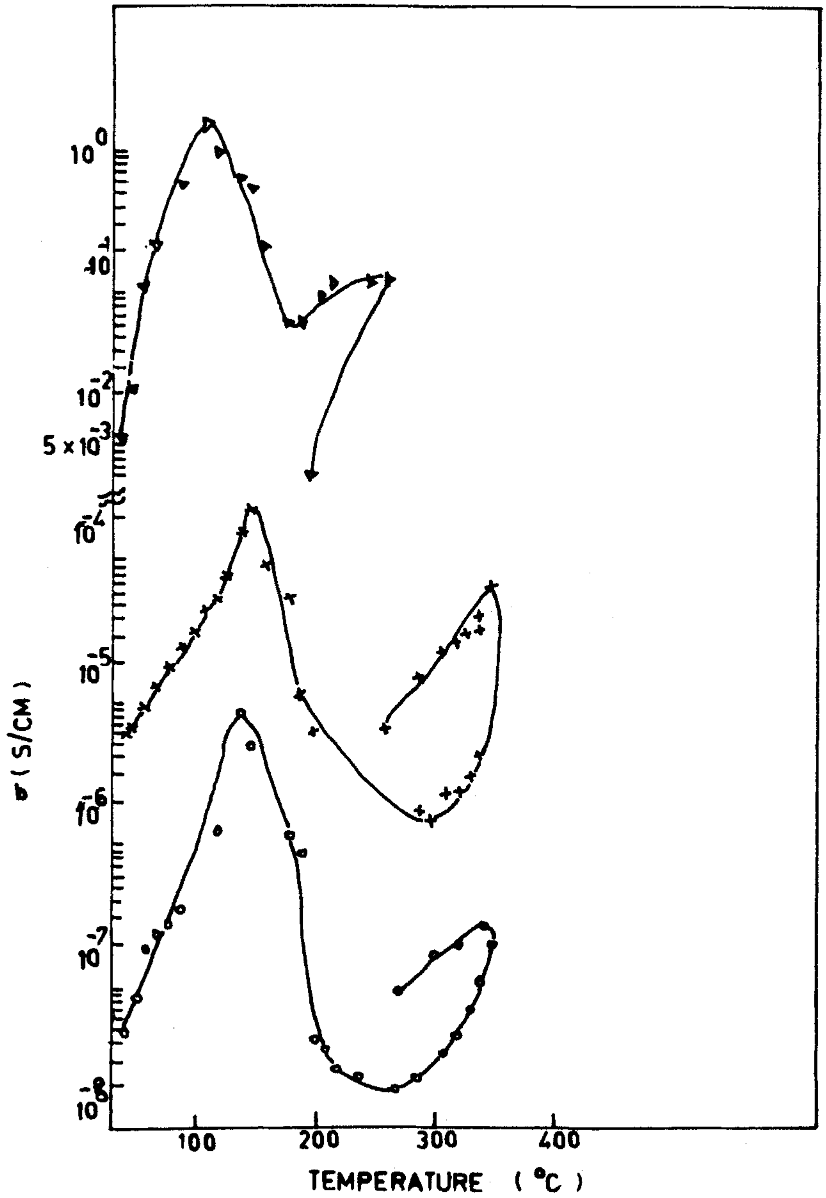

FIGURE 7 Plot of specific conductivity (σ) versus temperature (T) for chemically synthesized copolymers of benzidine with *o*-toluidine with comonomer ratio (△) 0:1; (×) 1:5; (○) 1:1.

