

Copolymerization of Benzidine with Anilines: A Comparative Study

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ABSTRACT: The copolymerization technique is an easy way to achieve better properties in a polymer. Copolymers of benzidine with aniline and its substituted derivatives in different comonomer proportions were synthesized using chemical and electrochemical methods. The characterization of the copolymers included elemental, IR, FTIR, XPS, TGA, thermal aging, and electrical conductivity studies. Specific conductivities of copolymers were obtained at different temperatures. Activation energies were calculated from the change in conductivity with temperature. The effect of steric influence on the electrical conductivities of copolymers was observed. Conductivity is also found to be highly dependent on factors like moisture and % doping. Thermal analysis shows a good thermal stability of the copolymers. The thermal aging process also supports the results obtained from TGA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2421–2432, 1997

INTRODUCTION

The field of copolymers is currently of great research interest. The obvious attraction is the high added value of the copolymers which may be obtained. In the field of conducting polymers, the research attraction is due mainly to its low cost of preparation and fabrication and their possible use in commercial applications like rechargeable batteries,¹ electrochromic windows,² and biosensors.³ Polyanilines,⁴ polypyrrole,⁵ and polythiophenes⁶ are very common examples, but like others, in this class, they are severely limited by their intractable and nonprocessable nature. To overcome such limitations and to obtain simultaneously both a conductive and processable nature, a copolymerization technique is used. Naguyen and Diaz⁷ recently prepared water-soluble copolymers from aniline and anthranilic acid. It led to the decrease of conductivity of the copolymers compared to polyaniline but resulted into their solubility in water. In this article, we attempted

to copolymerize benzidine with aniline and substituted anilines and studied the effect of the proportion of a comonomer on the thermal and electrical properties of the copolymers.

EXPERIMENTAL

The chemicals used in the present study were benzidine from National Chemicals, aniline from BDH, *o*- and *m*-chloroaniline from Fluka, and hydrochloric acid, ferrous sulfate, ammonium ferrous sulfate, and acetonitrile from Qualigens. The monomers chosen were benzidine (B), aniline (A), *o*-chloroaniline (OCA), and *m*-chloroaniline (MCA). Benzidine was purified from the water–alcohol mixture (70 : 30) and tested for its melting point. Aniline and its derivatives were purified by distillation at a constant temperature and stored under nitrogen. The copolymers were synthesized chemically (C) as well as electrochemically (EC). Different monomer compositions (w/w) were used.

The comonomer compositions used were

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Table I Elemental Analysis of the Copolymers

Copolymers	C	H	N	O	S	Cl	Empirical Formulas
B : OAC (C)							
1 : 0	52.64	4.63	9.72	20.27	9.71	3.00	C ₄₉ H ₅₂ N ₈ O ₁₁ ClS ₃
0 : 1	52.51	3.00	9.60	7.23	—	27.60	C ₁₉ H ₁₃ N ₃ O ₂ Cl ₃
1 : 1	52.28	4.66	9.80	18.50	8.83	5.93	C ₂₆ H ₂₈ N ₄ O ₇ ClS ₂
1 : 5	50.81	4.63	9.53	18.03	7.50	9.50	C ₁₈ H ₂₀ N ₃ O ₅ ClS
B : OAC (EC)							
0 : 1	55.25	3.64	8.53	10.06	—	22.52	C ₈ H ₆ NOCl
1 : 1	51.40	4.98	9.70	20.32	—	13.50	C ₁₂ H ₂₆ N ₄ O ₇ Cl ₂
B : MCA (EC)							
1 : 1	53.58	3.69	8.57	9.40	—	24.76	C ₁₂ H ₉ N ₂ O ₂ Cl ₂
1 : 5	51.60	3.01	8.60	8.99	—	27.89	C ₁₅ H ₁₁ N ₂ O ₂ Cl ₃
B : A (C)							
1 : 1	52.01	4.67	9.78	20.01	—	5.23	C ₂₉ H ₃₁ N ₅ O ₉ ClS ₂

Benzidine : anilinc (B : A = 4 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 4)

Benzidine : *o*-chloroaniline (B : OCA = 1 : 1, 1 : 5)

Benzidine : *m*-chloroaniline (B : MCA = 1 : 1, 1 : 5)

Synthesis : Benzidine–Aniline Copolymer (1 : 1)

Chemical Synthesis

A homogeneous solution of benzidine (0.1M) and aniline (0.1M) in HCl (1M) was prepared and cooled to approximately 7–8°C. A precooled solution of (NH₄)₂S₂O₈ (0.02M) was added to the comonomer solution with continuous stirring. A small amount of a dilute FeSO₄ solution was added to facilitate the reaction rate. The reaction mixture was washed with 1M HCl until the filtrate became colorless and additional water washings were given to remove unbound HCl. The copolymer obtained was dried in air at room temperature.

Electrochemical Synthesis

Benzidine (0.1M) and aniline (0.1M) were dissolved in 100 mL of aqueous HCl (1M) solution and subjected to electrolysis for 6 h under a N₂ atmosphere using platinum electrodes. Precipitates deposited on the anode indicated the polymer formation. Collected precipitates were washed with 1M aqueous HCl and water several times and finally dried in air at room temperature. Copolymers of benzidine with *o*-chloroani-

line and *m*-chloroaniline having different compositions were prepared by the same procedure.

Evolution of HCl from the copolymers was determined by the thermal aging process. A weighed amount of the copolymer was taken in a three-necked flask with an inlet for N₂ gas and an outlet. The polymer sample was heated for 4 h at 100°C and 4 h at 200°C. The HCl liberated from the polymer sample was swept by a continuous flow of N₂ gas and passed into the NaOH solution for pH change measurements. The pH change was noted at an interval of 1 h.

The thermogravimetric analysis of polymers was carried out with a Shimadzu TG analyzer in a nitrogen atmosphere at a run rate of 10°C/min. IR and FTIR spectra of copolymers in KBr were taken on a Shimadzu IR-408 spectrophotometer and a JASCO FT/IR-8000.

