Direct polymerization of aromatic diacid dimethyl esters with aromatic diamines
II. Control of copolyimide chemical structure

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Abstract

Control of the chemical structure of copolyimides through the sequence control of copolyamic acid methyl esters was tried. The copolyamic acid methyl esters were directly synthesized from 2,5-dicarbomethoxy terephthalic acid (*p*-PMDE) and two diamines, 4,4′-oxydianiline (ODA) and 2,2′-bis (trifluoromethyl) benzidine (PFMB), using phenyl phosphonic dichloride. The average sequence length of the copolyamic acid methyl esters was controlled by the stoichiometric unbalance and monitored by the proton nuclear magnetic resonance spectroscopy (^{1}H NMR). The inherent viscosity of the chemical structure-controlled copolyamic acid methyl ester was 0.39–0.53 dl/g. The average sequence length for the random copolymer was ca. 3 and that for the alternating copolymer was greater than 1. Control of the average sequence length became more difficult as the stoichiometric unbalance between the *p*-PMDE and the diamines increased. The maximum imidization temperatures of the ODA/*p*-PMDE and PFMB/*p*-PMDE polyamic acid methyl esters were around 237 and 252°C, respectively. Those of the copolyamic acid methyl esters were between these two temperatures. The maximum imidization temperature of the copolymer approached that of the PFMB/*p*-PMDE polyamic acid methyl ester as the average sequence length increased. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Direct polymerization; Copolyamic acid methyl ester; Chemical structure

1. Introduction

Aromatic polyimides have attracted attention due to their excellent thermal stability, high mechanical properties, and good chemical resistance and electrical properties. Various methods have been reported for the synthesis of aromatic polyimides, but the most common is the two-stage solution polycondensation of dianhydride with a diamine in an aprotic solvent [1]. A soluble polyamic acid is obtained as a polyimide precursor in the first stage.

The amic acid units of polyamic acid are initially depolymerized to give an anhydride and an amine moiety during the polyimidization reaction. This reaction was found to be associated with the presence of a carboxyl group in the ortho-position to the amide bond [2-4]. The acidic proton of the carboxylic acid is transferred to the oxygen atom of the amide group because of the possible resonance stabilization of the charge with the nitrogen and oxygen atoms as well as the π electron of the benzene ring. Attack by the carboxylate ion on the carbonyl carbon of the amide group results in the cleavage of the amide linkage. Furthermore, this acid-catalyzed re-equilibration reaction greatly influences the sequence of the copolyimide. Copolymerization is the most general and powerful method of effecting systematic changes in polymer properties, and is widely used in the production of commercial polymers [5]. In addition, the average sequence length of copolymers is a factor in modifying various physical properties.

The control of copolyimides chemical structure through the thermal conversion of the corresponding copolyamic acid prepared by the standard solution polycondensation is difficult, because a random copolyamic acid is always formed due to the re-equilibration reaction. This reaction is insignificant in chemical imidization because the *o*-carboxy carboxamide groups are quickly converted to the imide and isoimide moieties [6]. However, to control the copolyimide sequence during the thermal imidization, it is necessary to suppress the re-equilibration reaction, which

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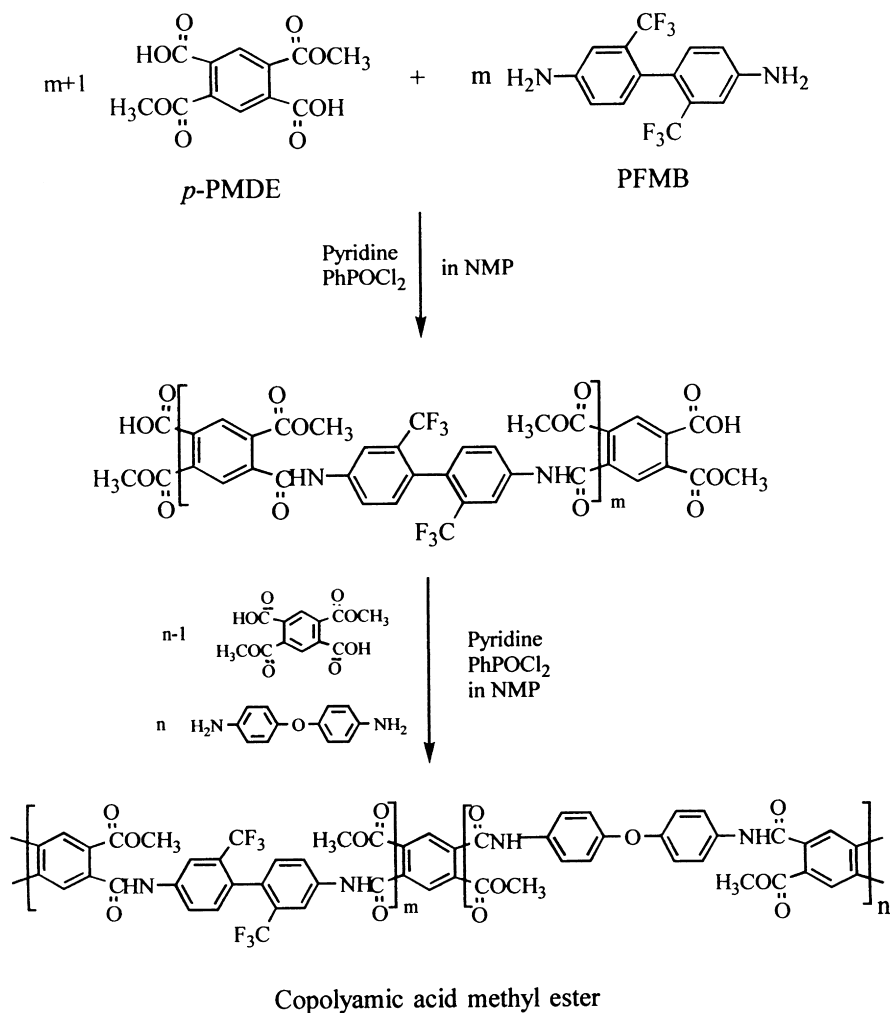
Scheme 1.

