Synthesis and Properties of Copolypyromellitimides

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Synopsis

Copolyamic acids with different proportions of diamine component were prepared by polymerizing different molar ratios of diamines—benzidine (B)/4,4'-diaminodiphenyl ether (E) and *p*-phenylene diamine (P)/4,4'-diaminodiphenyl methane (M)—with pyromellitic dianhydride (PMDA) in dimethylacetamide (DMAc) at room temperature. Diamine component can be arranged in regular sequence through various reaction processes, such as alternating, block, and partial block copolymers. In addition, it can also be arranged in random sequence to obtain random copolymers. Thermal cyclodehydration of polyamic acids results in the corresponding polyimides. Polymers are characterized by viscosity, thermal stability, crystallinity, and mechanical strength. It was found that an increase in the proportion of more flexible diamine component (such as E and M) incorporated in polymer chain results in copolyimides with better mechanical strength and causes a fall in viscosity of copolyamic acids and a decrease in thermal stability and crystallinity of copolyimides. Within the copolymers of the same composition, the thermal stability, crystallinity, and mechanical strength of ordered polymers are superior to those of random polymers. The results of viscosity measurements imply that the anhydride-terminated prepolymer is easily destroyed by water in the solution, so that the ultimate viscosities of alternating and block copolyamic acids are inferior to those of random ones, but this phenomenon can be improved through the preparation of the partial block copolymers.

INTRODUCTION

According to the combination of different functional groups, copolyimides can be referred to as copolyamide–imide,[1] copolyesterimide,[2] copolyoxadiazole–imide,[3] copoly(imide–benzimidazopiperidone),[4] copoly(quinazolone–amide–imide),[5] etc. Polyimides with the same type of imide linkage, but with different component, can also be called copolyimides, such as alternating, block, random copolyimides, and so forth. In general, the polymer condensated from single diamine and single dianhydride is called homopolyimide, and, when the polymer is prepared from single dianhydride and two or more kinds of diamines, or from single diamine and two or more kinds of dianhydrides, we also call them copolyimides according to the regularity of polymer chain or the composition.

Most of the copolyimide mentioned in the literature is random copolymer. For example, random copolyimides are prepared from one diamine with two dianhydrides,[6,7] from one dianhydride and two diamines,[8–10] or from the one dianhydride and two diisocyanates instead of diamines,[11,12] etc.

There are some papers describing the block copolyimides. Block copolyimides prepared from amine-terminated prepolymer with dianhydride was reported by Fukami[13] as well as de Visser and his co-workers.[14] Whereas the block copolyimides prepared from one dianhydride and two diamines

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were studied only by Babu and Samnt,[15,16] who prepared block copolyimides from the polycondensation of PMDA with *m*-, *p*-phenylene diamine and benzidine, and compared some of their physical properties with those random copolymers.

The preparation and properties of various homopolyimides can be seen in the work of Sroog and his co-workers.[17] They reported that the properties of polypyromellitimide films are largely relative to the component of diamines. The polymer chains derived from benzidine (B) and *p*-phenylene diamine (P) are more rigid and their polyimide films are brittle, but have better thermal stability, while the polymer chains derived from 4,4′-diaminodiphenyl ether (E) and 4,4′-diaminodiphenyl methane (M) are flexible and can be cast to flexible films. In this study we shall prepare two series of copolyimides with different arrangements of molecular chains, where A series is prepared from PMDA and the misture of diamines, B and E, and B series is prepared from the mixture of P and M. The differences of some physical properties, such as viscosity, crystallinity, mechanical strength, and thermal stability among the copolymers will be discussed.

EXPERIMENTAL

Reagents

Pyromellitic dianhydride (PMDA) (TCI-GR) was recrystallized from acetic anhydride before use. Benzidine (B), 4,4′-diaminodiphenyl ether (E) (TCI-GR), *p*-phenylene diamine (P), and 4,4′-diaminodiphenyl methane (M) (TCI-GR) were used without further purification. Dimethylacetamide (DMAc) was dehydrated with P_2O_5 or CaH_2 and distilled before being stored in 4 Å molecular seives.

Polymerization Procedures

The polymerization procedures of homopolymer and copolymer are as follows.

Homopolymer. Equimolar PMDA was gradually added to the solution of diamine in DMAc to obtain a homopolyamic acid.

Alternating Copolymer. Two equivalences PMDA were added to the solution of one equivalence of diamine **a** in DMAc. After the complete reaction, another equivalence of diamine **b** was added to the reaction medium to obtain an alternating copolyamic acid.

Block Copolymer. With the molar ratio smaller than 1/2, such as 3/2, the PMDA was added to the solution of diamine **a** to produce the condensation reaction. After the reaction was complete, we made up the unbalanced quantity of diamine with the other diamine **b** to yield a block copolyamic acid.

Partial Block Copolymer. Into the solution of diamine **a** in DMAc we added PMDA with the equivalence less than that of diamine. If the reaction was complete, another diamine **b** was added and finally the enough equivalence number of PMDA was added to react to a partial block copolyamic acid.

Random Copolymer. Into the solution of the mixture of diamines **a** and

b in DMAc, equimolar PMDA was added to yield a random copolyamic acid.

Preparation of Polyimide Film

The viscous polyamic acid solutions were spread on a glass plate and were made dry in an air oven at 80°C to yield films. The polyamic acid films were imidized by heating at a range from the room temperature to 250°C, with a heating rate of 5°C/min and heated continuously at 250°C, for 30 min to ensure complete imidization.