XPS measurements were made on a VG Escalab MKII spectrometer with a MgK α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. All core-level spectra were referenced to the Cls neutral carbon peak at 284.6 eV. Pressure in the analysis compartment was kept at or below 10⁻⁸ mbar during the measurements. Electrical conductivity of copolymers was measured by a two-probe technique at different temperatures, ranging from room temperature to 360°C (in air). Polymer pellets of equal weight (100 mg) were prepared by a KBr pellet press under approximately the same pressure of 4.5 kgf cm⁻² for conductivity measurements. A change in conductivity was recorded for heating and cooling temperatures. Each pellet was subjected twice to conductivity measurements.

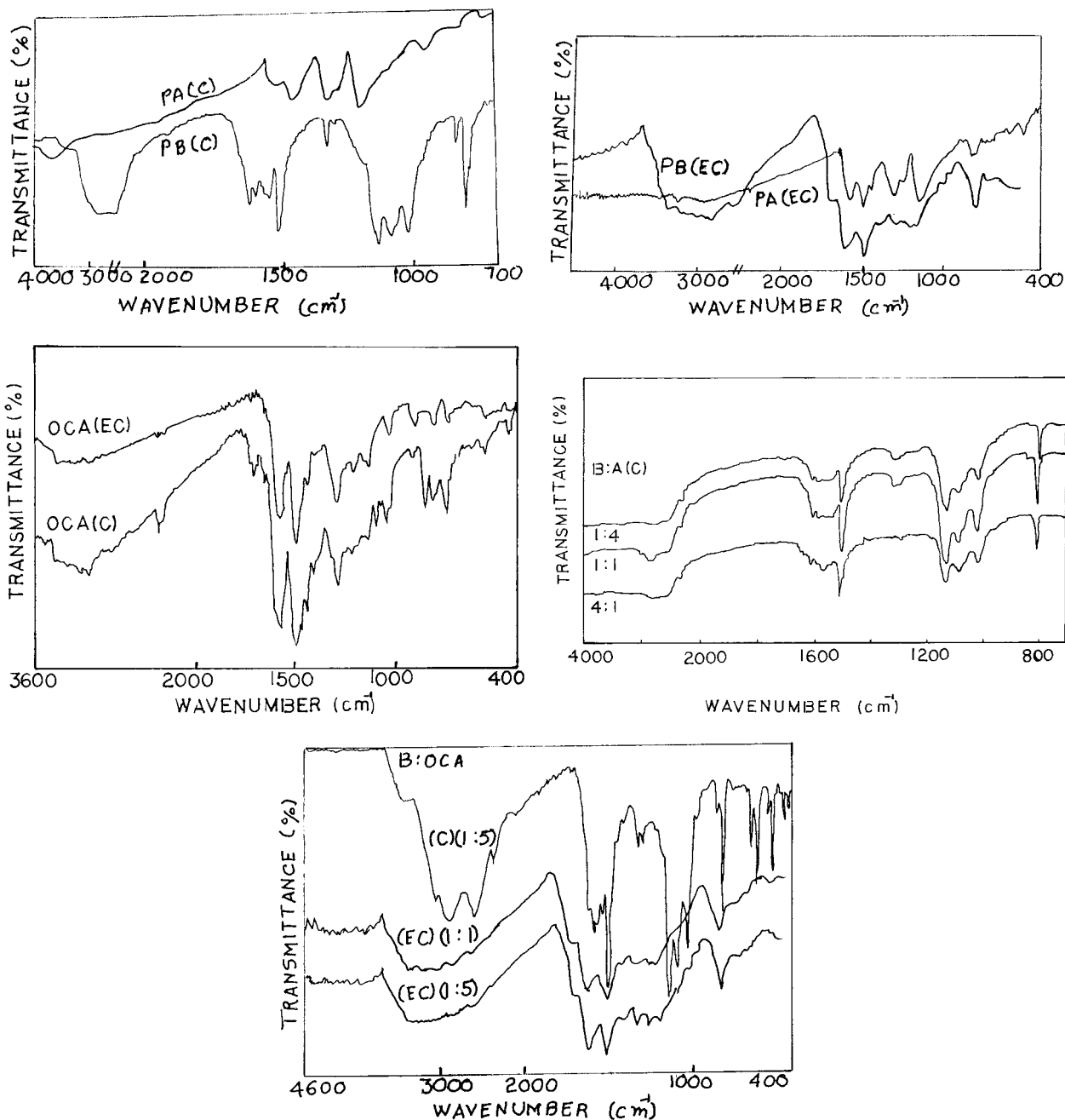


Figure 1 (a) IR spectra of PB (C) and PA (C). (b) FTIR spectra of PB (EC) and PA (EC). (c) FTIR spectra of OCA (C) and (EC). (d) FTIR spectra of B : A (C) (4 : 1, 1 : 1, and 1 : 4). (e) FTIR spectra of B : OCA (1 : 5 (C), 1 : 1 (EC), and 1 : 5 (EC)).

RESULTS AND DISCUSSION

The synthetic methods used by us are similar to those employed generally for polyanilines. The copolymers obtained chemically from benzidine and aniline vary in color from brown to green depending upon the comonomer composition. With increase in aniline content in the copolymer, there

is a shift in color from brown to green. A change of color from green to deep green was observed for B : OCA and B : MCA for different compositions. Polyanilines in salt form are generally green in color and polybenzidine is brown in color,⁸ so it is assumed that the predominance of one monomer over the other in the composition varies the physical properties like color. Electrochemically syn-