can be done by the esterification of acid groups with appropriate alkyl groups [7,8]. Thus, copolyamic acids should be replaced by copolyamic acid methyl esters as copolyimide precursors for the sequence control of copolyimides. In addition, polyamic acid esters have several advantages, including solution stability, better resistance to hydrolytic degradation, and freedom from the polyelectrolyte effect [9]. Babu and Samant [10,11] reported the synthesis of block copolyimides by the standard solution polycondensation, but the chemical structure of the copolyimide was not identified.

In a previous paper [12], the potential for the direct polycondensation of aromatic diacid dimethyl esters with aromatic diamines using phenyl phosphonic dichloride was investigated. The study revealed that a mixed carboxylic–phosphoric anhydride was formed as a polymerization intermediate. In continuation of this work, we have investigated the control of the chemical structure of copolyimides by this direct polymerization of copolyamic acid methyl esters. 4,4′-Oxydianiline (ODA) and 2,2′-bis(trifluoromethyl)benzidine (PFMB) were used as diamine

comonomers, and 2,5-dicarbomethoxy terephthalic acid as the diacid-diester. We focused on studying the chemical structure of the copolyimide by the proton nuclear magnetic resonance spectroscopy and the corresponding imidization properties by the differential scanning calorimetry.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA) and ODA were sublimed under reduced pressure before use. N-methyl pyrrolidone (NMP) was distilled over P_2O_5 under reduced pressure and stored in a desiccator. All other reagents, including pyridine and phenyl phosphonic dichloride (PhPOCl$_2$), were used as received.

2.2. Monomer synthesis

2.2.1. 2,5-Dicarbomethoxy terephthalic acid (p-PMDE)
Freshly sublimed PMDA (10 g) was introduced into

anhydrous methanol (100 ml) and the solution was heated to reflux with stirring until PMDA disappeared. After the clear solution was cooled to room temperature, the excess methanol was evaporated under reduced pressure to obtain dicarbomethoxy terephthalic acid (PMDE). PMDE was recrystallized from methanol to obtain 2.8 g of para-rich isomer. 2,6-Dicarbomethoxy terephthalic acid (*m*-PMDE) was extracted from butyl acetate using a Soxhlet extractor to obtain white *p*-PMDE (m.p. 237–238°C, 24%). ^{1}H NMR (DMSO-d_6, ppm): 8.0 (s, 2H aromatic); 3.8 (s, 6H methyl).

2.2.2. 2,5-Dicarbomethoxy terephthaloyl chloride

p-PMDE (1 g) was heated to reflux with stirring in thionyl chloride (5 ml) until a clear solution was obtained. The excess thionyl chloride was then removed by a water aspirator, and the residue was recrystallized from benzene/heptane (50/50, v/v) (m.p. 135–137°C).

2.2.3. 2,2′-Bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl [13]

Activated copper (45 g) was added to a solution of 50 g of 2-bromo-5-nitrobenzotrifluoride in *N*, *N*′-dimethyl formamide (100 ml) and the mixture was refluxed for 5 h. The mixture was filtered to remove copper, and the residue was poured into excess water. A brown precipitate was filtered off and dried at 60°C in vacuo. For purification, the product was recrystallized from ether (m.p. 138–140°C, 70%).

