

Analysis of chemical structure of fluoro-containing copolyamic acid methyl esters and its effect on the thermal imidization process

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Abstract

Copolyamic acid methyl esters were directly synthesized from 2,5-dicarbomethoxy terephthalic acid (*p*-PMDE) and 4,4'-oxydianiline (ODA) and fluoro-containing diamines using phenyl phosphonic dichloride. The average sequence lengths of the copolyamic acid methyl esters were controlled by stoichiometric unbalance and monitored by proton nuclear magnetic resonance spectroscopy (¹H-NMR). The effect of chemical structure of copolyamic methyl esters on thermal cyclization to the corresponding copolyimides was studied by differential scanning calorimetry and on thermal properties and solubility by thermogravimetry and solubility testing. The maximum imidization temperatures of the copolyamic acid methyl esters were between those of the homopolymers. The short sequence length of the fluoro-containing moiety of the copolyamic methyl esters made the copolyimide more soluble in organic solvents. The average sequence length of the copolymer did not affect the thermal properties of the corresponding copolyimide in this system. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aromatic polyimides (PIs) have been studied for several decades due to their excellent thermal stability, high mechanical properties, and good chemical resistance and electrical properties [1,2]. Since, however, PIs are generally insoluble in common organic solvents and infusible, it is not easy to process them. To overcome these drawbacks, new monomers which contribute to improvement in the solubility of PIs are developed and

introduced as comonomers to insoluble PIs systems. 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 [3]. In the case of thermal imidization of a 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 regeneration of 1–10 mol% of the anhydride groups depending on the chain flexibility [4,5]. This reaction was found to be associated with the presence of a carboxylic group in the *ortho*-position to the amide bond. The reaction is not significant in chemical imidization because the *o*-carboxy carboxamide groups are quickly converted to imide and isoimide moieties. Control of copolyimide chemical structure is important because the

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two-step method for polyimide synthesis is most common and the average sequence length of copolymers is a factor in modifying various physical properties. However, this reaction is suppressed effectively by esterification of acid group with alkyl group [6,7]. Therefore, the sequences of the two copolymers, the copolyamic acid methyl ester and the corresponding copolyimide, are identical. Polyamic acid esters have generally been synthesized by the reaction of diester–diacid chloride with diamine. However, this method is not easy to use on a large scale, since preparation and purification of acid chloride is complicated. In previous studies [8,9], the potential for direct polycondensation of aromatic diacid dimethyl esters with aromatic diamines using phenyl phosphonic dichloride and the control of the chemical structure of copolyimides by this direct polymerization of copolyamic acid methyl esters were investigated.

In a continuation of this work, we focused on studying the effect of the average sequence length of copolyamic methyl ester on thermal cyclization to the corresponding copolyimide by differential scanning calorimetry and on thermal properties and solubility by thermogravimetry and solubility testing. We have synthesized some fluoro-containing diamines with bulky and flexible groups and used them as comonomers to prepare Kapton[®]-based copolyimides with three kinds of average sequence length through the sequence control of copolyamic acid methyl ester. Kapton[®] is the polyimide from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).

2. Experimental

2.1. Materials

PMDA and ODA were sublimed under reduced pressure. *N*-methyl pyrrolidone (NMP) was distilled over phosphorus pentoxide under reduced pressure. All monomers and solvents were kept in a desiccator before use. All other reagents, including pyridine, phenyl phosphonic dichloride (PhPOCl₂), and 2,2-bis(4-aminophenyl)-hexafluoropropane (6FDAM), were used as received.

2.2. Monomer synthesis

2,5-Dicarbomethoxy terephthalic acid (*p*-PMDE) [9]: (m.p. 237–238°C, yield 24%). ¹H-NMR (DMSO-*d*₆, ppm): 8.0 (s, 2H aromatic); 3.8 (s, 6H methyl).

1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDAM) [10]: (m.p. 204–206°C; lit. m.p. 201–204°C, yield 80%). Elemental analysis (C, H, N): 70.48, 4.61, 8.02 (found); 70.17, 5.00, 8.18 (calc.). IR (KBr, cm⁻¹): 3486, 3385 (N–H str., pri. amine); 1624 (C=C str., ar-

omatic). ¹H-NMR (acetone-*d*₆, ppm): 6.6–7.4 (13H, aromatic); 4.8 (4H, pri. amine).