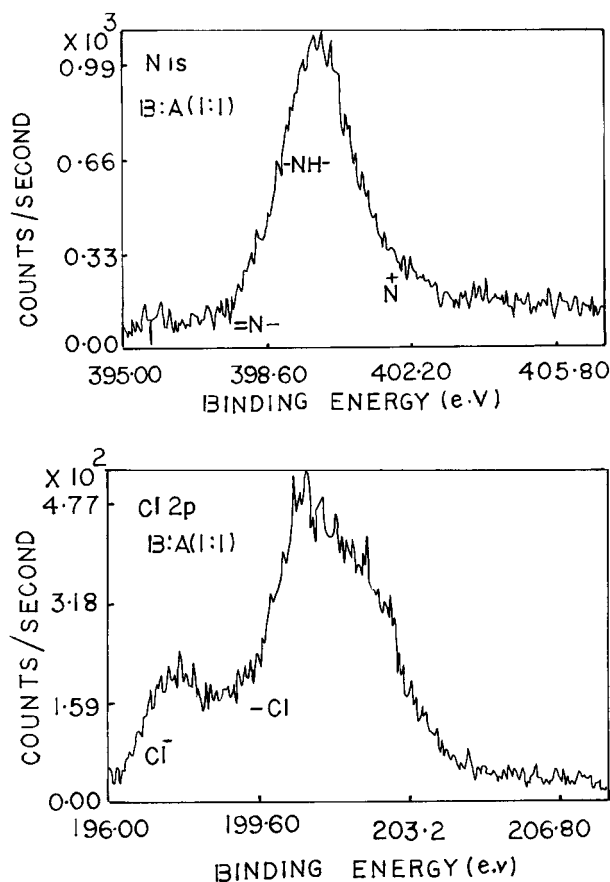


Figure 2 (a) XPS spectra for N 1s core level for B : A (1 : 1) (C). (b) XPS spectra for Cl 2p core level for B : A (1 : 1) (C).

thesized copolymers are basically dark brown in color. With increase in aniline content in the comonomer composition, the color shifts to black but there is a decrease in product yield. These copolymers are amorphous in nature. The copolymers obtained by the electrochemical method are comparatively more soluble in dimethyl sulfoxide, *N*-methyl pyrrolidone, and dimethylformamide than are those synthesised by the chemical method. This difference in solubility of the copolymers could be due to a lower molecular weight of the electrochemically prepared polymers.

Elemental, IR, FTIR, and XPS Analysis

Elemental analysis of different copolymers are tabulated in Table I and possible empirical formulas are derived for the copolymers. A high amount of oxygen may be due to the presence of sulfate or water.

IR and FTIR for homopolymers and copolymers are presented in Figure 1(a)–(e). The FTIR analysis of B : OCA (1 : 1, 1 : 5) (C) and (EC) show absorption bands at 1502 and 1589 cm^{-1} corresponding to quinoid and benzenoid structures, respectively. The absorption peak at 1300 cm^{-1} is associated with C—N stretching modes. Stretching modes at 754 and 800 cm^{-1} correspond to C—Cl and C—H modes. Absorption bands for 1100–1010 cm^{-1} indicated the presence of sulfate for chemically synthesized copolymers and poly-

Table II Specific Conductivity of Copolymers of B : A for Two Consecutive Runs

Copolymer Composition	First Run			Second Run		
	Conductivity at Room Temp $\times 10^8$ (S/cm)	Maximum Conductivity $\times 10^5$ (S/cm)	Temp ($^{\circ}\text{C}$)	Conductivity at Room Temp $\times 10^8$ (S/cm)	Maximum Conductivity $\times 10^8$ (S/cm)	Temp ($^{\circ}\text{C}$)
B : A (C)						
1 : 0	1.58	0.015	110	0.017	0.17	110
4 : 1	3.76	2.06	150	—	—	—
2 : 1	9.41	19.80	150	—	—	—
1 : 1	74.30	45.40	150	—	—	—
1 : 2	134.00	—	—	—	—	—
1 : 4	305.00	135.00	150	4.13	17100.00	160
0 : 1	2380.00	—	—	—	—	—
B : A (EC)						
4 : 1	1.24	6.20	85	3.38	9.22	115
2 : 1	3.72	34.10	120	1.73	32.10	80
1 : 1	4.96	70.90	130	—	—	—
1 : 2	224.00	1180.00	90	87.50	—	—
1 : 4	7410.00	26700.00	80	8520.00	—	—