2.2.4. 2,2′-Bis(trifluoromethyl)benzidine (PFMB) [13]

2,2′-Bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl (15 g) and stannous chloride dihydrate (63 g) were added to ethanol (50 ml). While the mixture was stirred at room temperature, hydrochloric acid (80 ml) was added carefully. The mixture was refluxed overnight and cooled to room temperature. The ethanol was removed under reduced pressure. Water was added to the residue, and the solution was alkalinized with 20% (w/v) sodium hydroxide aqueous solution. The precipitate was filtered off and dried at 60°C in vacuo. The product was extracted with acetone and sublimed at 130–140°C under reduced pressure to yield white needle crystals (m.p. 179–180°C, 80%). IR (KBr, cm^{-1}): 3445, 3343 (N–H str., pri. amine); 3225 (C–H str., aromatic); 1636, 1493 (C=C str., aromatic); 1337–1119 (C–F str., CF$_3$). ^{1}H NMR (acetone-d_6, ppm): 6.8–7.3 (6H, aromatic); 5.1 (4H, pri. amine).

2.3. Polymerization

2.3.1. Homopolymerization

After *p*-PMDE (4.1 mmol) was dissolved in NMP (10 ml) under nitrogen, pyridine (16.4 mmol) and phenyl phosphonic dichloride (8.2 mmol) were added to the solution carefully. When the exothermic reaction was completed, the aromatic diamine was introduced into the mixture with vigorous stirring for the direct polycondensation. It was

stirred for 24 h at room temperature. The polymer concentration was adjusted to 20% (w/v). After the reaction, the resulting viscous solution was poured into methanol, and the precipitate was filtered off and dried in vacuo at room temperature.
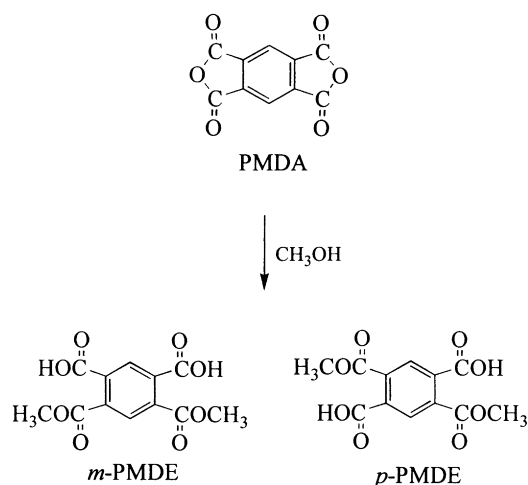
2.3.2. Copolymerization

Alternating or block copolymer was prepared as shown in Scheme 1 (Synthesis of copolyamic acid methyl esters). *p*-PMDE [(m + 1) mol] was dissolved in NMP under nitrogen. Pyridine (4 eq. to *p*-PMDE) and phenyl phosphonic dichloride (PhPOCl$_2$) (2 eq.) were then introduced into the solution. When the exothermic reaction was completed, PFMB (m mol) was added by vigorous stirring. The solution was stirred for 2 h at room temperature. In the same way, *p*-PMDE [(n − 1) mol] was added to the solution and dissolved completely. Pyridine (4 eq.) and PhPOCl$_2$ (2 eq.) were then introduced into the solution. Finally, ODA (n mol), the second diamine, was added at once with vigorous stirring. Copolymerization was carried out for 24 h. Here, m and n have the same value and are adjusted to 1, 5, 10 and 20. For random copolymerization, two diamines [(m + n) mol] were added to the NMP solution of *p*-PMDE [(m + n) mol] at the same time.

2.4. Measurements

IR spectra were recorded on a Midac® FTIR spectrophotometer. Proton nuclear resonance (^{1}H NMR) spectra were obtained on a Varian® Gemini 500. Differential scanning calorimetry (DSC) analyses were performed on a DuPont® DSC 2910 at a heating rate of 10°C/min. Inherent viscosity of all polymers was determined at 0.5 g/dl in *N*,*N*′-dimethyl acetamide (DMAc) at 25°C with an Ubbelohde viscometer.