3,5-Diaminobenzotrifluoride (3,5-DABTF) [11]: (m.p. 85°C; lit. m.p. 85°C, yield 86%). Elemental analysis (C, H, N): 48.05, 3.90, 15.69 (found); 47.73, 4.00, 15.90 (calc.). IR (KBr, cm⁻¹): 3334, 3216 (N–H str., pri. amine); 1611 (C=C str., aromatic); 1340–1125 (C–F str., CF₃). ¹H-NMR (acetone-*d*₆, ppm): 6.1–6.2 (3H, aromatic); 4.8 (4H, pri. amine).

2.3. Polymerization [9]

2.3.1. Homopolymerization

After *p*-PMDE (4.1 mmol) was dissolved in NMP (10 ml) under nitrogen, pyridine (16.4 mmol) and PhPOCl₂ (8.2 mmol) were added to the solution carefully. When the exothermic reaction was completed, the aromatic diamine (4.1 mmol) was introduced into the mixture with vigorous stirring for direct polycondensation. It was left with stirring for 24 h at room temperature. The polymer concentration was adjusted to 20% (w/v).

2.3.2. Copolymerization

Alternating or block copolymer was prepared as shown in Fig. 1. *p*-PMDE [(*m* + 1) mol] was dissolved in NMP under nitrogen. Pyridine (4 eq. to *p*-PMDE) and PhPOCl₂ (2 eq.) were then introduced into the solution. When the exothermic reaction was completed, fluoro-containing diamine (mmol) was added with vigorous stirring. The solution was left with stirring 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 PhPOCl₂ (2 eq.) were then introduced into the solution. Finally, ODA (nmol), the second diamine, was added all at once with vigorous stirring. Copolymerization was carried out for 24 h. Here, *m* and *n* are the same value and are adjusted to 1, 5. For random copolymerization, two diamines [(*m* + *n*) mol] were added to the NMP solution of *p*-PMDE [(*m* + *n*) mol] at the same time.

After the reaction, all of the resulting viscous solutions were poured into methanol, and the precipitates were filtered and dried in vacuo at 60°C until no weight change was observed.

2.4. Measurements

IR spectra were recorded on a Midac FTIR spectrophotometer. Elemental analyses were carried out with a Carlo Erba 116 Elemental Analyzer. Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained on a Varian Gemini 200 for monomer identification. A Varian Gemini 500 was used for the sequence analyses of copolyamic methyl esters. The imidization reaction was monitored by differential scanning calorimetry (DSC) and thermogravimetry (TG) using a DuPont