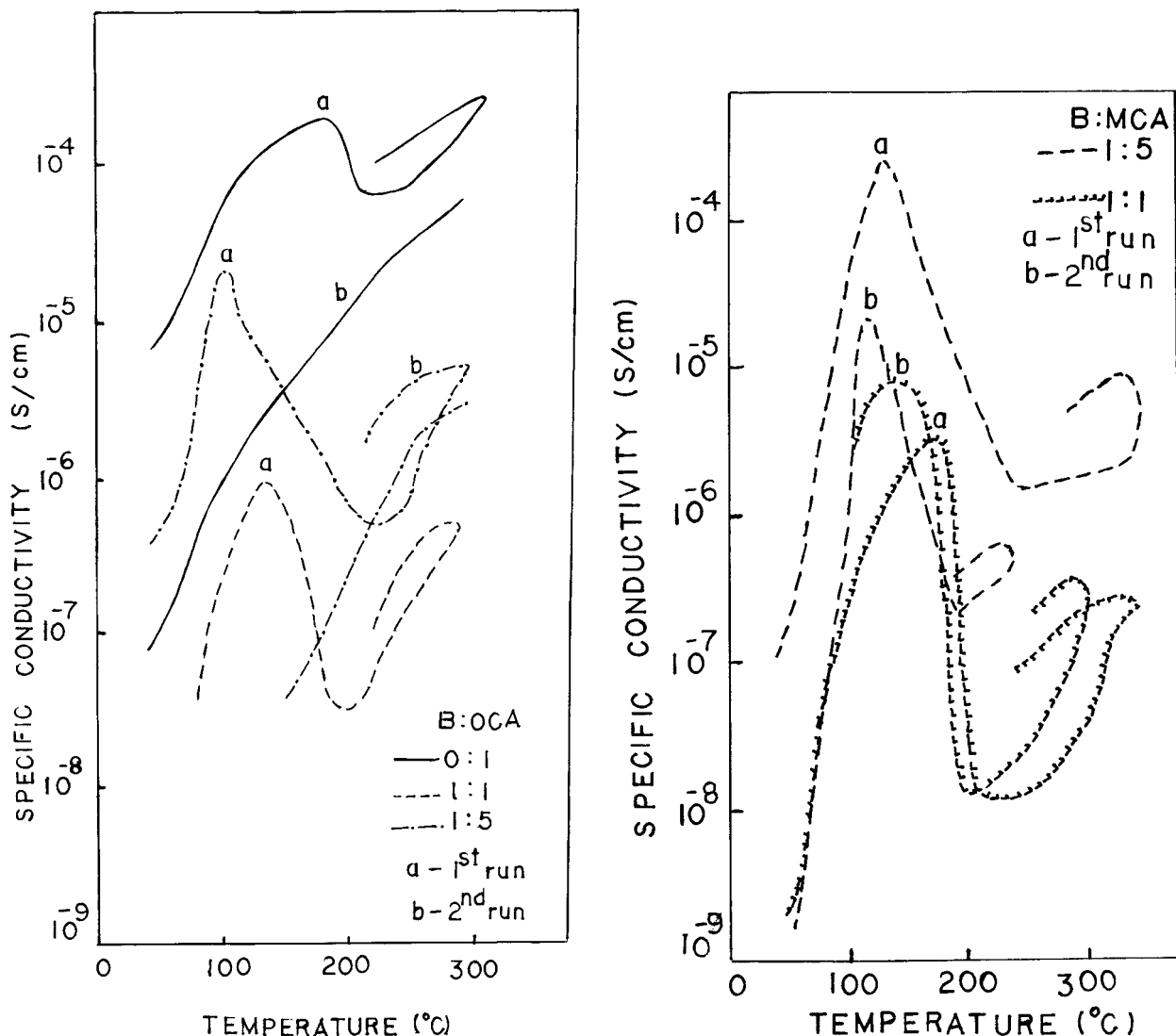


Figure 3 (a) Conductivities of B : OCA (C) (1 : 1 and 1 : 5) for two consecutive runs. (b) Conductivities of B : MCA (C) (1 : 1 and 1 : 5) for two consecutive runs.

benzidine. These peaks of sulfate were absent for electrochemically synthesized copolymers and polyaniline, poly(*o*-chloroaniline) and poly(*m*-chloroaniline) synthesized by the chemical method. The intensity of the C—Cl band is less in the copolymers of either composition (1 : 1 or 1 : 5) compared to their parent polymers. It indicates a random copolymerization with a predominance of benzidine moieties. Similar results were obtained for copolymers of B : A (C) [Fig. 1(d)]. From IR, it is difficult to determine the predominance of either monomer in the copolymers.

From XPS core-level spectra, characteristic binding energies (BEs) of the photoelectrons can be obtained and thus elements involved can be

identified. The peak intensity can be directly related to the atomic concentration in the sample. The shift of BE of core electrons is accompanied by changes in the chemical environment. Figure 2(a) and (b) presents the XPS N1s and Cl 2p core-level spectra for B : A = 1 : 1 (C). Nitrogen is obtained in three structural forms, corresponding to BEs of 398.2 eV (—N=), 399.4 (—NH—), and > 400 eV (—N⁺—). Qualitative analysis shows a —NH— structure in the maximum and —N— in the minimum proportions. The Cl 2p components are well resolved as ionic (Cl⁻) and covalent (—Cl) species corresponding to BEs of 197.2 and 200.3 eV. A qualitative amount of covalent chlorine is more than that of ionic chlorine

Table III Specific Conductivity of Copolymers of B : OCA and B : MCA for Two Consecutive Runs

Copolymer Composition	First Run			Second Run			
	Conductivity at Room Temp $\times 10^8$ (S/cm)	Maximum Conductivity $\times 10^7$ (S/cm)	Temp ($^{\circ}$ C)	Initial Conductivity $\times 10^8$ (S/cm)	Temp ($^{\circ}$ C)	Maximum Conductivity $\times 10^6$ (S/cm)	Temp ($^{\circ}$ C)
B : OCA (C)							
0 : 1	690.00	2186.00	200	7.60	40	—	—
1 : 1	3.81	9.59	120	191.00	30	253.00	120
1 : 5	38.30	218.00	90	3.83	50	—	—
B : OCA (EC)							
1 : 1	0.09	0.55	100	0.03	40	—	—
1 : 5	1.33	62.90	110	0.63	40	0.51	120
B : MCA (C)							
0 : 1	375.00	1184.00	150	300.0	100	—	—
1 : 1	0.22	37.0	150	208.00	50	8.00	140
1 : 5	9.1	2500.00	130	0.16	100	76.3	140
B : MCA (EC)							
1 : 1	6.78	11.30	170	0.01	100	—	—
1 : 5	15.40	17.60	90	0.07	40	—	—

and a small amount of ($-\text{N}^+-$) can therefore be due to covalent chlorine.

Thus, we observed that IR and FTIR studies gave absorption peaks for sulfate, chlorine, etc., but the peaks for covalent chlorine are not very sharp. The XPS analysis gave supportive evidence for chlorine in ionic and covalent forms. It also indicated the presence of variable oxidation states of nitrogen. This supports the possibility of the presence of sulfate as detected by IR and elemental analysis, as the sulfate ion may be held by ionic nitrogen.

Electrical Conductivity

Table II gives the specific conductivity for B : A (C) and (EC) at room temperature as well as at higher temperature. The polymers synthesized at low pH by either method are obtained in a doped state. In protonic acid doping, there is no electron transfer between the polymer chain and the dopants; instead, the protons are added directly to the polymer chain and may form bonds at available nitrogen sites and, subsequently, combine with π electrons of the polymer. This doping process results into a significant local modification of chain geometry leading to an introduction of the localized state in the gap like solitons, polarons, or bipolarons. But there are few other factors which affect the conductivity of polymers and vary with

temperature. When compared, the electrical conductivity of copolymers of B : A are found to be higher than that of polybenzidine and, as expected, the conductivity increases with the proportion of aniline in the copolymers. The electrochemically synthesized copolymers of B : A = 4 : 1, 2 : 1, and 1 : 1 have electrical conductivities lower than those of chemically synthesized polymers (Table II). The possible reason could be the low molecular weight of the polymers. But for B : A (EC) 1 : 2 and 1 : 4, the electrical conductivity is higher than that for B : A (C) 1 : 2 and 1 : 4. This discrepancy may be due to a higher dopant level of water or Cl^- . The presence of the sulfate ion can be one of the factors which could lead to the discrepancy in the observations. Similar results were obtained for copolymers of benzidine with *o*-chloroaniline and *m*-chloroaniline [Fig. 3(a) and (b) and Table III]. Polyaniline has a much higher conductivity (2.38×10^{-5} s/cm) compared to its substituted derivatives, i.e., poly(*o*-chloroaniline) (3.9×10^{-6} s/cm) and poly(*m*-chloroaniline) (3.75×10^{-6} s/cm). Poly(*o*-chloroaniline) has a higher conductivity than that of poly(*m*-chloroaniline), indicating the steric influence of the substitution. It is proposed that steric effects of the substituents indicate some ring twisting with the consequent reaction in π -conjugation in the polymer chain and, ultimately, reduction in the specific conductivity. Similar results were obtained for B : A,