3. Results and discussion

As aromatic polyimides are generally insoluble in common organic solvents and infusible, it is difficult to analyze their chemical structure. For such an analysis, the precursor polymer such as polyamic acid and polyamic acid ester might be used instead of the corresponding polyimide, because this precursor polymer is soluble in aprotic solvents such as NMP, DMAc, and *N*,*N*-dimethyl formamide (DMF). In the case of thermal imidization of the copolyamic acid, the sequence of the resulting polyimide is not the same as that of the initial copolyamic acid, because, as is well known, a depolymerization reaction occurs during imidization, resulting in regenerating 1–10 mol% of the anhydride groups [1,14,15]. However, this reaction is suppressed effectively by the esterification of the acid group with the alkyl group [7,8]. In this study, the copolyamic acid is replaced by the copolyamic acid methyl ester as a copolyimide precursor to control the sequence of the copolyimide. Therefore, the sequences of the two
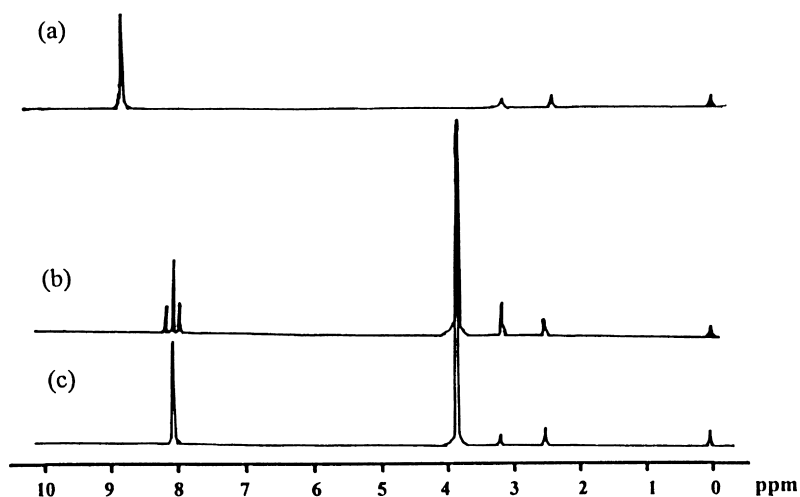
PMDA

CH₃OH

m-PMDE   p-PMDE

Scheme 2.

copolymers, the copolyamic acid methyl ester and the corresponding copolyimide, would be identical.

PMDA was treated with anhydrous methanol to prepare the diacid dimethyl ester monomer before polymerization. In this case, m-PMDE and p-PMDE isomers could be obtained, as shown in Scheme 2 (Two isomers of PMDE). If this isomer mixture is used in the polymerization, the resulting copolyamic acid methyl ester shows the complexity of the sequence analysis. For a simple sequence analysis of the copolyamic acid methyl ester by ^{1}H NMR, p-PMDE, whose aromatic proton is in an identical magnetic equivalence and has the same chemical shift, was separated from the isomer mixture and used for the preparation of the copolyamic acid methyl ester. Opening of the PMDA ring resulted in a change in the chemical shift of the aromatic proton (Scheme 2 (Two isomers of PMDE)). The chemical shift of the aromatic proton in PMDA was 8.8 ppm; it was separated into three peaks, at 7.9, 8.0 and 8.1 ppm, after the opening of the ring by anhydrous methanol as shown in

Fig. 1(a) and (b), i.e. the isomer mixture, m-PMDE and p-PMDE. After separation, the only remaining peak was at 8.0 ppm, assigned to the chemical shift of the aromatic proton in p-PMDE (Fig. 1(c)). This peak at 8.0 ppm was monitored to examine the average sequence length of the copolyamic acid methyl ester after polymerization. A new peak corresponding to the protons of the methyl group of the methyl ester appeared at 3.8 ppm after esterification with dry methanol, and this peak remained in the p-PMDE spectrum after the separation (Fig. 1(b) and (c)). As a result, p-PMDE could be completely seperated from the isomer mixture. Next, we synthesized copolyamic acid methyl esters directly, using PhPOCl₂ and pyridine, according to our previous results [12]. In this system, p-PMDE monomer reacted with PhPOCl₂ to form the corresponding mixed carboxylic–phosphoric anhydride as a polymerization intermediate. A nucleophilic substitution reaction by diamine then occurred at the carbonyl carbon of the carboxylic acids to form amide linkages. The copolyamic acid methyl esters were synthesized by the two-step procedure mentioned previously (Scheme 1 (Synthesis of copolyamic acid methyl esters)). In the first step, the p-PMDE-terminated oligomers were prepared by the reaction of PFMB with a calculated excess of p-PMDE in NMP. This first step continued for 2h, until the oligomers was completely formed. Oligomer length depends on the m, n values. The oligomer was used as a monomer in the second step. p-PMDE and ODA, the second diamine, were introduced into the solution in consideration of the oligomer to obtain stoichiometry. This method is probably the most versatile method for the synthesis of block copolymers [16].

