Aromatic-Aliphatic Polyimides. I. Preparation and Properties of Polypyromellitimides from Aromatic Diamines and Oxalyl Dihydrazide

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ABSTRACT

Copolyimides were prepared in two steps by ring-opening polyaddition of pyromellitic dianhydride (PMDA) with oxalyl dihydrazide (O) and an aromatic diamine; viz., diamino-diphenyl methane (M), p-phenylene diamine (P), or benzidine (B) in dimethylsulfoxide (DMSO), followed by thermal cyclodehydration. O content was restricted to 10%. Kinetics of imidization of polyamic acid samples was studied. The effect of structure and composition of copolymers on thermal properties was evaluated.

INTRODUCTION

Polyimides, among the class of heterocyclic polymers, have re-markable high temperature resistance [1-3]. They are, however, extremely intractible, being insoluble in most organic solvents. Various copolyimides have been reviewed to correlate their struc-ture-solubility relationships [4]. Polyimides have been prepared from hydrazine [5]. However, there have been no reports on the

synthesis of copolyimides containing oxalyl dihydrazide (O) units. The objective of the present work was to synthesize and characterize a series of copolyimides containing oxalyl dihydrazide and aromatic diamines such as diaminodiphenyl methane (M), p-phenylene diamine (P), or benzidine (B) in the polymer backbone and to compare the effect of O incorporation in the polymers on solubility and thermal behavior.

EXPERIMENTAL

Materials

O was prepared according to the method described by Chang and Vogl [6] (mp 240°C). PMDA (Koch-Light Laboratories) (mp 284-286°C), M (Koch-Light Laboratories) (mp 90°C), P (BDH) (mp 140°C), and B (Reanal) (mp 127-129°C) were sublimed under reduced pressure at temperatures of 220-240, 80, 130, and 110°C, respectively. All five monomers were vacuum dried for 10 h at 60-70°C before polymerization.

DMSO (BDH) was purified by refluxing with CaH_2 and distilling over molecular sieves (4A) under reduced pressure.

Dimethylformamide (DMF) (BDH) was similarly purified by keeping over anhydrous $MgSO_4$ for 24 h and distilling over molecular sieves (4A).

Xylene, hexane, and carbon tetrachloride were distilled before use.

Polymerization

The reaction of dianhydride and diamine was carried out in DMSO using 10% (w/v) solutions of equimolar quantities of the monomers. The reaction was carried out under nitrogen atmosphere to avoid oxidation of amine groups. The mixture was stirred for 6 h at 30°C and left overnight. The polymer was precipitated in water, washed with dilute hydrochloric acid, water, and finally acetone, and dried under vacuum at 80°C to constant weight.

The polyamic acid films were thermally converted to polyimide by heating in an air oven at 220°C for 3 h.

Characterization of Polymers

Viscosity measurements were done in DMF at 30°C by using an Ubbelohde suspension level viscometer. The polymer concentration was varied in the range 0.2-0.5 g/dL.

IR spectra of polyamic acids and polyimides were run in Nujol mull using a Perkin-Elmer spectrophotometer.

The densities of powdered polyamic acid and polyimide were deter-
mined by the suspension method using xylene and carbon tetrachloride
for the B and P series of polymers, and hexane and carbon tetrachlo-
ride for the M series [7].

X-ray diffraction diagrams were obtained using the Philips x-ray
unit PW1140/90 with Ni-filtered CuK$_\alpha$ radiation at 40 kV.

Cyclodehydration of polyamic acids was followed by measuring the
weight loss with time in a furnace that maintained a temperature of
±2°C.

Thermal analysis of the polymers was carried out under nitrogen
in a Stanton-Redcroft TG-750 thermal analyzer. A heating rate of
10°C/min was maintained and 5 mg of the polymer was used.

RESULTS AND DISCUSSION

Results of preparation of polymers are summarized in Table 1.
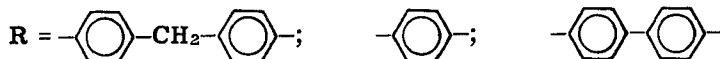The reaction scheme is as follows:

$$(X)NH_2-R-NH_2 \ + \ (Y)NH_2-NH-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-NH-NH_2$$
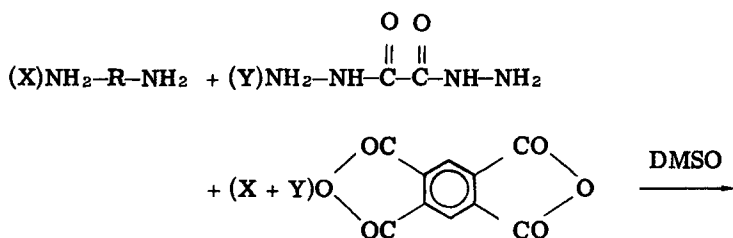
gave a random copolymer consisting of X units:
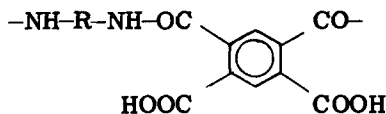
and Y units
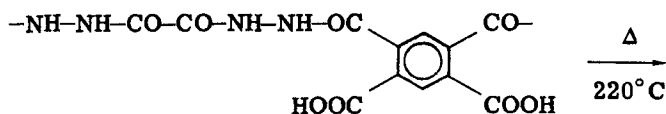
as a random copolyimide in which

$$R = \; -\!\!\left\langle \bigcirc \right\rangle\!\!-CH_2-\!\!\left\langle \bigcirc \right\rangle\!\!-; \qquad -\!\!\left\langle \bigcirc \right\rangle\!\!-; \qquad -\!\!\left\langle \bigcirc \right\rangle\!\!-\!\!\left\langle \bigcirc \right\rangle\!\!-$$

Viscosity

The viscosities of all polyamic acids drop with an increase of O content in the reaction mixture. This indicates the poor reactivity of O as compared to other diamines. The presence of an electron-withdrawing group vicinal to $-NH_2$ in O reduces its nucleophilicity, leading to the observed decrease in reactivity:
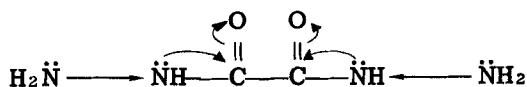
$$H_2\ddot{N} \longrightarrow \dot{N}H-C-C-\dot{N}H \longleftarrow \ddot{N}H_2$$