Characterization of Polymers

Viscosity measurements were made in DMAc at 30°C by using an Ubbelohde suspended level viscometer. The polymer concentration were in the range 0.5–0.25 g/dL. IR spectra of polyamic acids and polyimides were run by films by using a Jasco Infrared Spectrophotomer. X-ray diffraction patterns were obtained using a Jeol JDX-10RA Diffractometer with Ni-filtered Cr Radiation at 30 kV, 100 mA and wide-angle diffraction 2θ from 10° to 50°.

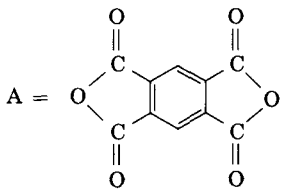
Mechanical Strength. The polyimide film was cut into a rectangular 6 cm long, less than 1 cm wide, and about 0.05 mm thick. An Instron Universal Tester with a load cell 5 kg was used to study the stress–strain behavior of the samples at the room temperature at a drawing speed of 5 cm/min.

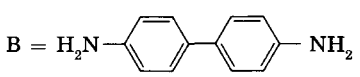
Thermal analysis of the polyimides was carried out in the air, nitrogen, or helium atmosphere. A Shimadzu DT-30B thermal Analyzer was used for evaluating the thermal behavior of polymers in the air. Daini Seikosha SSC/560GH, TG/DTA Scientific Instrument was used for the study of thermal behavior in nitrogen and helium atmosphere; 10 ± 2 mg of the polymer sample was taken and heated at a rate of 10°C/min.

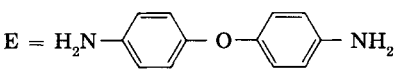
RESULTS AND DISCUSSION

Polymer Synthesis

The polymerizatio procedures of homopolymer and copolymer are shown in Schemes 1 and 2:







$$n\,B + n\,A \xrightarrow[r\cdot t]{DMAC} -(-A-B-)_n-$$

1 (polyamic acid)

$$1 \xrightarrow{250°C} 2 \text{ (corresponding polyimide)} \tag{1}$$

$$nx\,B + n(x+1)A \xrightarrow[r\cdot t]{DMAC} n[A-(-B-A)_x]$$

3

$$3 + n\,E \longrightarrow -[-E-A-(B-A)_x-]_n$$

4

$$4 \xrightarrow{250°C} 5 \text{ (corresponding copolyimide)} \tag{2}$$

$$ny\,E + n(y+1)\,A \xrightarrow[r\cdot t]{DMAC} n[A-(-E-A)_y]$$

6

$$6 + n\,B \longrightarrow -[-B-A-(E-A)_y-]_n$$

7

$$7 \xrightarrow{250°C} 8 \text{ (corresponding copolyimide)} \tag{3}$$

$$nx\,B + n\,E + n(x+y)A \xrightarrow[r\cdot t]{DMAC}$$

$$[-(A-E)_{y'}-(A-B)_{x'}-(A-E)_{y''}-(A-B)_{x''}-]_n$$

9

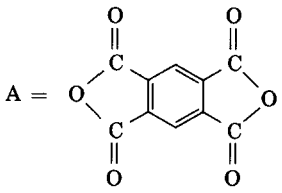
$$9 \xrightarrow{250°C} 10 \text{ (corresponding copolyimide)} \tag{4}$$

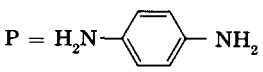
$$n\,E + n\,A \xrightarrow[r\cdot t]{DMAC} -(-A-E-)_n-$$

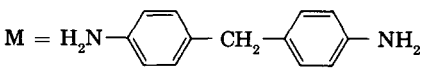
11

$$11 \xrightarrow{250°C} 12 \text{ (corresponding polyimide)} \tag{5}$$

Scheme 1. Preparation of A-series copolymers, copolypyromellitimide from benzidine (B) and 4,4′-diaminodiphenyl ether (E).







$$n\,P + n\,A \xrightarrow[r\cdot t]{DMAC} -(-A-P-)_n-$$

13 (polyamic acid) (6)

$$13 \xrightarrow{250°C} 14 \text{ (corresponding polyimide)}$$

$$nx\,\mathrm{P} + n(x-1)\mathrm{A} \xrightarrow[r\cdot t]{\mathrm{DMAC}} n[\mathrm{P}-(-\mathrm{A}-\mathrm{P})_{x-1}] \quad \underset{15}{} \tag{7}$$

$$15 + ny\,\mathrm{M} + n(1+y)\mathrm{A} \longrightarrow [-(\mathrm{A}-\mathrm{P})_x-(\mathrm{A}-\mathrm{M})_{y'}-]_n \quad \underset{16 \text{ (M as chain extender)}}{}$$

$$16 \xrightarrow{250°C} 17 \text{ (corresponding partial P block copolyimide)}$$

$$ny\,\mathrm{M} + n(y-1)\mathrm{A} \xrightarrow[r\cdot t]{\mathrm{DMAC}} n[\mathrm{M}-(\mathrm{A}-\mathrm{M})_{y-1}] \quad \underset{18}{} \tag{8}$$

$$18 + nx\,\mathrm{P} + n(x+1)\mathrm{A} \longrightarrow [-(\mathrm{A}-\mathrm{M})_y-(\mathrm{A}-\mathrm{P})_{x'}-]_n \quad \underset{19 \text{ (P as chain extender)}}{}$$

$$19 \xrightarrow{250°C} 20 \text{ (corresponding partial M block copolyimide)}$$