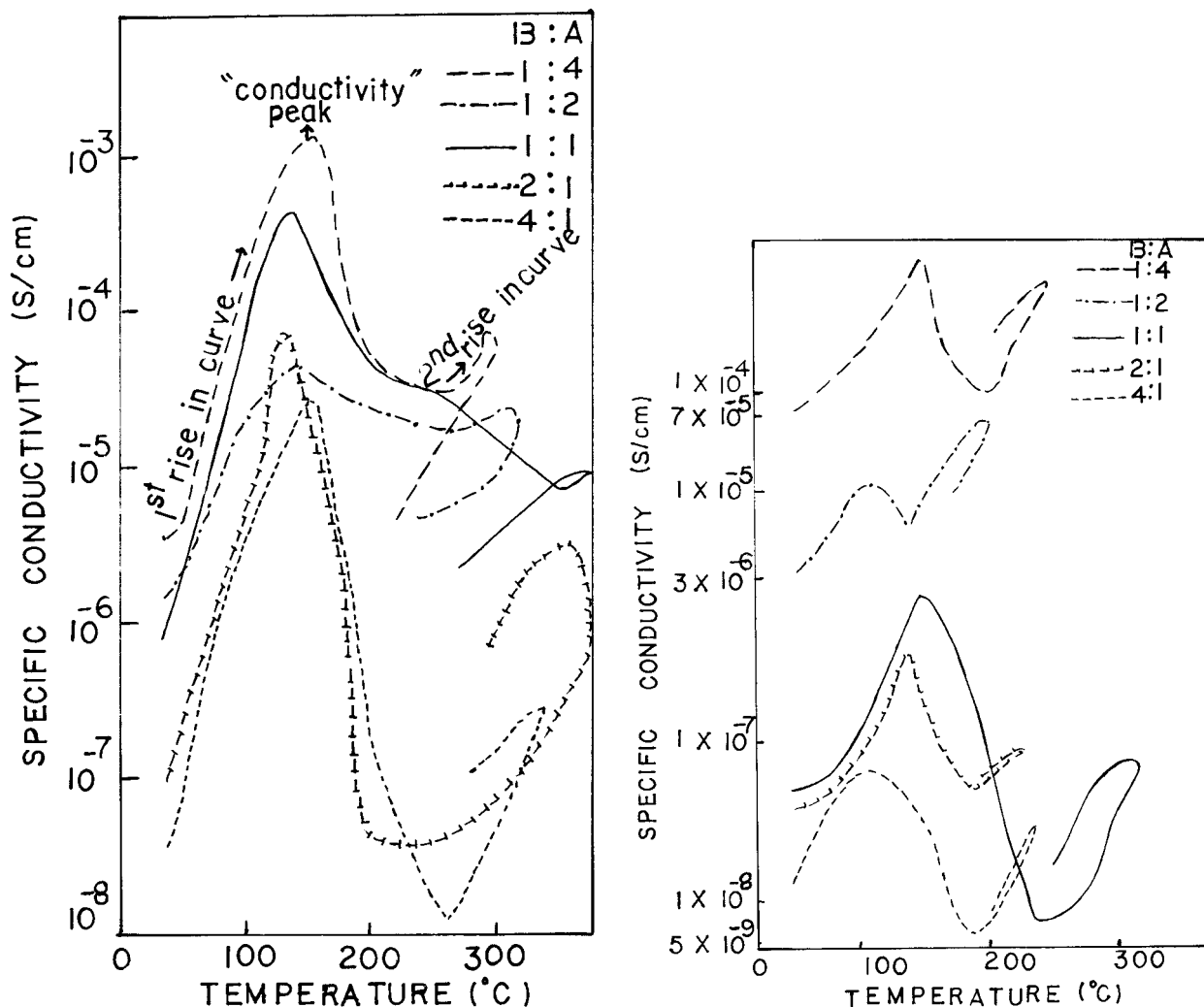


Figure 4 (a) Effect of temperature on conductivities of B : A (C) for first run. (b) Effect of temperature on conductivities of B : A (EC) for first run.

B : OCA, and B : MCA. Copolymerization of benzidine with aniline derivatives has led to an increase in the specific conductivity. With increase in aniline and its derivative content, a considerable increase of $\sim 10^3$ times was obtained.

Figure 4(a) and (b) shows the electrical conductivity (σ) for B : A (C) and (EC) as a function of temperature (T). In first run, the specific conductivity increases and then decreases with increase in temperature. A similar trend was observed for all the copolymers. During electrical conductivity measurements, a "conductivity peak" is obtained, which varies in peak height from one polymer to another. Figure 5(a) and (b) give a conductivity plot for second-run measurements. An absence or considerable decrease in peak height is observed. This observation is assumed to

be due to the removal of moisture or ionic chlorine present in the polymer. The effect of moisture or air on the conductivity of copolymer B : A (1 : 4) was tested by exposing the polymer overnight to the air after first run. The copolymer B : A (1 : 4) at room temperature shows a decrease in conductivity by 10^2 times in second run, but still the peak conductivity value is quite high. The hygroscopic nature and reaction with atmospheric oxygen can be one of the factors for this type of behavior.