TABLE 1. Preparation of Polyamic Acids

No.	Polymer code	O:D[a] (mole ratio)	Weight[b] (g)			Viscosity[c] (dL/g)
			PMDA	D	O	
1	M	O	0.2620	0.2380	–	0.56
2	$M_{98}O_2$	2:98	0.2630	0.2341	0.0029	0.40
3	$M_{96}O_4$	4:96	0.2641	0.2302	0.0057	0.38
4	$M_{94}O_6$	6:94	0.2651	0.2263	0.0086	0.38
5	$M_{92}O_8$	8:92	0.2661	0.2224	0.0115	0.33
6	$M_{90}O_{10}$	10:90	0.2672	0.2184	0.0144	0.15
7	P	O	0.3344	0.1656	–	1.02
8	$P_{98}O_2$	2:98	0.3342	0.1622	0.0036	0.54
9	$P_{96}O_4$	4:96	0.3339	0.1588	0.0073	0.42
10	$P_{94}O_6$	6:94	0.3337	0.1554	0.0109	0.40
11	$P_{92}O_8$	8:92	0.3335	0.1520	0.0145	0.36
12	$P_{96}O_{10}$	10:90	0.3333	0.1486	0.0181	0.18
13	B	O	0.2711	0.2289	–	1.63
14	$B_{98}O_2$	2:98	0.2720	0.2250	0.0030	0.62
15	$B_{96}O_4$	4:96	0.2729	0.2212	0.0059	0.46
16	$B_{94}O_6$	6:94	0.2738	0.2173	0.0089	0.42
17	$B_{92}O_8$	8:92	0.2748	0.2133	0.0119	0.38
18	$B_{90}O_{10}$	10:90	0.2757	0.2094	0.0149	0.22

[a]D represents the aromatic diamine M/P/B.
[b]Volume of DMSO added to make a 10% (w/v) solution.
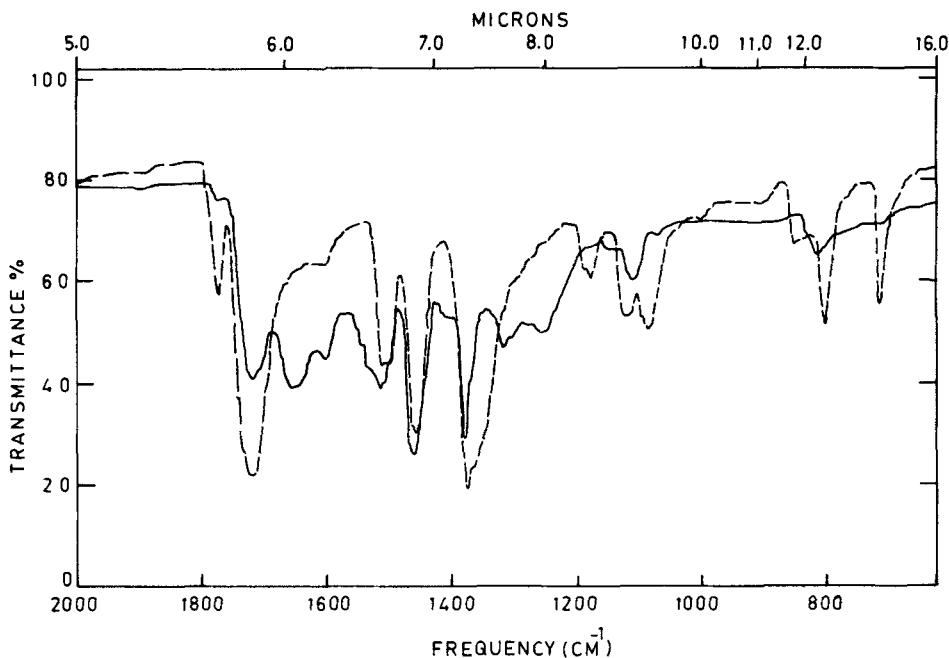[c]Intrinsic viscosity determined at 30°C for a 0.5% solution in DMF.

FIG. 1. Infrared spectra of B polyamic acid (—) and the corresponding cyclodehydration product (- -).

The decrease in viscosities of $P_{98}O_2$ and $B_{98}O_2$ is much higher than that of $M_{98}O_2$ with respect to the corresponding homopolymers. This may be due to the presence of an O unit in the copolymer chain which may significantly reduce the reactivity of end amino groups containing P and B where extended conjugation is possible.

The order of reactivity among the aromatic diamines toward polymerization as seen from the viscosity data is $M < P < B$. The reactivity depends on nucleophilicity of $-NH_2$ groups which, in turn, depends on inductive and resonance effects. Though there exists direct conjugation between the two amino groups in P as well as in B, the inductive effect is greater in P, leading to a decrease in electron density on the carbon atom bonded to the other amino group and hence the overall reactivity. Further, the nucleophilicity of amino groups of B is more than of P because of extended conjugation in the former. In M, such conjugation is not possible due to the presence of a methylene group between phenyl rings.
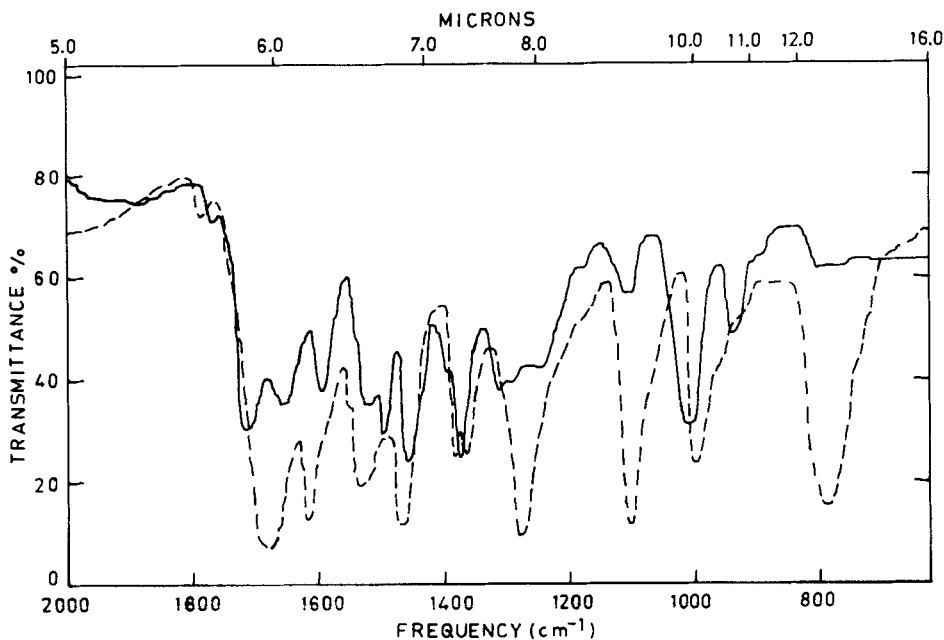
FIG. 2. Infrared spectra of $B_{90}O_{10}$ polyamic acid (—) and the corresponding cyclodehydration product (- -).