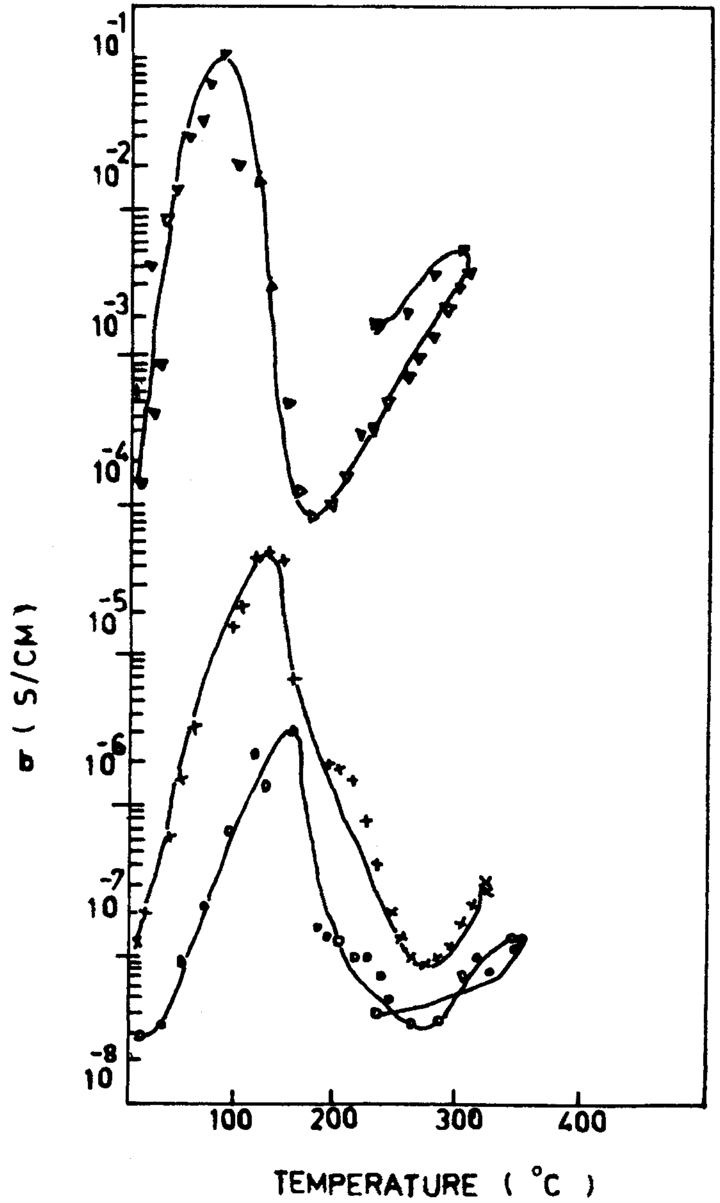

FIGURE 8 Plot of specific conductivity (σ) versus temeprature (T) for electrochemically synthesized copolymers of benzidine with *o*-toluidine with comonomer ratio (△) 0:1; (×) 1:5; (○) 1:1.

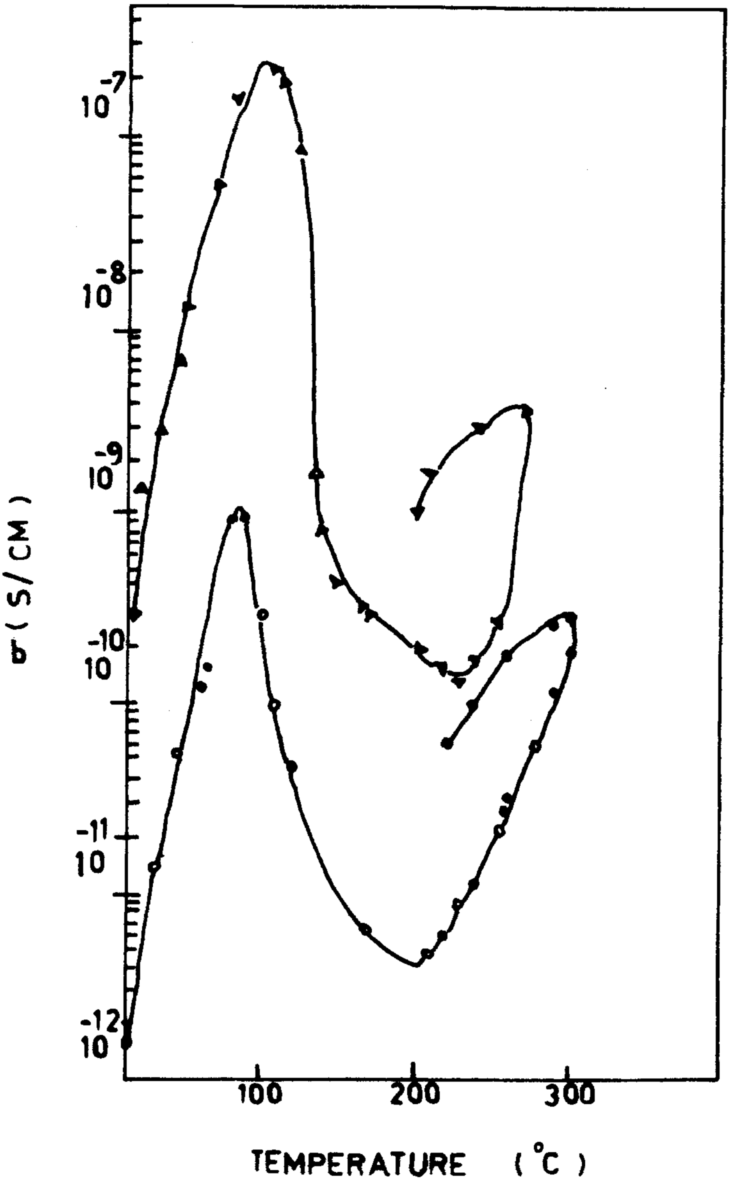

FIGURE 9 Plot of specific conductivity (σ) versus temperature (T) for chemically synthesized copolymers of benzidine with *m*-toluidine with comonomer ratio (△) 0:1; (×) 1:5 measured after two years.