$$nx\,\mathrm{P} + ny\,\mathrm{M} + n(x+y)\mathrm{A} \xrightarrow[r\cdot t]{\mathrm{DMAC}} [-(\mathrm{A}-\mathrm{P})_{x'}-(\mathrm{A}-\mathrm{M})_{y'}-(\mathrm{A}-\mathrm{P})_{x'}-(\mathrm{A}-\mathrm{M})_{y'}-]_n \quad \underset{21}{} \tag{9}$$

$$21 \xrightarrow{250°C} 22 \text{ (corresponding random copolyimide)}$$

$$n\,\mathrm{M} + n\,\mathrm{A} \xrightarrow[r\cdot t]{\mathrm{DMAC}} -(-\mathrm{A}-\mathrm{M}-)_n- \quad \underset{23}{} \tag{10}$$

$$23 \xrightarrow{250°C} 24 \text{ (corresponding homopolyimide)}$$

Scheme 2. Preparation of B-series copolymer, copolypyromellitimides from *p*-phenylene diamine (P) and 4,4′-diaminodiphenyl methane (M).

Block and Alternating Copolymers

The first step consists of preparation of prepolymer. Excess PMDA was added to the solution of diamine in DMAc to obtain a prepolymer terminated with anhydride group. Stirring was continued for 30 min at the room temperature under a continuous flow of nitrogen. In the second step, the second diamine was added to the above solution to complete the unbalanced stoichiometry. The reaction was continued for another hour to obtain viscous solution of polyamic acid with regular sequences. the molar ratios of two diamines were 1:1, 1:2, and 2:1. The reaction equations are shown as eqs. (2) and (3) in Scheme 1.

Random Copolymers

Equimolar PMDA was added to the solution of mixed diamine monomers in DMAc to attain a highly viscous polyamic acids after the reaction was carried out under N_2 for 2 h at room temperature with continuous stirring. The molar ratios of diamines B and E were 2:1, 1:1, and 1:2 and those of P and M were 3:1, 2:1, 1:1, 1:2, and 1:3. The reaction formulas are shown as eq. (4) in Scheme 1 and eq. (9) in Scheme 2.

Partial Block Copolymers

Dissolving one of the diamines into DMAc and adding PMDA with the quantity smaller than that of the diamine, such as 9/10 molar ratio, to the diamine solution, the amine-terminated prepolymer could be obtained by this process. Adding the second diamine to the above prepolymer solution and making up the unbalanced quantity of PMDA after the diamine dissolved completely, we could get the highly viscous solution of polyamic acid. Because these polymer chains contain the partial regular block sequences, we name them partial block copolymers. Further, we divide them in to partial P block and partial M block copolymer according to the order of addition of the diamines P and M. The reaction formulas are shown as eqs. (7) and (8) in Scheme 2 and the molar ratios of P/M are 1/1, 1/2, and 1/3.

The obtained polymer can be precipitated in methanol, or coated on a glass plate with the solvent removed at 80°C to produce a polyamic acid film, which is converted to polyimide by a further heating at 250°C.

Viscosity

Results of a A-series copolymers prepared under similar conditions are summarized in Table I. In the synthesis of three-step copolymers [such as reaction equations (2) and (3) in Scheme 1] the addition of a diamine to the lower viscosity solution of anhydride-terminated prepolymer 3 and 6 in Scheme 1 increases the viscosity gradually, indicating the formation of block

TABLE I
Preparation of A-Series Copolyamic Acids

Sample no.	Polymer	B:E (mol. ratio)	Weight (g)[a]			Viscosity[b] (dL/g)	
			PMDA	B	E	η_{sp}/C[c]	$[\eta]$
A-1	1 (Homopolymer)	—	0.542	0.458	—	3.56	1.83
A-2	4 (Block)	2:1	0.535	0.301	0.154	2.48	1.50
A-3	9 (Random)	2:1	0.535	0.301	0.164	3.35	1.79
A-4	4 (Alternating)	1:1	0.531	0.224	0.244	1.77	1.35
A-5	9 (Random)	1:1	0.531	0.224	0.244	3.12	1.75
A-6	7 (Block)	1:2	0.528	0.149	0.323	1.70	1.10
A-7	9 (Random)	1:2	0.528	0.149	0.323	3.04	1.68
A-8	11 (Homopolymer)	—	0.522	—	0.478	2.83	1.67[d]

[a] DMAc was added to give solutions of concn = 10 wt%.

[b] Viscosity was determined at 30°C in DMAc.

[c] C = 0.5 g/dL.

[d] Applying the Mark–Haouwink relation, $[\eta] = 1.84 \times 10^{-4} \overline{M}_w^{0.8}$, derived by Wallach[18] for homopolymer 11, this value correspondes to $\overline{M}_w \doteqdot 88{,}500$.

or alternating copolyamic acids. Results of viscosity measured are also shown in Table I. It can clearly be observed that the viscosity of block or alternating copolymer is lower than that of the corresponding random copolymer. This viscosity behavior is different from the result, $[\eta]_{block} \geq [\eta]_{random}$, observed by Babu and Samant.[15,16] Presumably the anhydride-terminated prepolymer is easily destroyed by the water in the solution; therefore, the next polycondensation can not proceed smoothly, and the viscosity is inferior to that of corresponding random copolymer synthesized by only one step. The solvent can't be easily treated to the state without any water; in addition, the heat given off in the polymerization brings about, more or less, some amic acid linkages to convert the imide structure and to relieve water. The little water is enough to destroy the anhydride-terminated prepolymer and retard the formation of high molecular weight of polyamic acid. Moreover, the longer the prepolymer stays in the solution, the more seriously it is destroyed and so the lower the viscosity of polymer. The various effects on the formation of high molecular weight polyamic acid will be investigated in part B at length.