Infrared Spectra

The spectra of all polyamic acids showed broad absorption bands around 1610, 1650, and 3400 cm^{-1} (Figs. 1 and 2). The band at 3400 cm^{-1}, however, is not clearly resolved due to C–H absorption of Nujol. The absorption band at 1650 cm^{-1} is peculiar to secondary amide groups. In homopolyimides both these bands disappear and new absorption peaks appear at about 1775, 1710, 1080, 800, and 710 cm^{-1}. The bands at 1775 and 1710 cm^{-1} are related to the stretching vibrations of two carbonyls that are weakly coupled. The bands at 1080, 800, and 710 cm^{-1} can be associated with vibrations of cyclic structures. In addition, spectra of copolyimides showed two peaks at 1610 and 1680 cm^{-1} (overlapped with 1710 cm^{-1} peak) which are characteristic of –CO–NH–NH– grouping [8]. This indicates that O does not participate in cyclization. Similar observations were made by Frost et al. for polyamic acids containing hydrazide groups [9].

Density Measurements and X-Ray Diffraction Studies

The densities of polyamic acid and polyimides are reported in Table 2. B and P polymers showed higher densities in comparison to

TABLE 2. Densities of Copolyamic Acids and Copolyimides

Polymer code	Density[a] (g/cc)	
	Polyamic acid	Polyimide
M	1.058	1.158
$M_{98}O_2$	0.865	0.869
$M_{96}O_4$	0.863	0.864
$M_{94}O_6$	0.859	0.862
$M_{92}O_8$	0.855	0.858
$M_{90}O_{10}$	0.851	0.858
P	1.277	1.369
$P_{98}O_2$	1.158	1.227
$P_{96}O_4$	1.158	1.207
$P_{94}O_6$	1.129	1.207
$P_{92}O_8$	1.096	1.158
$P_{90}O_{10}$	1.096	1.129
B	1.382	1.424
$B_{98}O_2$	1.315	1.376
$B_{96}O_4$	1.315	1.376
$B_{94}O_6$	1.303	1.353
$B_{92}O_8$	1.303	1.345
$B_{90}O_{10}$	1.227	1.277

[a]Probable deviation is less than 1%.

M polymers. This may be explained in terms of the rigid rodlike structure of B and P polymers due to resonance. In M the resonance is disturbed by introduction of the methylene group. All copolymers showed lower densities than the corresponding homopolymers and decreased further with an increase of O content. This has been further substantiated by x-ray diffraction diagrams obtained from powdered polymers using CuK_α radiation. Typical x-ray diffraction patterns of samples are shown in Fig. 3. All copolyimides showed an increase in density upon cyclodehydration. This may be due to the reduction of the molar volume of the polymers.

Solubility

Qualitative solubility of the polymers in excess solvent was determined on powdered samples. The solubility of copolyamic acids in various aprotic solvents (NMP, HMPA, DMF, DMAc, DMSO) is higher than that of the corresponding homopolymers. This further supports the density and crystallinity measurements described above.
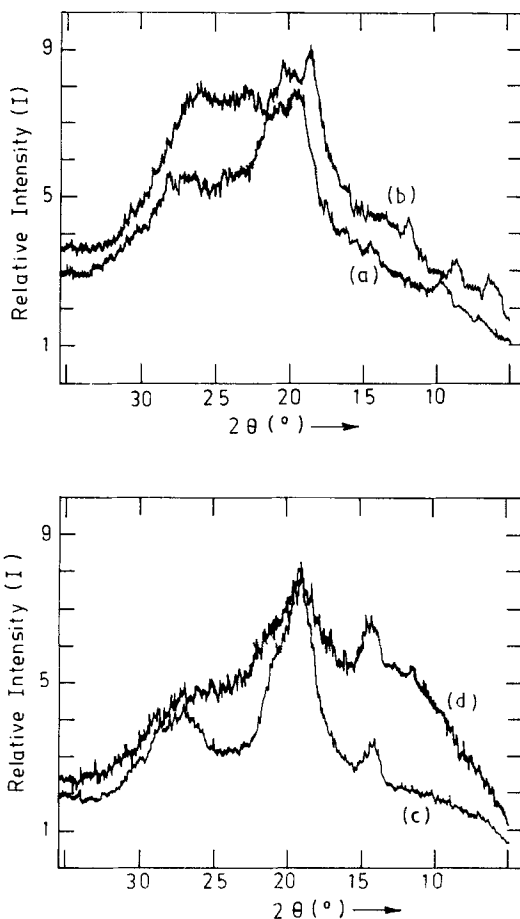
FIG. 3. X-ray diffraction patterns: (a) P polyamic acid, (b) $P_{96}O_4$ polyamic acid, (c) P polyimide, and (d) $P_{96}O_4$ polyimide.