When ODA and PFMB were used as diamine comonomers and copolymerized with p-PMDA, three types of the sequence were formed in the copolyamic acid methyl ester: two ODA moieties linked together through p-PMDE; ODA and PFMB moieties linked through p-PMDE; and two PFMB moieties linked through p-PMDE (Scheme 3

Fig. 1. ^{1}H NMR spectra of (a) PMDA; (b) PMDE; and (c) p-PMDE.
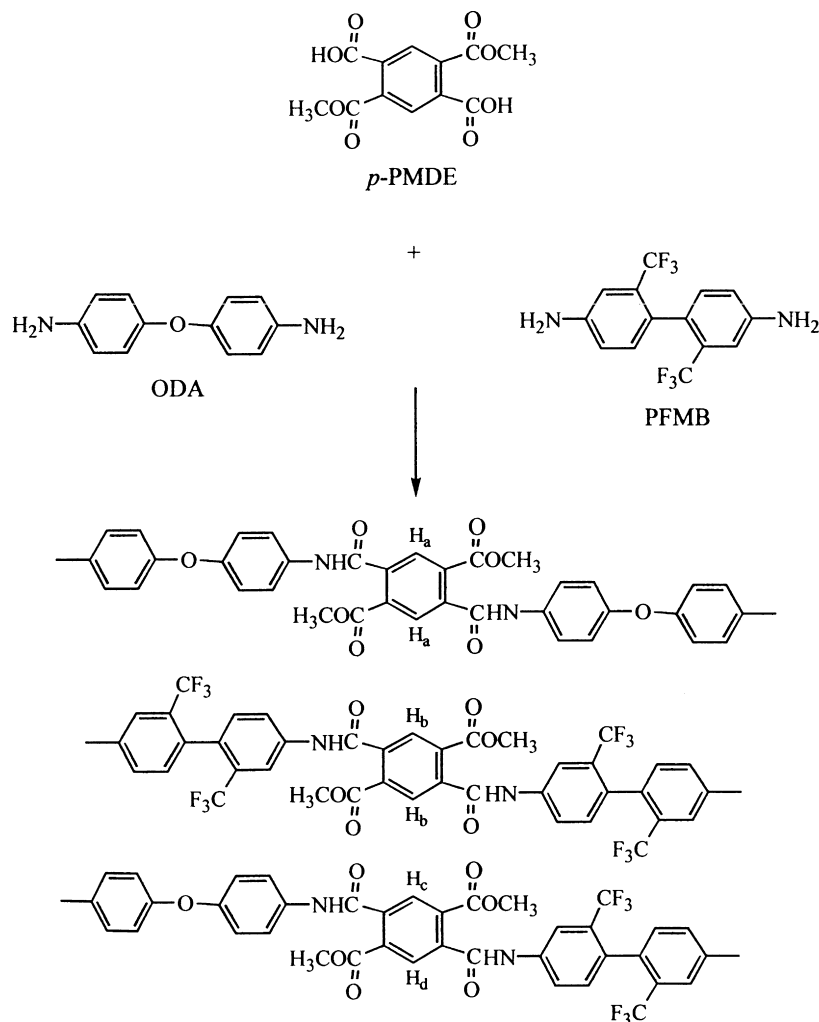
Scheme 3.

(Three types of copolyamic acid methyl ester sequence))
For the analysis of the copolymer chemical structure, the
chemical shifts of the aromatic proton of *p*-PMDE in each
magnetic environment had to be identified. H_a is the
aromatic proton of *p*-PMDE when two ODA moieties are
linked through *p*-PMDE, and H_b, when two PFMB moieties
are linked. H_c is the aromatic proton of the *p*-PMDE moiety
in the ortho position of the amide bond formed by ODA
when ODA and PFMB moieties are linked through
p-PMDE, and H_d is the aromatic proton of the *p*-PMDE
moiety in the ortho position of the amide bond formed by
PFMB. As shown in Fig. 2, the chemical shifts of H_a and H_b
were 8.05 and 8.21 ppm, respectively. It was thought that
the values of H_c and H_d might be between 8.05 and
8.21 ppm. Homo- and copolymerizations were carried out.
Here, the homopolyamic acid methyl ester of *p*-PMDE and
ODA is abbreviated to PO, and that of *p*-PMDE and PFMB,
to PP. Copolyamic acid methyl esters are abbreviated to
POP1, POP5, POP10, POP20, and POPR, which designate
copolymers with m = n = 1, 5, 10, 20, and a random
number, respectively. The inherent viscosity of these

polymers is summarized in Table 1. The inherent viscosity
of PO and PP homopolymers was 0.38 and 0.54 dl/g, respec-
tively and that of the copolymers was between 0.38 and
0.54 dl/g, which was good enough for film casting. Fig. 3
shows ^{1}H NMR spectra of the copolyamic acid methyl
esters POP1, POP5, POP10, POP20 and POPR between
8.0 and 8.4 ppm. The chemical shifts of H_c and H_d were
8.12 and 8.15 ppm, respectively, which were between
those of H_a and H_b as expected. The intensity of the peaks
at 8.12 and 8.15 ppm decreased as the values of m and n
increased, which indicated an increase in the average
sequence length.