TABLE VI Decomposition Temperatures at 10%, 30%, and 50% Weight Loss and Activation Energies for Degradation of Copolymers

	Decomposition temperatures (t) in °C			Activation energy transition	
Copolymer	10%	30%	50%	First cycle (KJ)	Second cycle (KJ)
B:OT (C)					
0:1	180	515	715	5.7	15.5
1:5	305	355	>450	50.84	81.48
1:1	313	360	>360	57.75	119.56
B:OA (C)					
1:5	380	450	735	23.1	–
1:1	405	470	770	19.2	–
B:OA (EC)					
1:5	310	625	780	32.4	–
1:1	340	660	>850	25.9	–
B:MT (C)					
1:5	415	480	810	15.7	–
1:1	400	460	810	38.47	–
B:MA (C)					
1:1	293	338	355	41.85	–
B:MT (EC)					
1:5	200	>445	–	9.7	–
1:1	230	395	>585	23.3	–
B:MA (EC)					
1:5	270	>450	–	17.5	–
1:1	250	470	–	23.2	–

anisidine have $\approx 10^4$–10^5 times more conductivity than the corresponding copolymers. All the copolymers irrespective of different comonomer ratios and method of synthesis show the same conductivity trend with temperature. The increase in conductivity varied with toluidine/anisidine ratios. This increase was more prominent with ortho substituents. The increase in conductivity (σ_m) with increase in temperature was found to be at least two orders.

The effect of thermal aging was studied by subjecting the copolymers to a second run of conductivity measurements (Tables IV and V). It is observed that the initial conductivity of polymers decreased by a factor of 10 on thermal aging. The initial increase and then decrease in conductivity

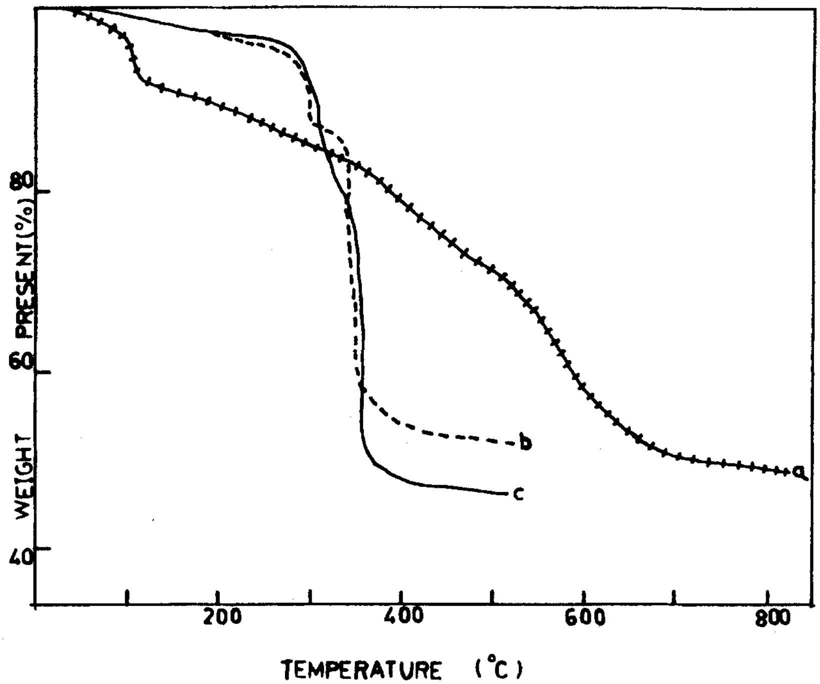

FIGURE 10 Thermogravimeteric analysis of chemically synthesized copolymers of benzidine with *o*-toluidine with comonomer ratio (a) 0:1; (b) 1:5; (c) 1:1.

(conductivity pattern) was not observed after thermal aging, indicating the removal of ionic species from the polymer chain. Another possibility could be that the new modified structure acquired on conversion of ionic chlorine to the covalent form or due to surface oxidation products, etc.