Table II gives the temperature at which maximum conductivity is obtained. The temperature ranges from 140 to 150 (°C) for B : A (C) and 80 to 120 (°C) for B : A (EC). This observation can be correlated assuming that electrochemically obtained polymers are more hygroscopic in nature (both runs). From Figure 5(a) and (b), it is obvi-

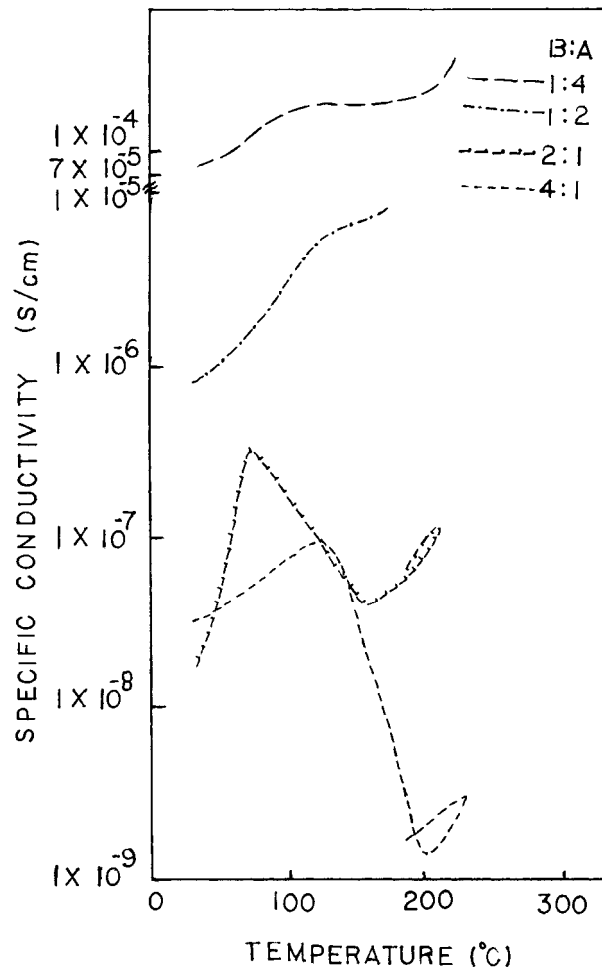
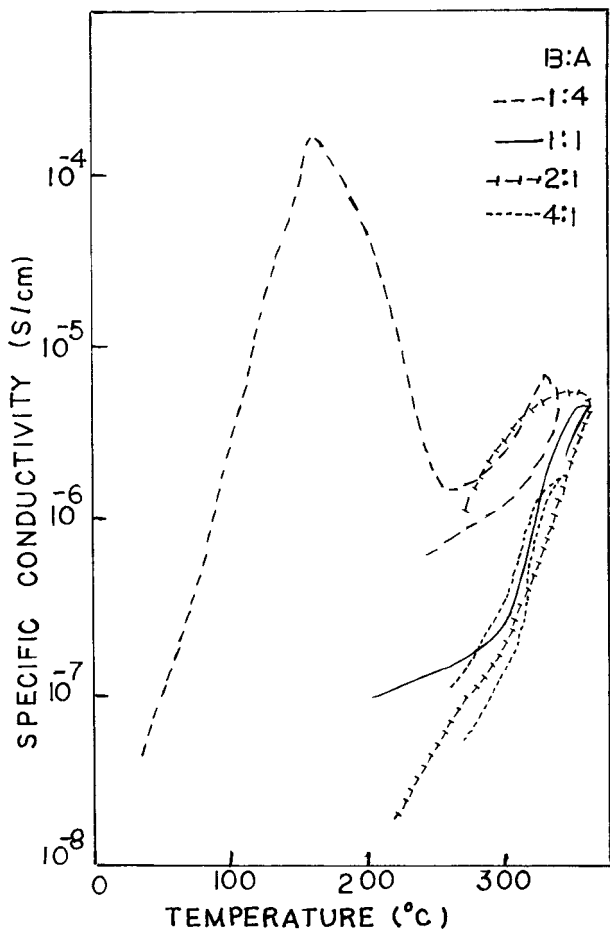


Figure 5 (a) Effect of temperature on conductivities of B : A (C) for second run. (b) Effect of temperature on conductivities of B : A (EC) for second run.

ous that the second increase in conductivity values occurs in the same temperature range irrespective of the number of runs. This could be due to the basic structure of polymers, which is principally responsible for electrical conduction. Many factors such as pressure, pH of the electrolyte

used, moisture, and % doping play a role in electrical conduction and, hence, it is difficult to optimize conditions to obtain reproducible values as supported by other authors also.⁹⁻¹²

Table IV Activation Energies for Conductivity in First and Second Rise in the Curve of First Run

Copolymers B : A (C)	First Rise $E_g \times 10^4$ (eV)	Second Rise $E_g \times 10^4$ (eV)
4 : 1	6.17	9.59
2 : 1	5.75	6.25
1 : 1	6.16	—
1 : 4	5.89	7.84

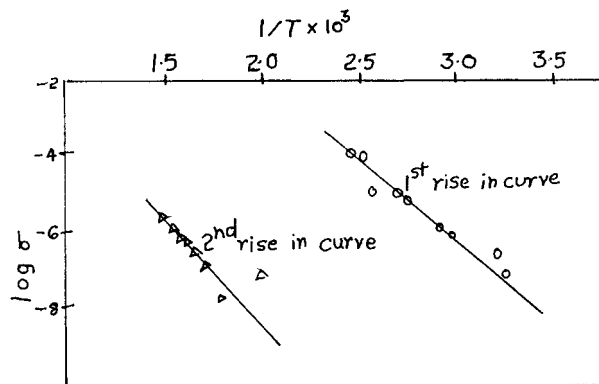


Figure 6 Plot of $\log \sigma$ vs. $1/T$.

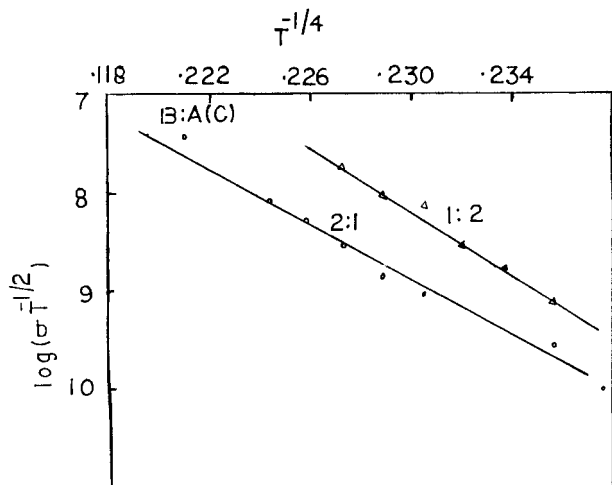


Figure 7 Plot of $\log \sigma T^{1/2}$ vs. $T^{-1/4}$.