The average sequence length in the copolymer can be
calculated from the mole fraction of each monomer partici-
pated in the copolymerization and the run number as
follows: [17,18]

Average "A monomer" sequence length = {(A)/[run
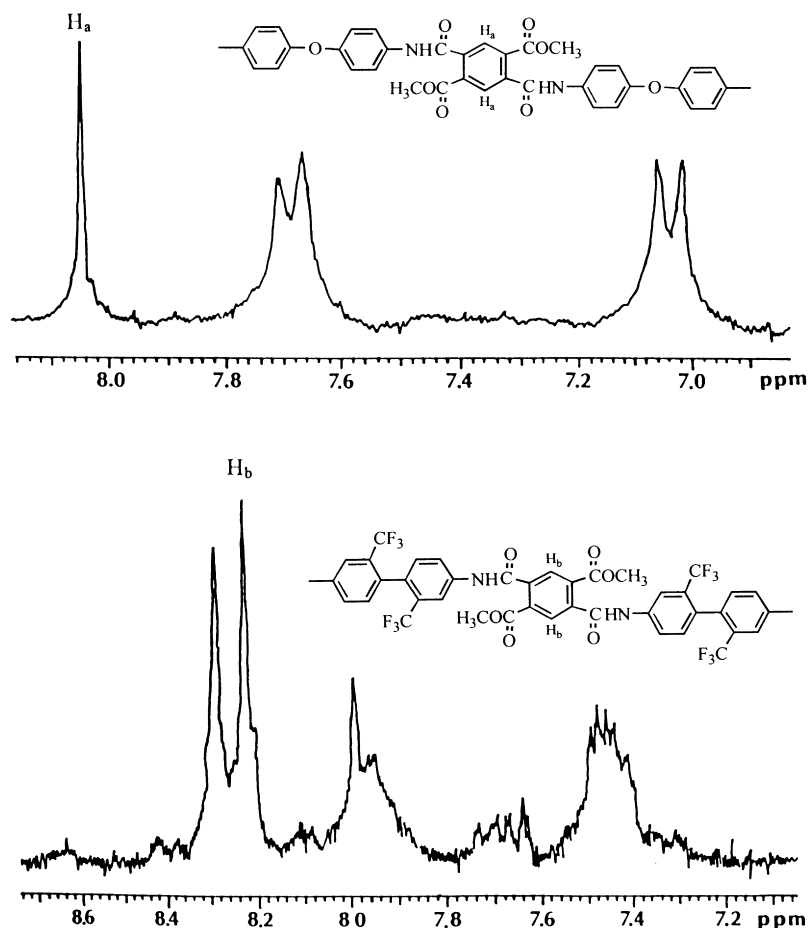number/2]} × 100;
Average "B monomer" sequence length = {(B)/[run
number/2]} × 100;

Fig. 2. ^{1}H NMR spectra of (a) PO and (b) PP homopolyamic acid methyl ester.

$(AB) = [\text{run number}/2]/100;$

$(BA) = [\text{run number}/2]/100;$ and

$\text{Run number} = [(AB) + (BA)] \times 100$

where (A) is the mole fraction of monomer A; (B) the mole fraction of monomer B; (AB) the mole fraction of AB diad in AB copolymer; (BA) the mole fraction of BA diad in AB copolymer; and the run number the average number of sequences of either type per 100 monomer units.

The mole fractions of ODA, (A), and PFMB, (B), in the copolyamic acid methyl ester were obtained from the fractions of the total area of the peaks at 10.6 and 11.1 ppm, which were assigned to the protons in the amide bonds formed by ODA and PFMB, respectively. The total mole fraction of the ODA-p-PMDE-PFMB, (AB), and PFMB-p-PMDE-ODA, (BA), triads was calculated from the sum of the areas of the peaks at 8.12 and 8.15 ppm. The resulting

Table 1
Inherent viscosity of polyamic acid methyl esters

Polymer	PO	POP1	POP5	POP10	POP20	POPR	PP
η_{inh} (dl/g)[a]	0.38	0.51	0.39	0.44	0.53	0.45	0.54

[a] Measured by 0.5 g/dl in DMAc at 25°C.

quantitative mole fraction, run number, and average sequence length are shown in Table 2. It can be seen that the ODA and PFMB participated in the polymerization in similar quantities, but slightly more PFMB than ODA was incorporated into the copolymer. Comparison of the chemical shift of the primary amine proton in ODA (4.7 ppm, acetone-d_6) and that in PFMB (5.1 ppm, acetone-d_6) shows that the reactivity of ODA is greater than that of PFMB, but the difference in reactivity between the diamines may not be important due to the low reactivity of the carbonic–phosphoric mixed dianhydride to diamines. In this case, it was possible that PFMB participated more in the formation of the copolymer because PFMB was introduced into the system before ODA.