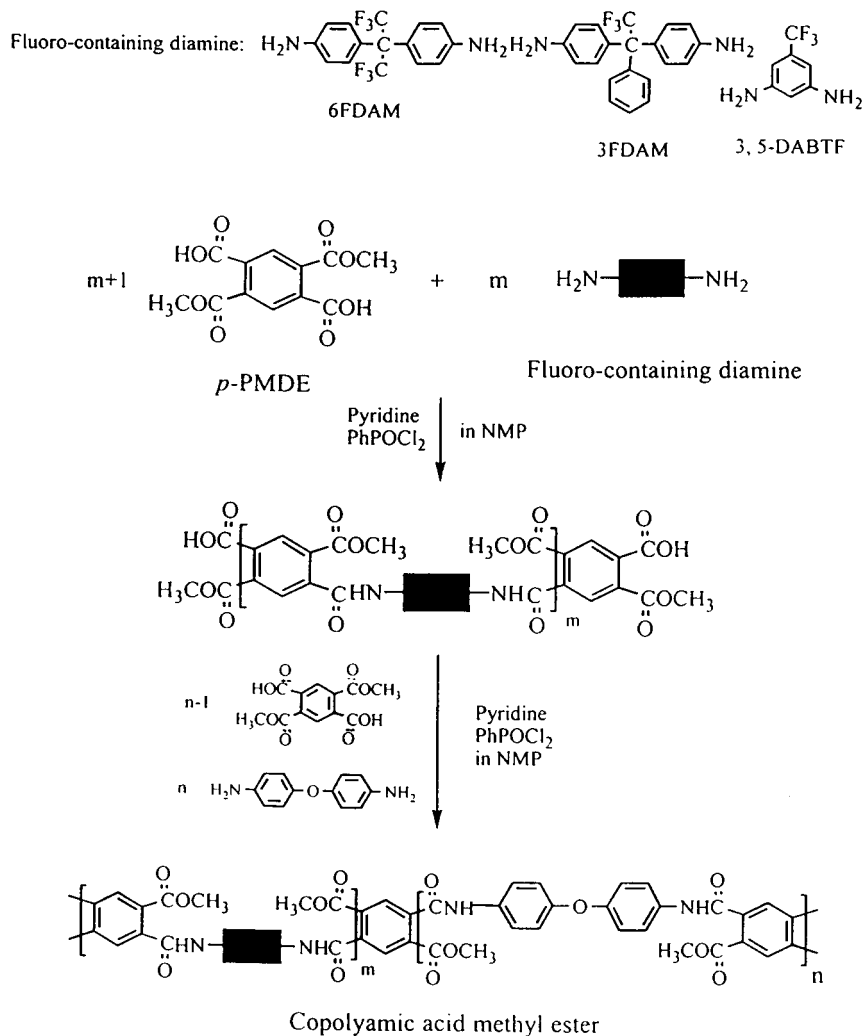


Fig. 1. Synthesis of copolyamic acid methyl ester.

DSC 2910 and TGA 2950 under nitrogen at a heating rate of 10°C/min. The 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

The copolyamic acid methyl esters were synthesized by the two-step procedure mentioned previously (Fig. 1). In the first step, the *p*-PMDE-terminated oligomers were prepared by the reaction of fluoro-containing diamine with a calculated excess of *p*-PMDE in NMP. This first step continued for 2 h, until the oligomers were completely formed. Oligomer length depends on the m , n values. The oligomers were used as monomers in the second step. *p*-PMDE and ODA, the second diamine,

were introduced into the solution in consideration of the oligomer to obtain stoichiometry.

Table 1 shows the inherent viscosity of homo and copolyamic acid methyl esters synthesized from ODA, 6FDAM, 3FDAM, and 3,5-DABTF by direct polymerization. The inherent viscosity of copolymers was between that of their homopolymers, which was good enough for film casting.

For a simple sequence analysis of the copolyamic acid methyl ester by ¹H-NMR, *p*-PMDE, whose aromatic proton is in an identical magnetic equivalence and has same chemical shift, was separated from the isomer mixture containing 2,6-dicarbomethoxy terephthalic acid (*m*-PMDE) and used for the preparation of the copolyamic methyl ester. The chemical shift (H_a) of the aromatic proton of *p*-PMDE in the homopolymers synthesized from 6FDAM, 3FDAM, and 3,5-DABTF

Table 1
Inherent viscosity of polyamic acid methyl esters

Homopolymer	η_{inh} (dl/g)			
ODA	0.38			
6FDAM	0.23			
3FDAM	0.11			
3,5-DABTF	0.17			
Copolymer	η_{inh} (dl/g)			
		$m = n = 1$	$m = n = 5$	random
ODA/6FDAM	0.34		0.29	0.21
ODA/3FDAM	0.33		0.27	0.16
ODA/3,5-DABTF	0.30		0.27	0.21

was 8.10, 8.07, and 8.14, respectively. The chemical shift of this proton in the homopolymer synthesized from ODA was previously determined to be 8.05 (H_a) [9].

When ODA and a fluoro-containing diamine were used as diamine comonomers and copolymerized with *p*-PMDA, three types of sequence were formed in the copolyamic acid methyl ester: two ODA moieties linked together through *p*-PMDE; ODA and fluoro-containing diamine moieties linked through *p*-PMDE; and two fluoro-containing diamine moieties linked through *p*-PMDE. For analysis of the copolyamic acid methyl ester 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_d when two fluoro-containing diamine moieties are linked. H_b is the aromatic proton of the *p*-PMDE moiety in the ortho position of the amide bond formed by ODA when ODA and fluoro-containing diamine moieties are linked through *p*-PMDE, and H_c is the aromatic proton of the *p*-PMDE moiety in the ortho position of the amide bond formed by fluoro-containing diamine.