Cyclodehydration Studies

A study of the isothermal weight loss at 200°C reveals that all samples showed rapid cyclization in the first 3 min (Figs. 4-6). Beyond this, the rate decreased. M and P polymers lose about 11% of their original weight in 7 min in comparison to only 6% for B. This means that the relative ease of cyclization for M and P is much greater than that of B. The rigid nature of B may hinder cyclization. This fact is further evident in comparing B and $B_{96}O_4$ where ease of cyclization of the latter is found to be much greater. At 200°C, the
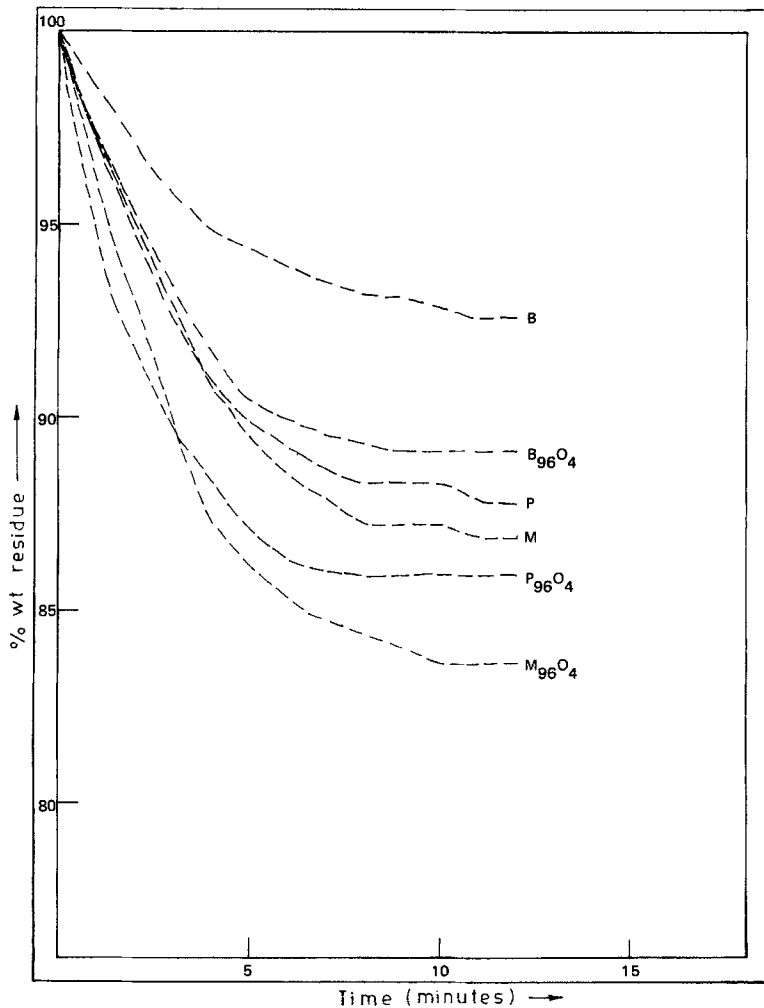
FIG. 4. Isothermal cyclization at 200°C: B, $B_{96}O_4$; P, $P_{96}O_4$; and M, $M_{96}O_4$.
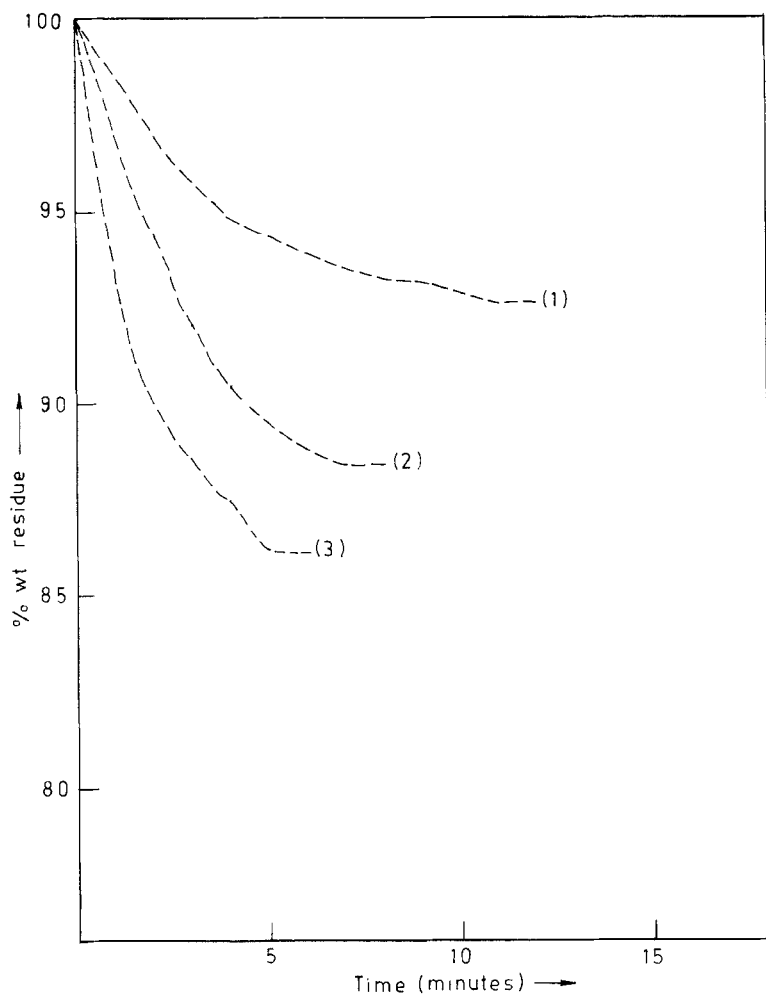
FIG. 5. Isothermal cyclization of B: (1) 200°C, (2) 240°C, and (3) 280°C.
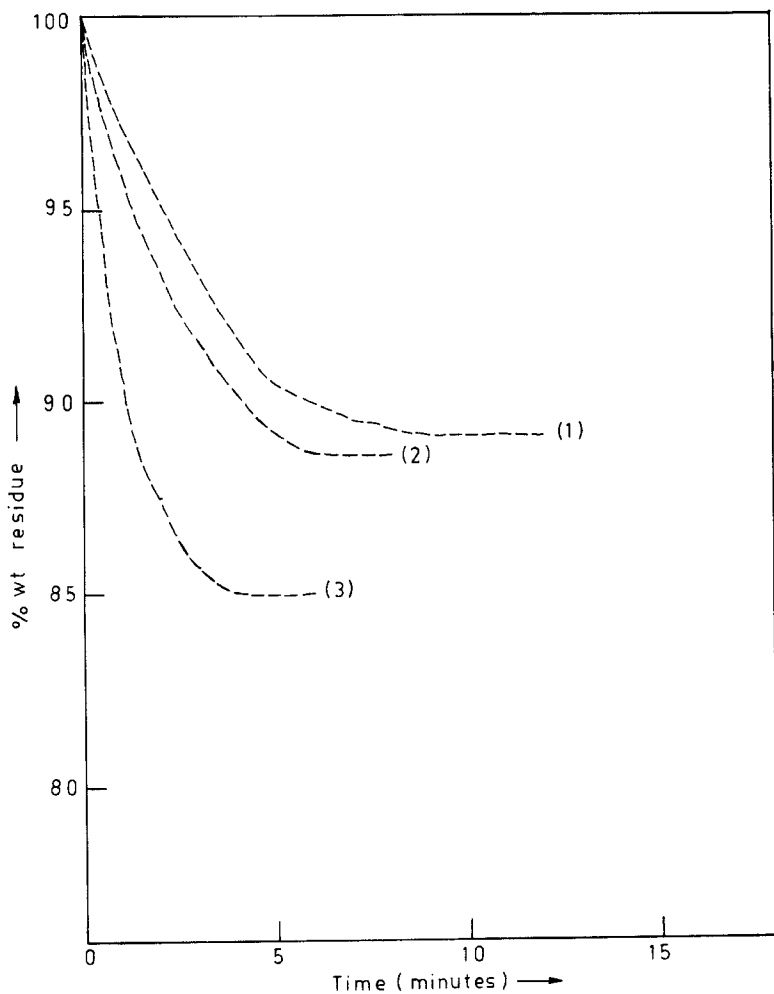
FIG. 6. Isothermal cyclization of $B_{86}O_4$: (1) 200°C, (2) 240°C, and (3) 280°C.