For copolyamic acid methyl ester synthesized with $m = n = 1$, the real average sequence lengths of ODA and PFMB were 2.1 and 2.1. For $m = n = 10, 20$, the real average sequence lengths of ODA and PFMB were shorter than expected, i.e., 6.0, 7.1 and 8.0, 8.4, respectively. When the two diamine comonomers were introduced at the same time, the average sequence lengths were 2.7 and 3.3. For this copolymerization system, the real average sequence lengths could be controlled as intended when $m = n = 5$, i.e., 4.5, 5.8. Alternating character in the copolymer with $m = n = 1$
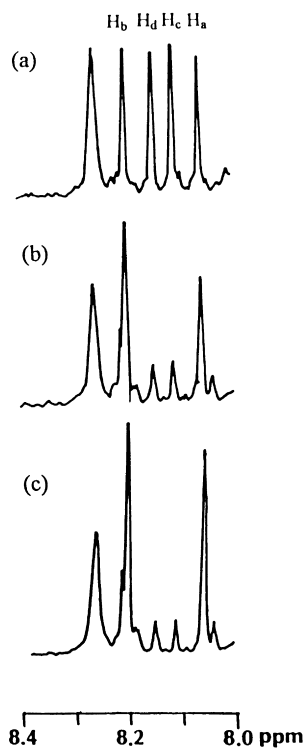
Fig. 3. ¹H NMR spectra of (a) POP1; (b) POP5; (c) POP10; (d) POP20; and (e) POPR copolyamic acid methyl ester.
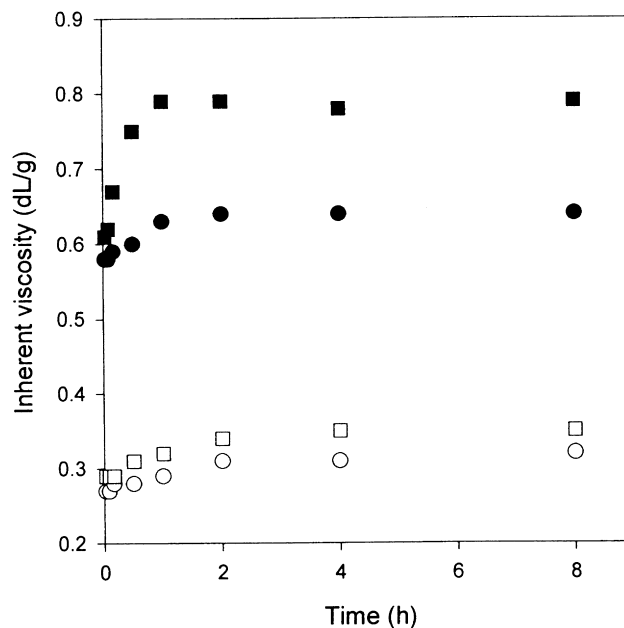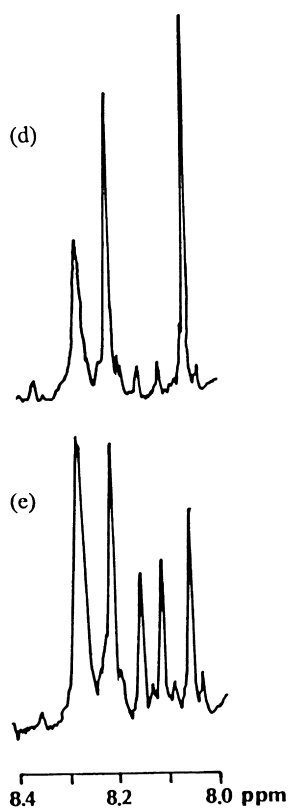

Fig. 4. The reactivity of ODA and PFMB under various polycondensation conditions: ODA/*p*-PMDE by direct polycondensation (○); ODA/2,5-dicarbomethoxy terephthaloyl chloride by acid-chloride method (●); PFMB/*p*-PMDE by direct polycondensation (□); and PFMB/2,5-dicarbomethoxy terephthaloyl chloride by acid-chloride method (■).

was not perfect due to a low reactivity of the polymerization intermediate to diamines in the system.