Fig. 2 shows the 1H -NMR spectra of the copolyamic acid methyl esters synthesized from ODA/6FDAM, ODA/3FDAM, and ODA/3,5-DABTF. The intensity of the H_b and H_c peaks decreased as the values of m and n increased, which indicated an increase in average sequence length. These peaks could not be identified in the copolyamic acid methyl ester synthesized from ODA/3FDAM, since the difference in chemical shift between H_a and H_d of the homopolymer synthesized from ODA and 3FDAM is very small, 0.02.

Average sequence length in the copolymer can be calculated from the mole fraction of each monomer participating in the copolymerization and the run number as follows [12]:

average “A monomer” sequence length

$$= \{(A)/[\text{run number}/2]\} \times 100,$$

average “B monomer” sequence length

$$= \{(B)/[\text{run number}/2]\} \times 100,$$

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

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

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

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

The mole fractions of the ODA moiety, (*A*), and the fluoro-containing diamine moiety, (*B*), in the copolyamic acid methyl ester were obtained from the fractions of the total area of the peaks, which were assigned to the protons in the amide bonds formed by ODA and fluoro-containing diamine, respectively. The total mole fraction of the ODA-*p*-PMDE-fluoro-containing diamine, (*AB*), and fluoro-containing *p*-PMDE-ODA diamine, (*BA*), triads was calculated from the sum of the areas of the H_b and H_c peaks. The resulting quantitative mole fractions, run numbers, and average sequence lengths are shown in Table 2. The fluoro-containing copolyamic acid methyl esters with around 2, 3, and 5 of average sequence length was obtained in this system. It can be seen that slightly more fluoro-containing diamine than ODA was incorporated into the copolymer because fluoro-containing diamine was introduced into the system before ODA. The sequence of the corresponding copolyimides would be identical to that of the polyamic acid methyl esters due to esterification of acid group with methyl group.

Fig. 3 shows the imidization characteristics of copolyamic acid methyl esters according to average sequence length. The maximum imidization temperature of homopolyamic acid methyl ester synthesized from ODA was around 237°C, and for that synthesized from 6FDAM, 3FDAM, and 3,5-DABTF the temperature