Further, in all the copolymers the viscosity increases with the increasing proportion of biphenyl component in the backbone. In step-growth polymerization the degree of polymerization is directly proportional to the percentage of conversion. In the polyamic acids, which were prepared from PMDA under similar conditions, the reactivity of amines will affect the extent of conversion and the degree of polymerization. The intrinsic viscosity measurements of polyamic acid reveals the following reactivity order of the diamine: B > E. The nucleophilicity of B and E depends on the inductive and resonance effects; an amino group by induction is an electron-withdrawing group and by resonance, anelectron-donor group. The direct conjugation of two amino groups in B will increase the electron density of carbon carrying the amino group, and consequently the nucleophilicity of amino group will increase. In addition, the intrinsic viscosity is also affected by the dimensions of a polymer molecule in solution. The biphenyl structure would tend to lie in extended conformation, thereby behaving as rodlike molecules difficult to move. However, the diphenyl ether unit is more flexible than biphenyl and has a tendence to show folded conformatios in solution, so that the viscosity of polymer derived from E is lower.

The results of B-series partial block and random copolymers synthesized under similar conditions are summarized in Table II. In the syntheses of A-series block and alternating copolymers, it was found that the anhydride-terminated prepolymer is easily destroyed by the water in the solution so that the ultimate viscosity can't be raised as that of random copolymers. Hence when B-series copolymers are synthesized, we prepare, according to the process shown in Scheme 2, an improved partial block copolymer. The characteristic of this process is not to leave unreacted anhydride group in the solution; instead, the amine-terminated prepolymer is prepared. The prepolymer isn't inacted by the water existing in the solution; therefore, the ultimate viscosity of polymer can be raised significantly. As given in Table II, partial block copolymers even have a tendence to show a higher viscosity than that of the corresponding random copolymers. Based on the similar molecular weight of each copolymer, the effects of structure and

TABLE II
Preparation of B-Series Copolyamic Acids

Sample no.	Polymer	P:M (mol. ratio)	Weight (g)[a]			Viscosity[b] (dL/g)	
			PMDA	P	M	η_{sp}/C	$\eta_{inh.}$
B-1	13 (Homopolymer)	—	0.669	0.331	—	3.54	2.04
B-2	21 (Random)	3:1	0.626	0.232	0.142	2.91	1.80
B-3	21 (Random)	2:1	0.613	0.202	0.185	2.75	1.73
B-4	21 (Random)	1:1	0.588	0.145	0.267	2.56	1.65
B-5	16 (Partial P block)	1:1	0.588	0.145	0.267	2.54	1.64
B-6	19 (Partial M block)	1:1	0.588	0.145	0.267	2.63	1.68
B-7	21 (Random)	1:2	0.565	0.093	0.342	2.17	1.47
B-8	16 (Partial P block)	1:2	0.565	0.093	0.342	2.36	1.56
B-9	19 (Partial M block)	1:2	0.565	0.093	0.342	2.54	1.64
B-10	21 (Random)	1:3	0.554	0.069	0.377	2.29	1.53
B-11	16 (Partial P block)	1:3	0.554	0.069	0.377	2.29	1.53
B-12	19 (Partial M block)	1:3	0.554	0.069	0.377	2.21	1.49
B-13	23 (Homopolymer)	—	0.524	—	0.476	2.23	1.50

[a] DMAc was added to give solutions of concn.= 10 wt %.
[b] Viscosity was determined at 30°C in DMAc with concn.= 0.5 g/dL.

composition on the properties of copolymers can be investigated more precisely.

Furthermore, the viscosity of this series copolyamic acid also decreases as the proportion of more flexible component, M, in polymer chain increases. The reason is similar to the assumption accounting for the viscosity behavior of A-series copolymeres, i.e., the reactivity of diamine is P > M and the molecular chain with an increasing proportion of *p*-phenylene is more difficult to move in solution.

IR spectra

Polyimide and polyamic acid samples have been examined as films. The spectra of all polyamic acids showed characteristic absorption around 3200 and 1660 cm^{-1}. The band around 3300 cm^{-1} is ascribed to the stretching of N—H linkage, the band in the range 2400–3200 cm^{-1} is due to the stretching of O—H, and the absorption band at 1660 cm^{-1} is peculiar to secondary amide groups. In the spectra of polyimides the 3200 and 1660 cm^{-1} absorption bands are absent, and new absorption peaks appear at

about 1780, 1100, and 720 cm^{-1}. The band at 1780 cm^{-1} is related to the stretching vibrations of two carbonyls that are weakly coupled. The bands at 1100 and 720 cm^{-1} can be associated with the vibrations of the cyclic imide structure. Figure 1 shows examples of the IR spectra of polyamic acid and its corresponding polyimide for sample A-5 (B/E=1/1, random copolymer).