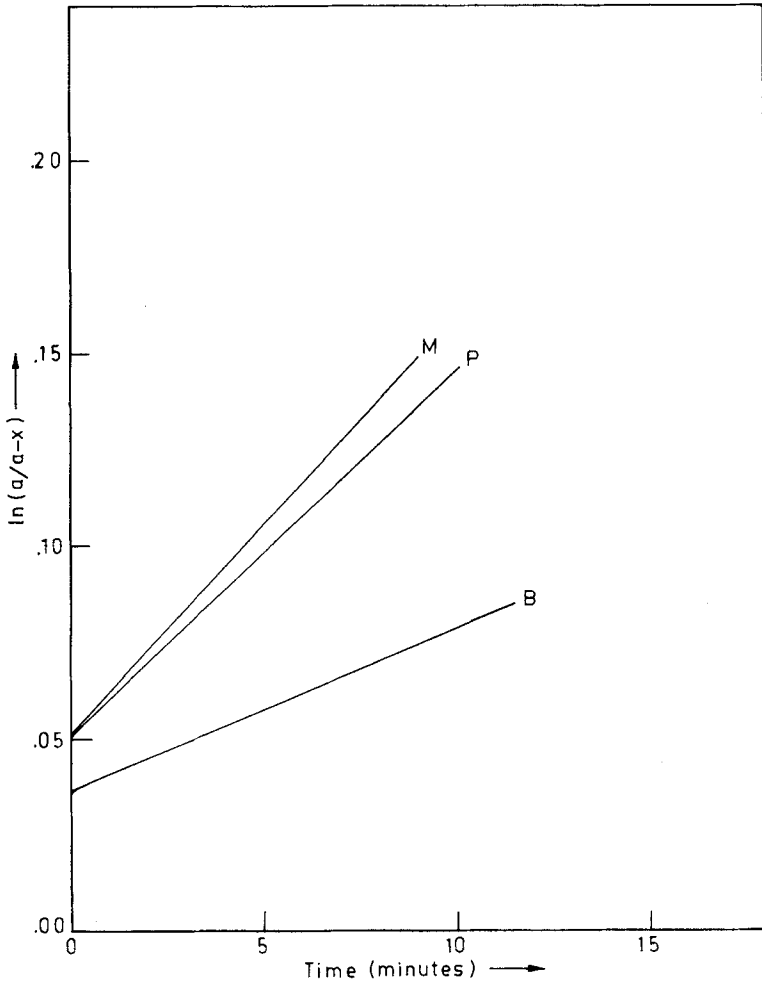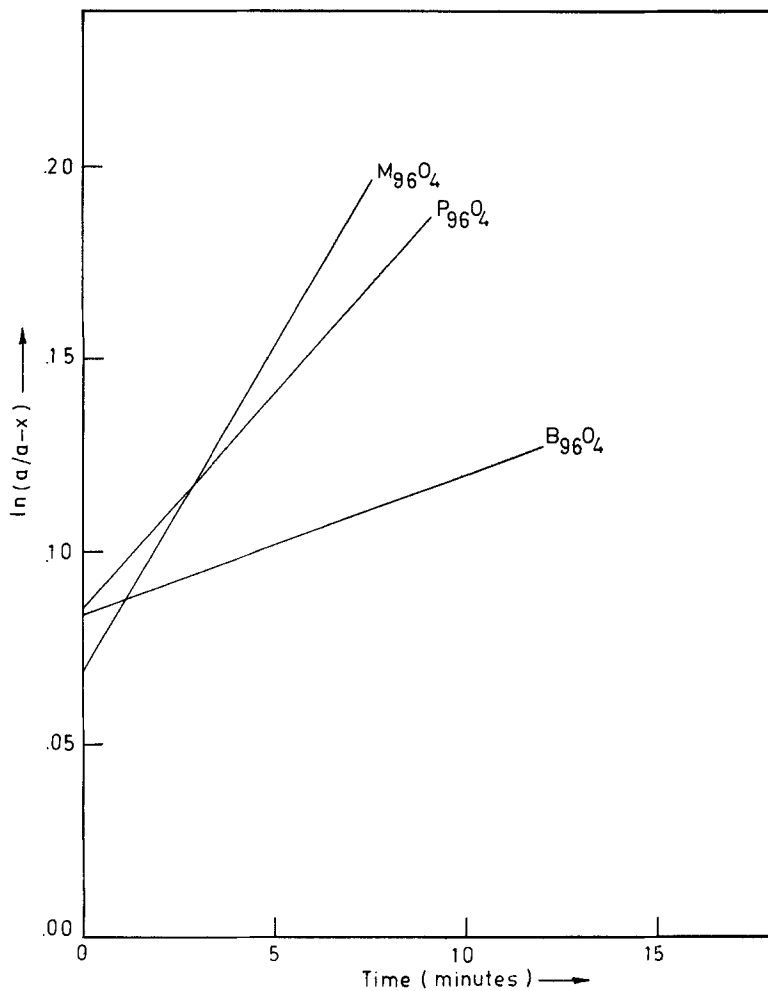FIG. 7. First-order plot at 200°C: B, P, and M.