We studied the reactivities of ODA and PFMB to the mixed carboxylic–phosphoric anhydride, a polymerization intermediate in the direct polymerization, in comparison to the reactivity to acid chloride (Fig. 4). The reactivities of ODA and PFMB to acid chloride was higher than to the mixed carboxylic–phosphoric anhydride. When 2,5-dicarbomethoxy terephthaloyl chloride was used, the rate of polymerization was also higher than that in the direct copolycondensation. In the direct polymerization, it seemed that the reactivity of ODA to the mixed carboxylic–phosphoric anhydride was similar to that of PFMB owing to the low reactivity of the polymerization intermediate to nucleophiles. The degree of polymerization in the direct polycondensation was half that obtained when the acid

Table 2
Quantitative determination of mer distribution and average sequence length

Copolymer	(A)[a]	(B)[b]	(AB) + (BA)	Run number	Average sequence length (ODA/PFMB)
POP1	0.4987	0.5013	0.4744	47	2.1/2.1
POP5	0.4343	0.5657	0.1941	19	4.5/5.8
POP10	0.4593	0.5407	0.1592	16	6.0/7.1
POP20	0.4978	0.5022	0.1194	12	8.0/8.4
POPR	0.4487	0.5513	0.3366	34	2.7/3.3

[a] Distribution of ODA.
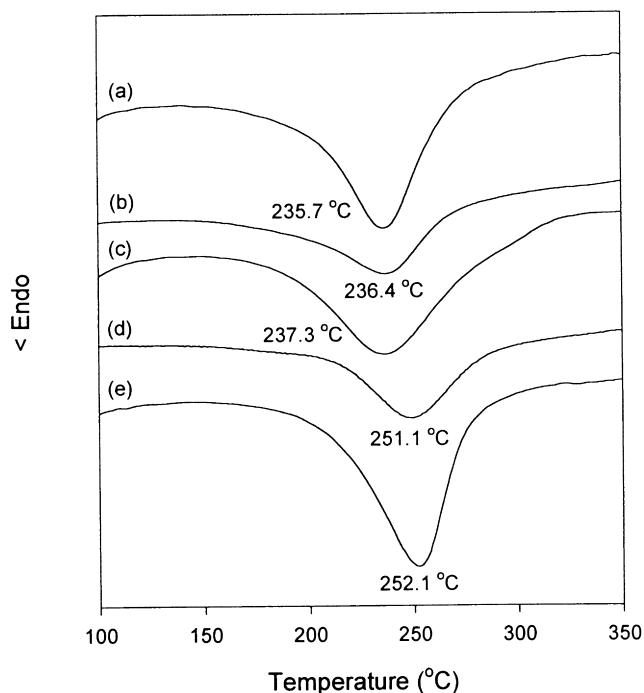
[b] Distribution of PFMB.

Fig. 5. DSC thermograms of polyamic acid methyl esters: (a) PO; (b) POP1; (c) POPR; (d) POP5; and (e) PP.

chloride method was used. The polymerization reached equilibrium after 2 h in all cases.

Fig. 5 shows the imidization characteristics of copolyamic acid methyl esters according to the average sequence length. Imidization properties of polyamic acid alkyl esters in comparison to alkyl esters have been studied [19-21]. However, the effect of average sequence length on these imidization properties has not been examined. The maximum imidization temperature of ODA/p-PMDE polyamic acid methyl ester was around 237°C and that of PFMB/p-PMDE was 252°C. The maximum imidization temperature of the copolymer with the long average sequence length approached that of the PFMB/p-PMDE polyamic acid methyl ester and reached 252°C when the average sequence length was ca. 5. When the average sequence length is long, the ODA/p-PMDE block moiety is thermally cyclized to the corresponding polyimide before the cyclization of the PFMB/p-PMDE block moiety. Therefore, a block of PFMB/p-PMDE moiety, the maximum imidization temperature of which is greater than that of ODA/p-PMDE, may be crucial for the thermal imidization when the average sequence length is greater than ca. 5 [1].

4. Conclusion

The average sequence length of copolyimides was controlled via copolyamic acid methyl esters as a precursor

by direct copolycondensation. The degree of polymerization of the copolyamic acid methyl esters was high enough for film casting. A perfect alternating copolyimide was not obtained, but the average sequence length was less than that of random copolyimides. Control of the average sequence length was difficult as the stoichiometric unbalance between p-PMDE and diamine increased due to the low reactivity of carbonic–phosphoric mixed dianhydride to diamines. The maximum imidization temperature of copolyamic acid methyl ester with the long average sequence length approached that of the PFMB/p-PMDE polyamic acid methyl ester, and was higher than that of the ODA/p-PMDE polyamic acid methyl ester, because the polymeric unit with high imidization temperature was crucial in thermal cyclization to the corresponding copolyimide.

In the future, we will study possibilities for better control of the average sequence length and investigate the relationship of other physical properties with the average sequence length of copolyimides.

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