Further, by adopting IR spectra analysis we can carry on the quantitative experiment of the imidization of polyamic acid through cyclodehydration. The percentage of imidization of polyamic acid was calculated by using the following equation[19]:

$$\% \text{ imidization} = \frac{[A(1)/A(2)]_t - [A(1)/A(2)]_{t=0}}{[A(1)/A(2)]_{t=\infty} - [A(1)/A(2)]_{t=0}}$$

where $A(1)$ is absorbance of imide peak at 1780 cm^{-1}, $A(2)$ is absorbance of standard reference peak at 1500 cm^{-1}, and $t = \infty$ was taken as the time beyond which no further changes in the imide peak were observed at 300°C. Take sample A-5 for example: The sample was made into a film and cured at increasing temperatures of 80, 100, 150, 180, 200, 220, 250, and 300°C at each temperature. IR spectrum was recorded at each curing stage. the extent of imidization can be evaluated according to the above equation and the results are shown in Table III. The result indicates that this polymer needs longer time to reach complete imidization at below 220°C, while above 250°C it can be completely converted into polyimide in a very short time. Moreover, polyamic acid films with the same thickness are cured at various temperatures and are determinated IR spectra periodically. The percent imidization vs. time of various temperatures is plotted in Figure 2, which

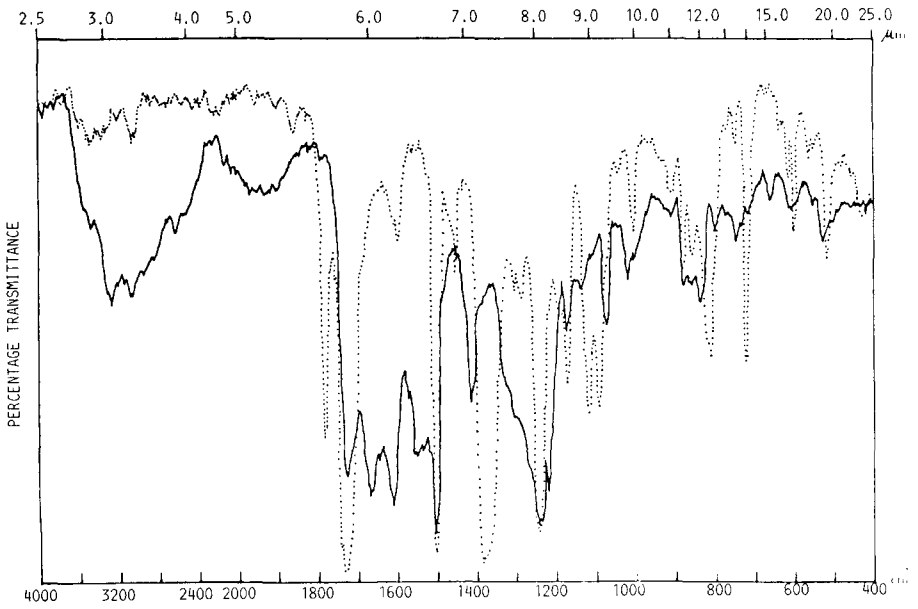


Fig. 1. IR spectra of copolyamic acid A-5 (—) and its corresponding copolyimide (···).

TABLE III
Quantitative Analysis of IR Spectra of Copolyimide A-5, Percent Imidization at Each Curing Stage

Stage no.	Cure temp (°C)	Cure time (min.)	Total % imidization
1	80	0	0
2	80	60	3.3
3	80	40	3.6
4	100	50	7.9
5	100	50	10.1
6	100	20	14.5
7	150	20	55.7
8	150	20	68.1
9	150	30	69.5
10	150	120	77.5
11	180	20	84.0
12	180	20	86.2
13	180	100	89.1
14	200	10	91.3
15	200	20	92.7
16	220	10	95.6
17	220	20	98.5
18	250	10	100.0
19	250	20	100.0
20	300	30	100.0

also shows that there is a rapid cyclization at above 250°C and the polymer requires a longer time to imidize completely below 220°C.

Crystallinity

The crystallinity of copolyimide samples with various compositions was determined by X-ray diffractometer with 2θ from 10° to 50°. In A-series copolymers the diffraction pattern of sample A-8, which is derived from

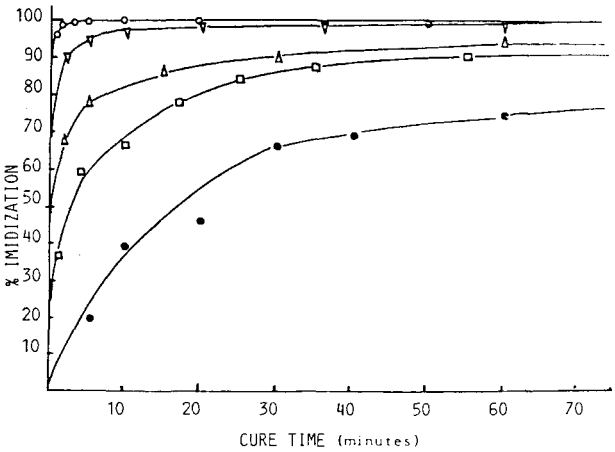


Fig. 2. Imidization of copolyamic acid A-5 at various temperatures (●) 150°C; (□) 180°C; (△) 200°C; (▽) 220°C; (○) 250°C.