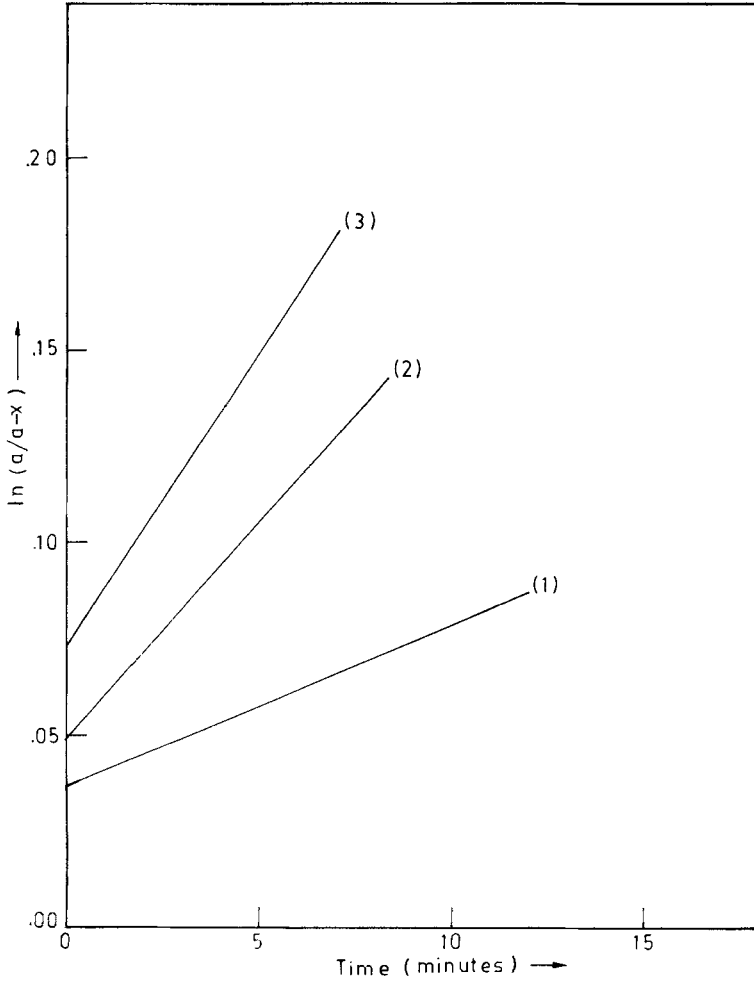FIG. 8. First-order plot at 200°C: $B_{96}O_4$, $P_{96}O_4$, and $M_{96}O_4$.

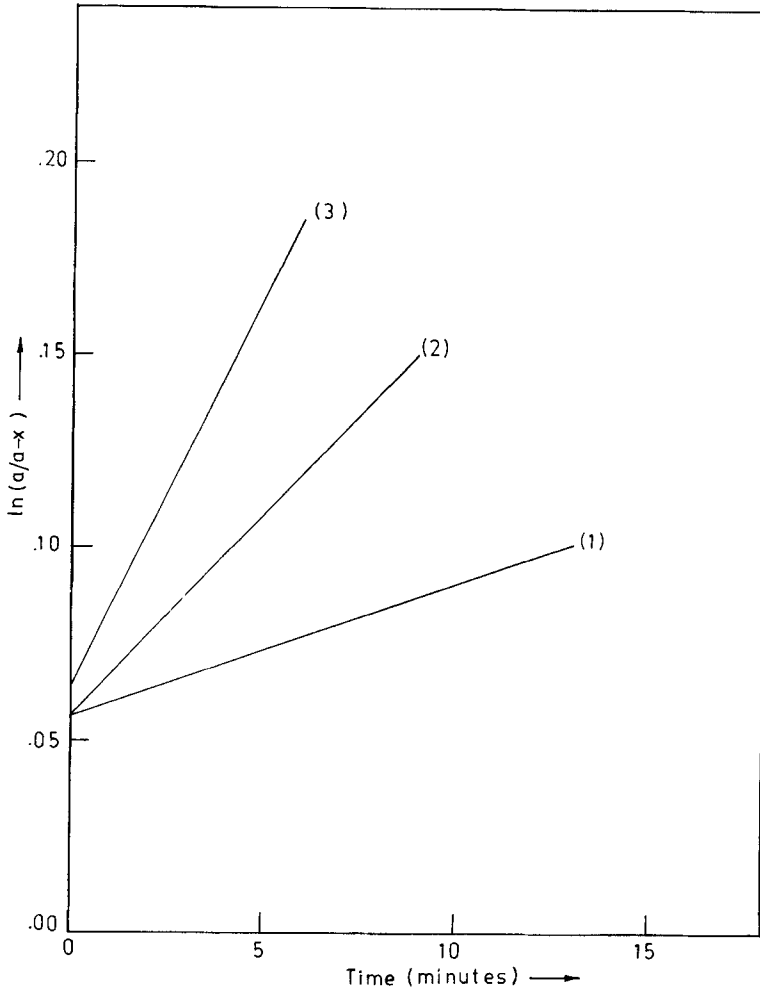FIG. 9. First-order plot of B: (1) 200°C, (2) 240°C, and (3) 280°C.

FIG. 10. First-order plot of $B_{36}O_4$: (1) 200°C, (2) 240°C, and (3) 280°C.

TABLE 3. Rate Constants for Cyclization

Polymer code	$k \times 10^3$ (°C/min)		
	200	240	280
B	4.2	11.4	15.4
$B_{96}O_4$	3.8	10.6	20.0
P	9.6	11.8	13.6
$P_{96}O_4$	11.0	17.2	18.8
M	10.8	13.0	22.6
$M_{96}O_4$	9.2	17.0	18.2

TABLE 4. Activation Energy E_a for Cyclization

Polymer code	E_a (kcal/mol)[a]
B	25
$B_{96}O_4$	17
P	10
$P_{96}O_4$	9
M	7
$M_{96}O_4$	5

[a]Probable deviation is less than 10%.

total weight loss for the cyclodehydration process in B is 7.5% whereas under similar conditions the weight losses due to cyclization for B at 240 and 280°C are 11.5 and 13.8%, respectively. This shows that at high temperature, besides cyclization, cross-linking of pendant −COOH groups might be taking place. A similar change in weight loss was observed in all other homo- and copolymer systems. Figures 7-10 show first-order kinetics of cyclization at 200, 240 and 280°C. The rate constants (k) for cyclization of the polymers were derived from the slopes of these plots and are given in Table 3. The rate constant values vary in the range 4×10^{-3} to 18×10^{-3} min^{-1}. The activation energy values obtained from Arrhenius plots are given in Table 4.