Activation energies for conduction were calculated for the temperature range investigated (Table III). All the measured points are approximated to a straight line through the equation

$$\sigma(T) = \sigma_0 \exp(-Eg/KT)$$

showing temperature dependence. The activation energies (Table IV) from the slope of first rise in the curve (Fig. 6) for electrical conductivities are more or less same for all B : A copolymers, but in

the second rise of curve, it is found that Eg values decrease with increasing aniline content. This supports the earlier observation that the copolymer composition may play a major role in modifying the properties.

Different people have suggested different equations for various modes of conduction. The hopping conduction mechanism as suggested by Greeves¹³ is given by the equation

$$\sigma T^2 = \exp(-B/T^{1/4})$$

where B is a constant and the equation

$$\sigma = AT^{1/2} \exp(-Ea/KT)$$

by Matare¹⁴ indicates a grain boundary barrier type of conduction mechanism where A is a constant and Ea is a potential barrier. The tunneling equation by Zeller¹⁵ is expressed as

$$\sigma = \sigma_0 \exp(-A/T^{1/2})$$

Various plots for all the modes were prepared for the copolymer of B : A (C). Plots of $\log(\sigma T^{1/2})$ vs. $T^{-1/4}$ (Fig. 7) were found to be straight lines, whereas the plots $\log(\sigma T^{-1/2})$ vs. $1/T$ and $\log \sigma$ vs. $T^{-1/2}$ were not linear, suggesting a hopping mechanism for the electrical conduction. The presence of defects like water or ionic chlorine create polaron sites which be-

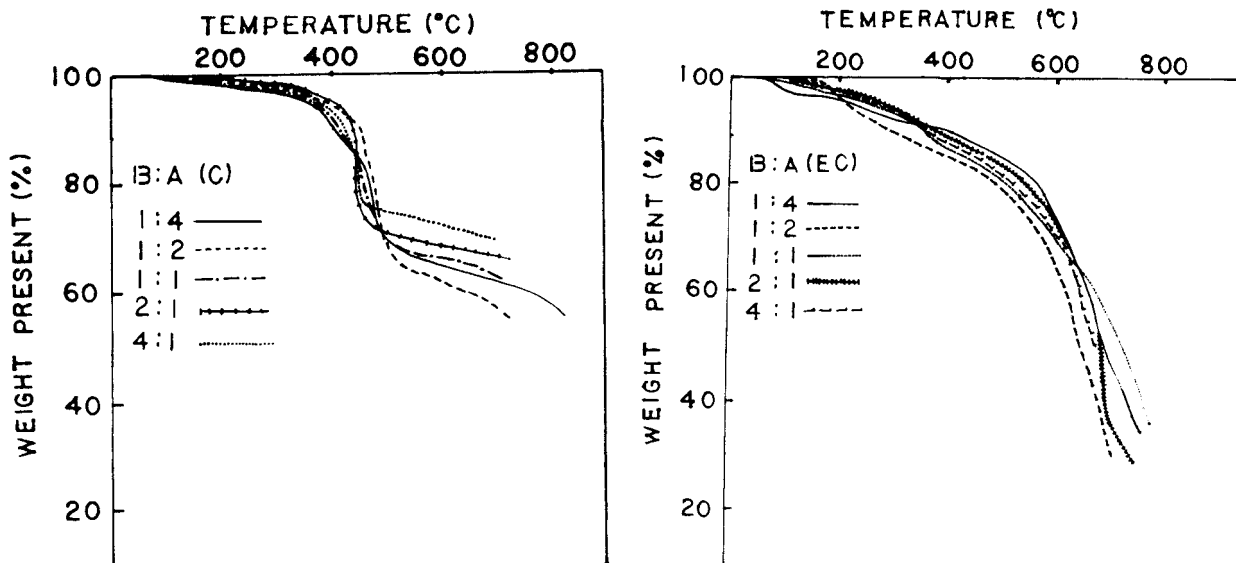


Figure 8 (a) Thermal analysis for B : A (C). (b) Thermal analysis for B : A (EC).

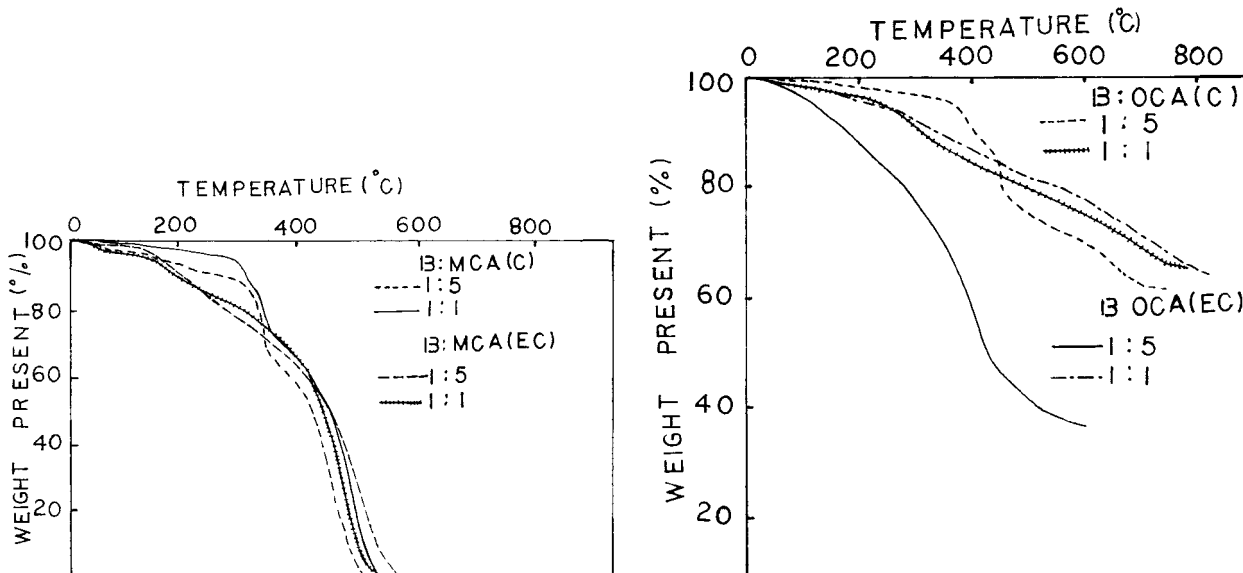


Figure 9 (a) Thermal analysis for B : MCA (C) and (EC). (b) Thermal analysis for B : OCA (C) and (EC).

have as charge carriers and give rise to a metal-like band structure. However, the extent of conduction depends upon the concentration of defects in the polymer, morphology of polymer, etc. Polaron hops from one state to another and leads to the conductivity of the copolymers.