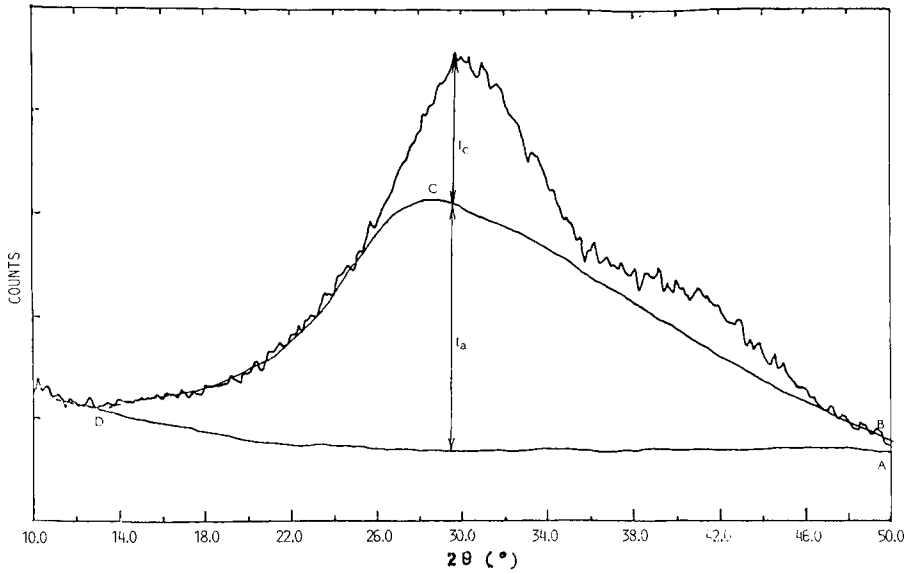


Fig. 3. X-ray diffraction pattern of partially crystalline copolyimide A-3.

PMDA and 4,4′-diaminodiphenyl ether, is a smooth curve, so that this sample can be regarded as a fully amorphous polymer. In B-series copolymers the samples B-10 and B-13 also show little crystalline scattering. The diffraction pattern of highly crystalline polyimide B-1, which is derived from PMDA and benzidine, is shown in Figure 4. In addition to the strong diffraction intensity around 32° of 2θ, there is also a weak scattering around 42°.

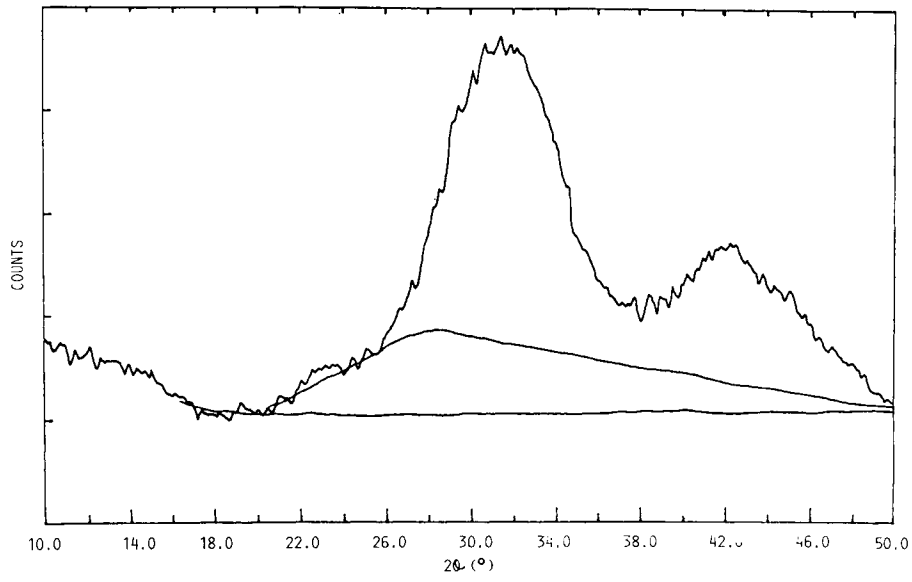


Fig. 4. X-ray diffraction pattern of highly crystalline polyimide B-1.

Taking the sample A-3 as an illustration for the calculation of crystallinity, the total area above the curve BCD in Figure 3 is now taken to be proportional to the intensity of crystalline scattering, I_c, and the area between the lines AD and BCD is taken to be proportional to the intensity of amorphous scattering, i_a, while the region beneath AD line is related to the scattering of air and the Scotch tape which is used to settle the sample. The degree of crystallinity is taken as the ratio of crystalline (I_c) to total scattering ($I_a + I_c$). The degree of crystallinity for this example is 22%. Some polyimide samples are determined by X-ray diffraction and the crystallinity is calculated by using the above method. The results are summarized in Table IV. It was found that the crystallinity of all copolymers increases as the proportion of B or P component increases. This may be due to the fact that the molecular chain containing B or P component is more rigid and is easy to be packed well; therefore, polyimides A-1 and B-1 show a high degree of crystallinity.

Mechanical Properties

Mechanical properties of B-series partial block and random copolymers are determined. For the simlar molecular weight they are used in the test to study the effects of the composition and the structure on mechanical properties. In stress–strain test, the buildup of force is measured as the specimen in being deformed at a constant rate. Figure 5 illustrates the typical strees–strain behavior of all copolyimides. The large slope of the stress–strain curve, no yield point, and a low elongation at the breakdown point indicate that these polymers are hard and brittle materials. The ultimate tensile strength of copolyimides varies with composition. The more the highly crystalline P component is found in the polymer chain, the lower the ultimate tensile strength of polymer is (Table V). This may be due to the unwanted microscopic cracks which are stress concentrators in highly crystalline polymers. And the ultimate tensile strength of partial block is a little superior to that of random ones. This may can be explained by the

TABLE IV
Crystallinity of the Copolyimides

Sample no.	Intensity of amorphous scattering I_a	Intensity of crystalline scattering I_c	$\frac{I_a}{I_c}$	Degree of crystallinity $X_c = (1+k \cdot I_a/I_c)^{-1}$, $k=1$[a]
A-1	51.87	48.13	1.08	0.48
A-3	77.51	22.49	3.45	0.22
A-5	82.05	17.95	4.57	0.18
A-7	87.22	12.78	6.82	0.13
A-8	100	—	—	—
B-1	30.87	69.13	0.45	0.69
B-2	68.11	31.89	2.14	0.32
B-4	82.55	17.45	4.73	0.17
B-10	100	—	—	—
B-13	100	—	—	—

[a] See Ref. 19.