   Isothermal weight loss due to cyclization was compared with dynamic weight loss. A typical comparison is shown in Fig. 11. The
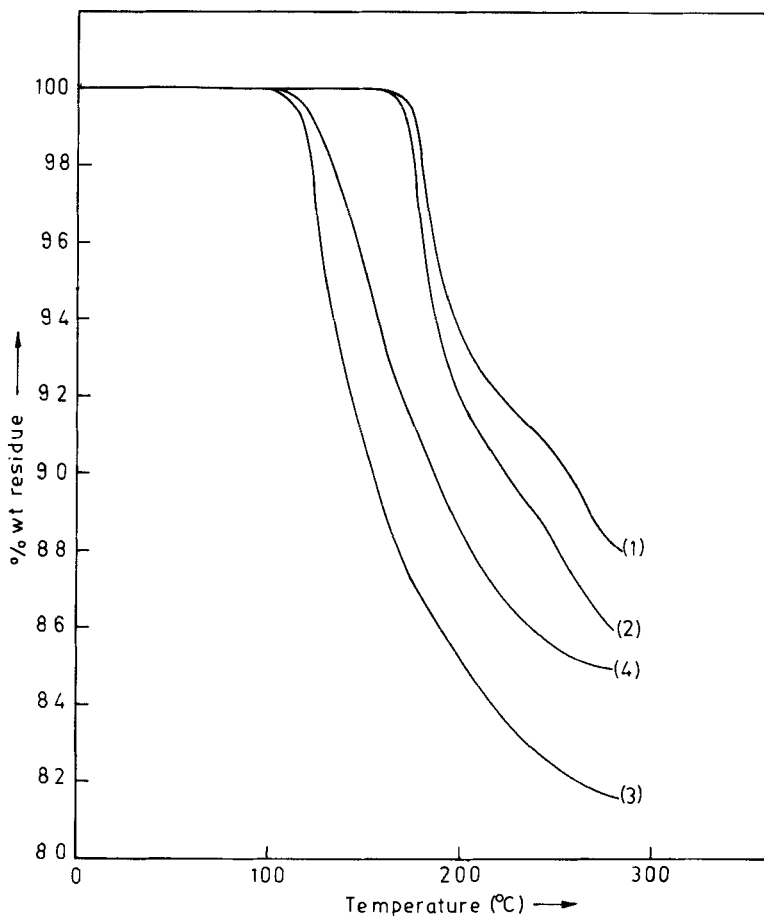
FIG. 11. Comparison of dynamic and isothermal cyclodehydration: (1) B (dynamic), (2) B (isothermal), (3) $B_{96}O_4$ (dynamic), and (4) $B_{96}O_4$ (isothermal).

slopes of the curves were approximately the same, thus indicating a similar dependence on cyclization rate.