To study the effect of aging of polymer with time, B:MT(1:1)C and B:MT(1:5)C were subjected to the conductivity measurements after two years (Figure 9). A three- to four-order decrease in the specific conductivity was observed. This decrease could be due to the removal of volatile ionic chloride or HCl trapped in the polymer chain. After two years, the copolymers had similar conductivity, behavior with temperature. From the effect of the temperature on the specific conductivity, we can say that the homopolymers as well as the copolymers behave like semiconductors.

Thermal Analysis

All the homopolymers and copolymers were subjected to thermogravimetric analysis under a nitrogen atmosphere. Table VI gives the decomposition temperatures for 10%, 30%, and 50% degradation. All the copolymers show 50% degradation at temperatures above 500°C. The polymers show a small weight loss near 100°C from the moisture present in the sample. The copolymers initially degraded slowly, but after 300°–350°C degraded quite quickly, as shown in Figure 10. This effect could be due to the removal of dopants like Cl^-, due to chlorination reaction as suggested by Hagiwara et al.[15], or due to decomposition of low-molecular-weight polymers. The different thermal stabilities of copolymers can be attributed to different substituents on the aniline derivatives. The electrochemically synthesized polymers also show good thermal stability (Table VI). These polymers also show weight loss near 100°C. The TGA curve levels off at higher temperatures. Approximately above 200°C, it shows slow degradation. Overall the copolymers were found to be thermally stable with a small weight loss near ~100°C, indicating the presence of water and ionic chlorine. The activation energies for the deprotonation of homopolymers and copolymers were calculated and tabulated in Table VI.

CONCLUSION

All the copolymers obtained either by electrochemical or by chemical synthetic method were found to be semiconducting in nature. Electrical conductivity of ploybenzidine increases with copolymerization of benzidine with toluidine or anisidine. The thermal analysis supports the electrical conductivity studies. The factors partly responsible for conductivity (i.e., ionic species) are quite visible in thermal analysis. The thermal properties of homopolymers of toluidine and anisidine were improved with copolymerization with benzidine.

ACKNOWLEDGMENT

We wish to thank the University Grants Commission, New Delhi, India, for the financial assistance for this work.

REFERENCES

[1] A. Kitami, M. Kaya, and K. Sasaki. (1986), *J. Electrochem. Soc.*, *133*, 1069.
[2] A. G. Macdiarmid, L. S. Yang, W. S. Huang, and B. D. Humphrey. (1987), *Synth. Met.*, *18*, 393.
[3] T. Nakajima and T. Kawagoe. (1989), *Synth. Met.*, *28*, C629.
[4] M. Mizumoto, M. Namba, S. Nishimura, H. Miyadera, M. Kosehi, and Y. Kobayashi. (1989), *Synth. Met.*, *28*, C639.

[5] T. Kobayashi, H. Voneyama, and H. Tamura. (1984), *J. Electroanal. Chem., 161-4*, 19.

[6] S. Gottesfeld, A. Redondo, and S. W. Feldberg. (1987), *J. Electrochem. Soc., 134*, 134.

[7] E. M. Genies, M. Laploeski, C. Santier, and E. Vieil. (1987) *Synth. Met., 18*, 631.

[8] M. T. Nguyen and L. H. Dao. (1989), *J. Electrochem. Soc., 136*, 2131.

[9] L. H. Dao and M. T. Nguyen. (1989) Proc. 24th Intersoc. *Energy Conversion Eng. Conf. (IECEC-89), 4*, 1737.

[10] T. Nagaoka, K. Kakuno, M. Fugimoto, H. Nakao, Y. Yano, and K. Ogura. (1994), *J. Electroanal. Chem., 368*, 315.

[11] A. G. Macdiarmid and I. B. Kaner. (1986) in *Handbook of Conducting Polymers*, ed. Skothiem, T. A., and Dekker, M., New York, Chapter 20.

[12] B. Rawat and H. S. Rama. (1997) *J. App. Polym. Sci.*, 2421.

[13] B. Rawat, S. S. Kansara, and H. S. Rama. (1991) *Polym. Int., 26*, 233.

[14] W. R. B. Liedberg, O. Ingane, R. Erlandson, I. Lundstrom, A. G. Macdiarmid, M. Halpern, and N. I. D. Somasiri. (1985), *Mol. Cryst. Liq. Cryst., 124*, 191.

[15] T. Hagiwara, M. Yamura, and K. Iwata. (1988), *Synth. Met., 25*, 243.