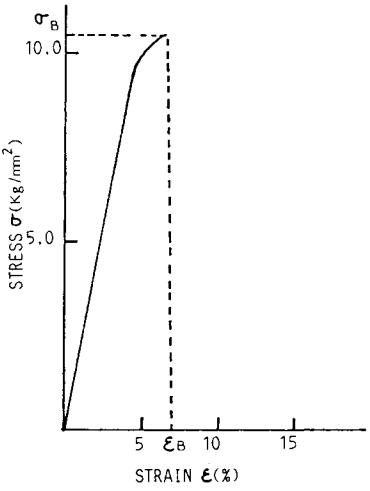


Fig. 5. Stress–strain curve of copolyimide film B-11.

fact that in the partial block copolymers there esists a short segment of P or M block which is dispersed in the polymer chain, leading to a better packing and hence to a higher strength.

Thermal Stability

Thermal stabilites of copolyimides were evaluated from their thermogravimetric curves (TG curves). From the TG curves of A-series random copolyimides in helium (Fig. 6) and in air (Fig. 7), we can find that the copolymer containing biphenyl structure is more stable than that containing diphenyl ether. Bruck[21] has suggested the graphitelike product of thermal decomposition of H-film in vacuum. Heacock and Berr[22] have described that the principal gaseous products are CO and CO_2 from the thermal decomposition of the polypyromellitimide derived from 4,4′-diaminodiphenyl ether in closed system at 540°C and have presumed that the primary scission process appeared to occur at the imide bonds (C—N), followed by a secondary cleavage (C—C) resulting in the elimination of CO groups. This

TABLE V
Strength at Breakdown Point of Partial Block and Random Copolyimides

Sample no.	Molar ratio P:M	Sequences of polymer chain	Strength at break σ_B (kg/mm^2)
B-4	1:1	Random	5.58
B-5	1:1	Partial P block	5.90
B-6	1:1	Partial M block	5.64
B-7	1:2	Random	6.25
B-8	1:2	Partial P block	7.20
B-9	1:2	Partial M block	6.80
B-10	1:3	Random	8.87
B-11	1:3	Partial P block	10.27
B-12	1:3	Partial M block	9.45

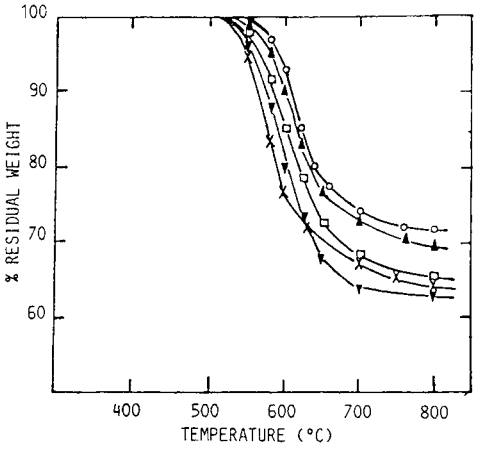


Fig. 6. Thermogravimetric curves of A-series polyimides: (○) A-1; (▲) A-3; (□) A-5; (▼) A-7; (X) A-8. Heating rate = 10°C/min in He.

presumption is in harmony with the mechanism proposed by Bruck for the thermal decomposition of the aromatic polyimides. The better stability of polyimide derived from benzidine (B) may be due to its rodlike molecular chain which is easy to be well-packed and restricts the motion of molecular chain and hence gives the better thermal stability. Furthermore, in the polymer with biphenyl groups the C—N scission would lead a radical that could be stabilized by resonance over the benzene ring. This may be another critical reason, and the percentage of residual weight of copolymers at 800°C in a helium atmosphere has a slight difference. Because the oxygen atom of the polymer derived from E will be eliminated finally in a high temperature, its residual weight is lower. In the air, however, the stability of all polymers was weaker and a complete degradation occurred at about 40 min after isothermal heating at 600°C. Because the oxygen in the air was in-

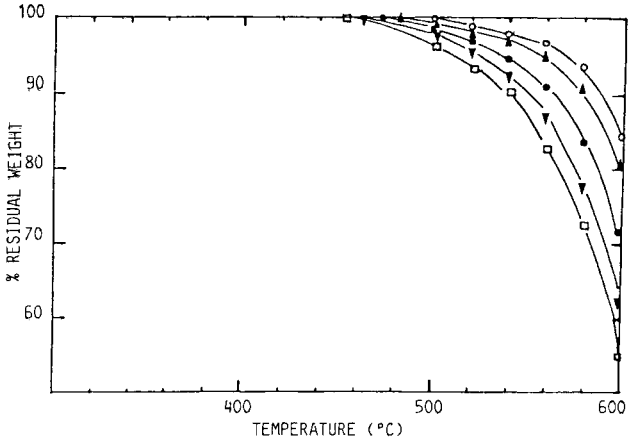


Fig. 7. TG curves of polyimides in air: (○) A-1; (▲) A-3; (●) A-5; (▼) A-7; (□) A-8. Heating rate = 10°C/min.