Thermal Analysis

Thermograms obtained by plotting percentage residual weight against temperature for homo- and copolyimides are given in Figs. 12-14. The thermal analysis data show that the threshold degradation temperature is lowered in all copolyimides. The rate of decomposition
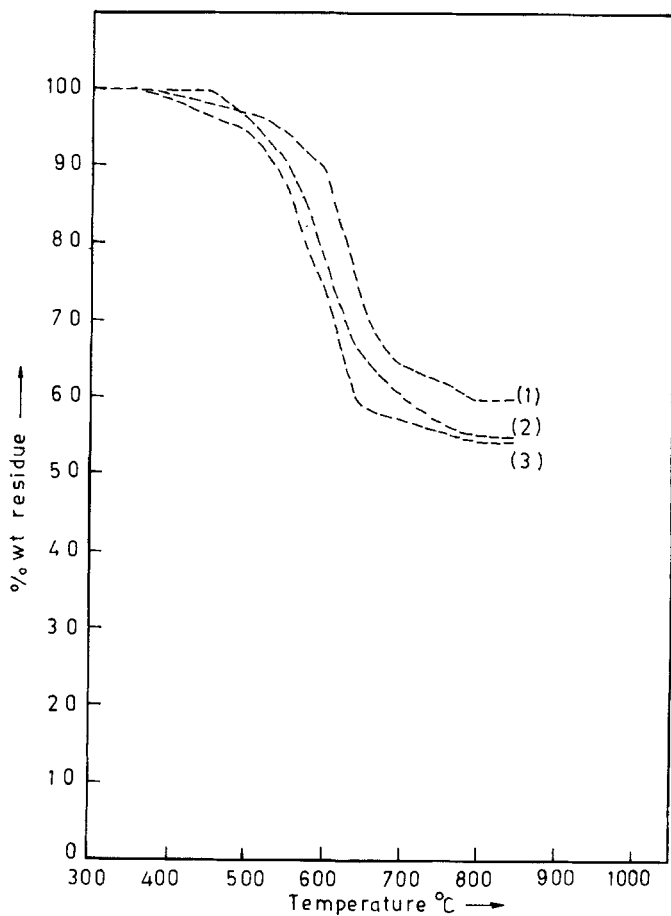
FIG. 12. Thermogravimetric analysis of polyimides: (1) B,
(2) $B_{96}O_4$, and (3) $B_{90}O_{10}$.
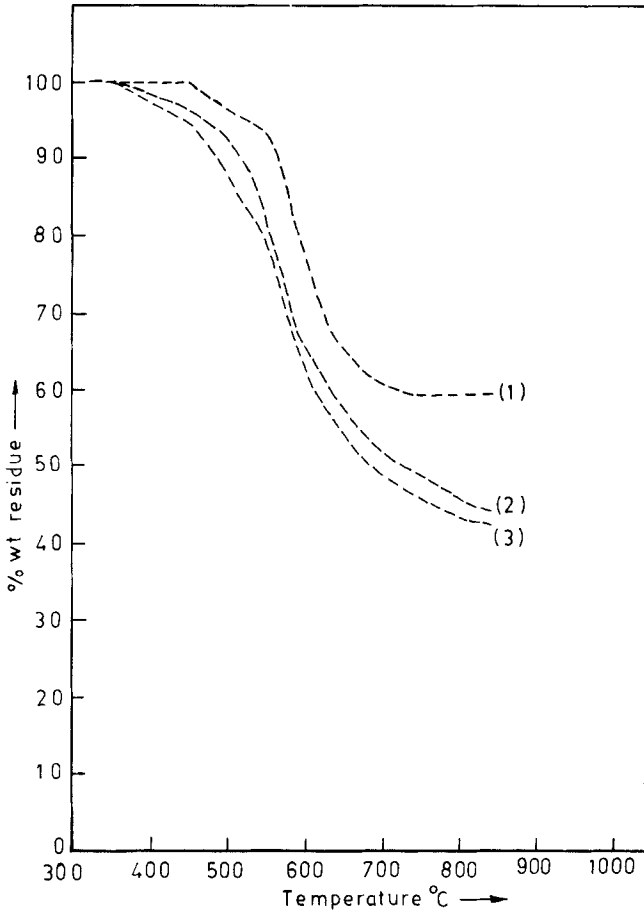
FIG. 13. Thermogravimetric analysis of polyimides: (1) P, (2) $P_{96}O_4$, and (3) $P_{90}O_{10}$.
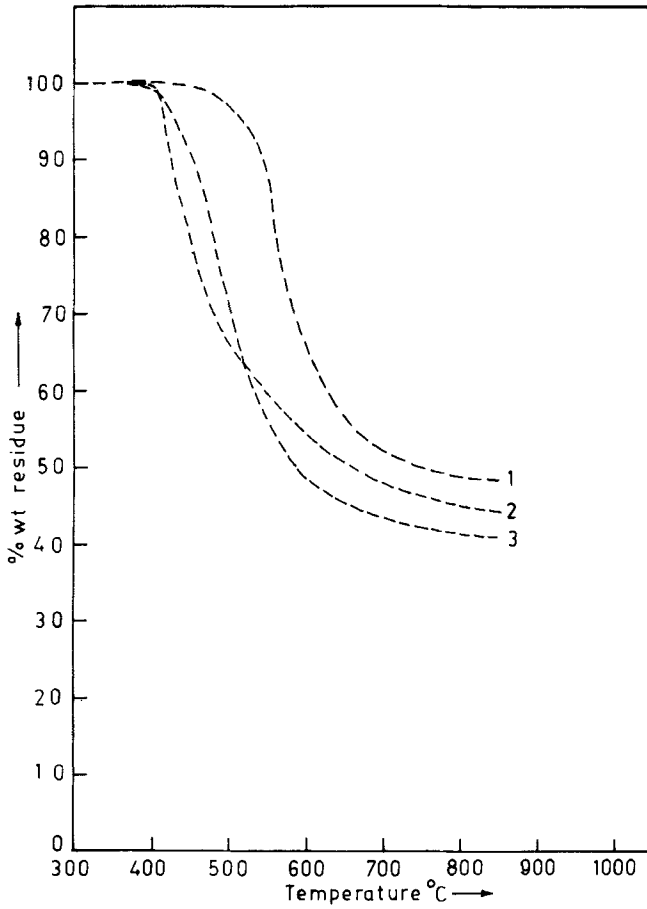
FIG. 14. Thermogravimetric analysis of polyimides: (1) M, (2) $M_{96}O_4$, and (3) $M_{90}O_{10}$.

TABLE 5. Thermal Analysis of Polyimides

Polymer code	I.D.T. ($°C$)[a]	Temperature at 40% wt. loss, $°C$	T_{max} ($°C$)	IPDT ($°C$)[c]
M	425	625	615	714
$M_{96}O_4$	370	535	555	659
$M_{90}O_{10}$	370	545	540	650
P	450	720	595	745
$P_{96}O_4$	370	630	545	709
$P_{90}O_{10}$	350	610	535	688
B	385	795	575	761
$B_{96}O_4$	450	705	425	739
$B_{90}O_{10}$	365	640	435	726

[a]IDT = initial decomposition temperature.
[b]T_{max} = maximum decomposition temperature.
[c]IPDT = integral procedural decomposition temperature.

is also much higher in copolymers than for fully aromatic polyimides.
The maximum decomposition temperature of $B_{90}O_{10}$ is $575°C$ whereas
in B it is about $625°C$. Consequently, decomposition of these copoly-
mers starts even before the probable cyclization to oxadiazole. In
such a case, copolyimides would have exhibited stability greater than
or equal to that of homopolyimide. Further investigations are neces-
sary to understand the probability of cyclization of polyamic acid to
polyimide or polyoxadiazole.

The integral procedural decomposition temperature (IPDT), as
proposed by Doyle [10], provides a semiquantitative means of com-
parison of the relative stability of various polymers.

Although the overall stability of the copolymers as seen from the
IPDT values in Table 5 is smaller (by about $40°C$) than that of the
corresponding homopolymers, incorporation of O increases the
solubility and hence the processability.

ACKNOWLEDGMENTS

REFERENCES

[1] J. Gagliani, German Offen. 2,903,347 (1979); Chem. Abstr., 91, 59171g (1979).

[2] T. L. St. Clair and D. J. Progar, National SAMPE Symposium Proceedings, Vol. 24, 1979, p. 1081; Chem. Abstr., 91, 58264j (1979).

[3] Y. Karasawa and H. Kokame, Jpn. Kokai Tokkyo Koho, 79, 95, 697 (1979); Chem. Abstr., 92, 24451y (1980).

[4] T. L. St. Clair, A. K. St. Clair, and E. N. Smith, Structure Solubility Relationships in Polymers, Academic, New York, 1977, p. 199.

[5] I. K. Varma, R. N. Goel, and D. S. Varma, Angew. Makromol. Chem., 64, 103 (1977).

[6] Chang and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 15, 311 (1977).

[7] E. M. McCaffey, Laboratory Preparations for Macromolecular Chemistry, McGraw-Hill, New York, 1970, p. 20.

[8] A. H. Frazer and W. P. Fitzgerald, Jr., J. Polym. Sci., C, 24, 89 (1968).

[9] L. W. Frost, G. M. Bower, J. H. Freeman, H. A. Burgman, E. J. Trayner, and C. R. Ruffing, J. Polym. Sci., A-1, 6, 215 (1968).

[10] C. D. Doyle, Anal. Chem., 33, 77 (1961).