Thermal Analysis

Thermal analysis was done for B : A [Fig. 8(a) and (b)], B : MCA [Fig. 9(a)] and B : OCA [Fig.

9(b)]. All the polymers show a small weight loss near 100°C, indicating a loss of water which could be bonded weakly to the polymer. The B : A (EC) copolymer is found to be more thermally stable than is polyaniline prepared under the same conditions.

A major weight loss around 250–300°C could be due to decomposition of very low molecular weight polymers as indicated by JaCroix and Diaz¹⁶ and Wei and Hsueh¹⁷ or by chlorination of the benzene ring as suggested by Hagiwara et al.¹⁸ To support this fact, the thermal aging process was carried out. The lowering of the pH of

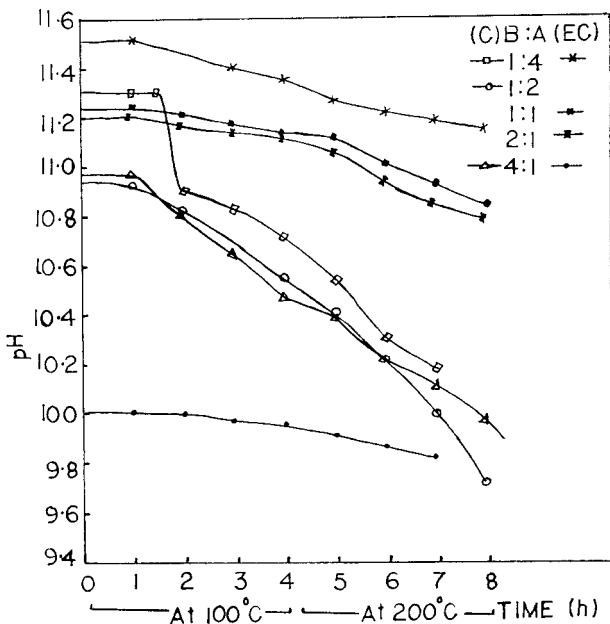


Figure 10 Plot of pH vs. time.

Table V Amount of HCl Liberated During Thermal Aging

Copolymers	% Cl ⁻ Liberated	
	100°C	200°C
B : A (C)		
4 : 1	0.17	1.35
2 : 1	2.94	2.93
1 : 1	3.94	2.61
1 : 2	4.30	4.53
1 : 4	5.30	5.80
B : A (EC)		
4 : 1	—	—
2 : 1	—	—
1 : 1	1.91	0.27
1 : 2	2.27	6.61
1 : 4	4.50	8.36

NaOH solution could be due to volatiles liberated which we believe to be hydrogen chloride. The amount of HCl liberated during the aging process increases with heating time and temperature as shown in Figure 10 and Table V. It is observed that with an increase in the amount of aniline in the copolymer B : A the percent of Cl^- liberated increases and it is also observed that the conductivity is higher in copolymers with a higher proportion of aniline. This shows that the extent of doping or the presence of ions has a great influence on the electrical conductivity of polymers.

Activation energies for the major degradation of copolymers were calculated by the Broido¹⁹ method. Figure 11 is a plot of $\ln(\ln 1/Y)$ vs. $1/T$, where Y is the weight fraction of the original weight of the polymer. The values of the activation energies are given in Table VI. All the copolymers were found to be thermally stable at least up to 300°C.

CONCLUSION

The copolymers of benzidine with aniline and its derivatives show an increase in electrical conductivity with an increased aniline feed ratio. There is a steric influence of chlorine in the *o*- or *m*-position on the electrical conductivity of the copolymers. The thermal stabilities of these co-

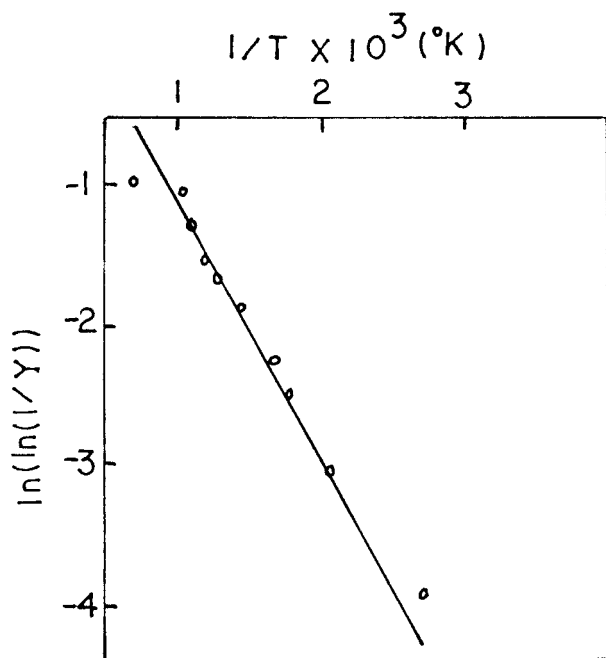


Figure 11 Plot of $\ln(\ln 1/Y)$ vs. $1/Y$.

Table VI Activation Energies for Decomposition of Copolymers of B : A, B : OCA, and B : MCA

Copolymers	E (kJ)
B : A (C)	
4 : 1	45.11
2 : 1	—
1 : 1	35.64
1 : 2	48.25
1 : 4	47.14
B : OCA (C)	
1 : 1	12.68
1 : 5	23.70
B : MCA (C)	
1 : 1	31.32
1 : 5	—
B : A (EC)	
4 : 1	16.3
2 : 1	23.2
1 : 1	14.31
1 : 2	16.04
1 : 4	20.73
B : OCA (EC)	
1 : 1	—
1 : 5	46.32
B : MCA (EC)	
1 : 1	48.19
1 : 5	35.15

polymers were found to be quite high. No specific conclusion could be drawn for the effect of copolymerization on the thermal behavior of these polymers.

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