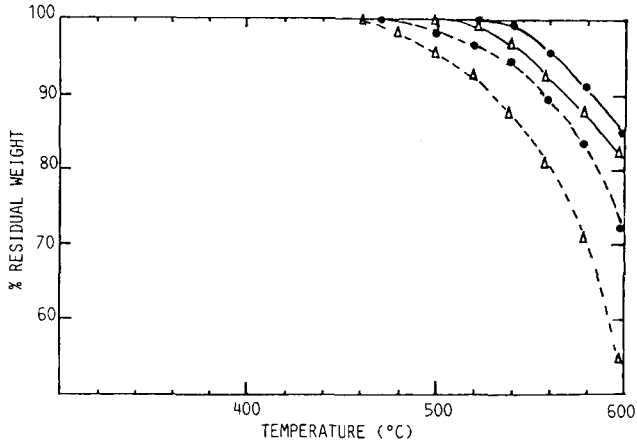


Fig. 8. TG curves of alternating copolyimide A-4 (●) and random copolyimide A-5 (△) in N_2 (—) and in air (···).

corporated in decomposition reaction and destroyed the structure of graphite, the complete decomposition took place in a high temperature. In the air the thermal behavior of the copolyimide with different compositions behaved as in helium, i.e., the thermooxidative stability of polymers decreased with an increase on E component in the backbone. The presumption described as above can also be applied to explain this behavior.

Figure 8 shows TG curves obtained for polyimide A-4 and A-5 in the air and helium, respectively. Apparently, alternating copolyimide A-4 (with B/E = 1/1) shows a better stability than the corresponding random copolyimide A-5. This may be due to the symmetrical structure of the former which might lead to a better packing of the polymer chain. In general, thermal decomposition of polymers occurs first in an amorphous region.

The thermal analysis in helium of B-series copolyimides of different com-

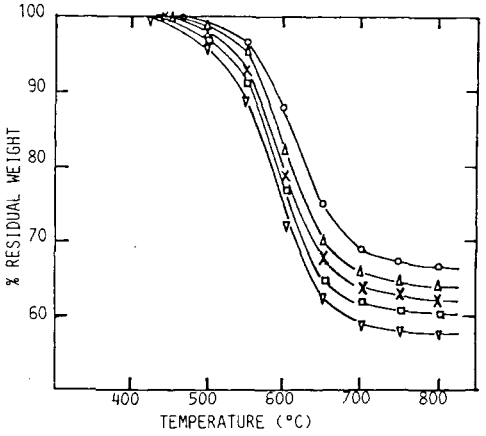


Fig. 9. TG curves of polyimides B-1 (○), B-2 (△), B-4 (X), B-10 (□), and B-13 (▽), with heating rate 10°C/min in N_2.

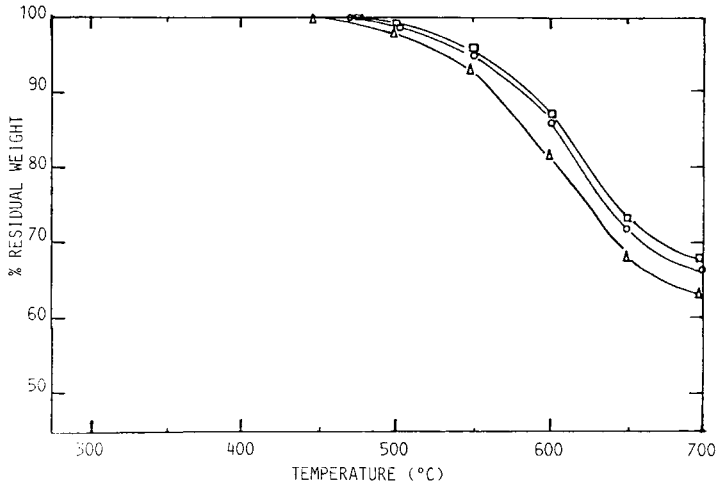


Fig. 10. TG curves of copolyimides B-4 (△, random), B-5 (□, partial P block), and B-6 (○, partial M block), heating rate 10°C/min in N_2.

positions is shown in Figure 9. When the ratio of M in polymer increases, the thermal stability decreases. Exclusive of the reasons described in A-series, the poor stability of the—CH_2—linkage in M component is another principal factor. It can be seen from the TG curves in Figure 10 that partial block copolymers (B-5 and B-6) show a better stability than the corresponding random copolyimide (B-4). This may be due to the introduction of more symmetrical P or M segments, a fact that leads to a better packing and hence to a higher stability. In addition, the introduction of higher crystalline P block into polymer chain contributes to a slightly larger improvement on the thermal stability. Because the M block itself is a more flexible polymer chain, its introduction can't effect a good improvement on the packing of polymer chains as that P block does.

From the decomposition temperatures of different weight losses, we can

TABLE VI
Thermal Properties of Copolyimides

Sample no.	Molar ratio of diamines	Sequences of polymer chain	Atoms	Wt % at temp. (°C) 10	20	30	T_0 (°C)	$T_{max.}$ (°C)
A-4	B/E = 1/1	Alternating	Air	584	620	—	524	580
A-5	1/1	Random	Air	570	608	—	500	574
A-4	1/1	Alternating	N_2	558	589	603	471	574
A-5	1/1	Random	N_2	533	563	583	462	558
B-4	P/M = 1/1	Random	N_2	563	608	620	455	575
B-5	1/1	Partial P block	N_2	583	620	665	473	588
B-6	1/1	Partial M block	N_2	587	625	675	475	589

[a] T_0 = initial decomposition temperature.
[b] T_{max} = temperature at maximum decomposition.

compare clearly the thermal stability of copolymers with regular and random sequences of polymer chain. (Table VI).

Thus it is possible to enhance the thermal stability of copolyimides by preparing block or partial block copolymers if polyimide segments are interpersed with single imide units of a different monomer.

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