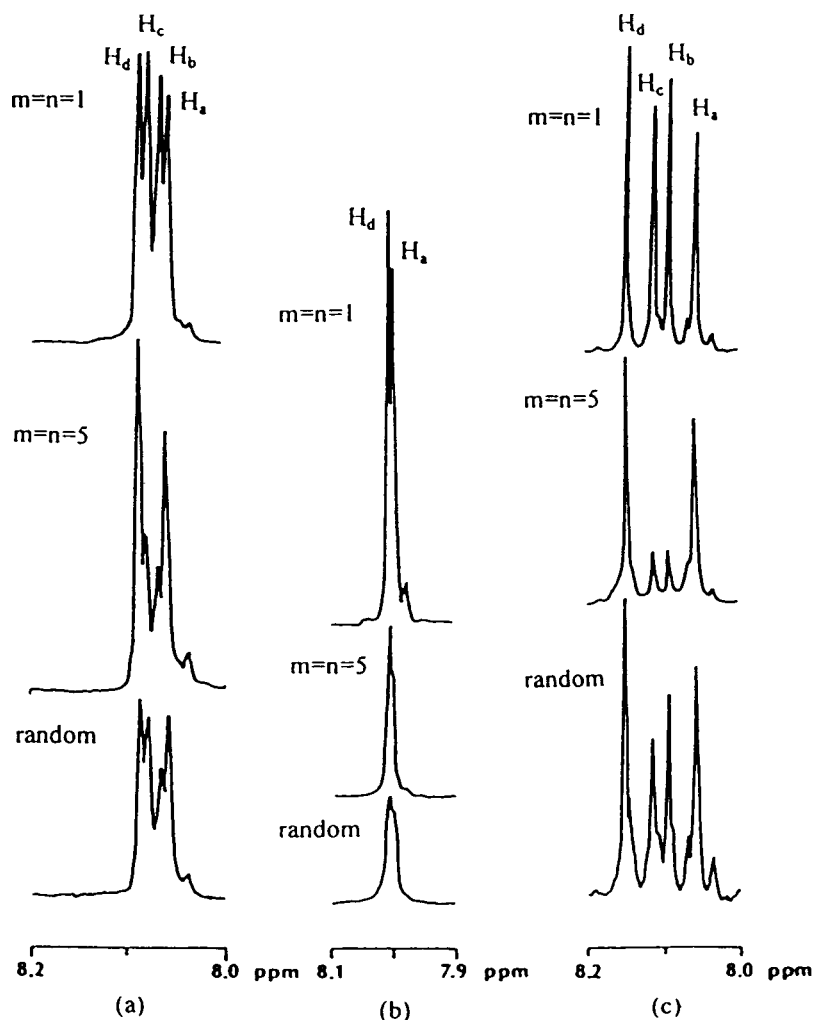


Fig. 2. ^1H -NMR spectra of copolyamic acid methyl esters synthesized from (a) ODA/6FDA, (b) ODA/3FDAM and (c) ODA/3,5-DABTF.

was 250°C, 260°C, and 243°C, respectively. These temperatures were between those measured for each homopolymer. The maximum imidization temperature of the copolymers with an average sequence length of 3 approached that of polyamic acid methyl esters synthesized from fluoro-containing diamines. Therefore, a block of fluoro-containing diamine-*p*-PMDE moiety, the maximum imidization temperature of which is greater than that of the ODA-*p*-PMDE moiety, may be crucial for thermal imidization when the average sequence length is around 3.

Table 3 shows the thermal properties of homopolyamic acid methyl ester and copolyamic acid methyl ester. The found weight loss during imidization was slightly greater than the theoretical value, which means the cyclization reaction fully occurs. NMP might not remain in the polymer after full drying, because the

carboxylic acid group was blocked with methanol [13]. The decomposition temperature (T_d) of the homopolyamic acid methyl ester synthesized from 6FDA and 3FDAM was lower than that for any other homopolymer due to their hinge type moiety [2]. However, at 800°C, the residue of polyimide from 3FDAM was high. The T_d of the copolyamic acid methyl esters was between that of their homopolymers irrespective of the average sequence length.

The solubility of the polyimides is shown in Table 4. The homopolyimide synthesized from 3FDAM had excellent solubility. It was well known that introducing a polar, bulky, and flexible group to a polyimide backbone improves solubility [14]. Park et al. [15] reported that perfect alternating character in copolyimides improves their solubility in organic solvents. The solubility of the copolyimide increased when 3FDAM and

Table 2

Quantitative determination of mer distribution and average sequence length of various fluoro-containing copolyamic acid methyl esters

Copolymer	(A) ^a	(B) ^b	(AB + BA)	Run number	Average sequence length
<i>ODA/6FDAM</i>					
<i>m</i> = <i>n</i> = 1	0.4693	0.5307	0.5248	52	1.8 ^c /2.0 ^d
<i>m</i> = <i>n</i> = 5	0.4536	0.5464	0.1988	20	4.6/5.5
random	0.4732	0.5268	0.3754	38	2.5/2.8
<i>ODA/3FDAM</i>					
<i>m</i> = <i>n</i> = 1	0.4444	0.5556	– ^e	–	–
<i>m</i> = <i>n</i> = 5	0.4350	0.5650	–	–	–
random	0.4025	0.5971	–	–	–
<i>ODA/3,5-DABTF</i>					
<i>m</i> = <i>n</i> = 1	0.4768	0.5232	0.4929	49	1.9/2.1
<i>m</i> = <i>n</i> = 5	0.4913	0.5087	0.2087	21	4.7/4.9
random	0.4602	0.5398	0.4203	42	2.2/2.6

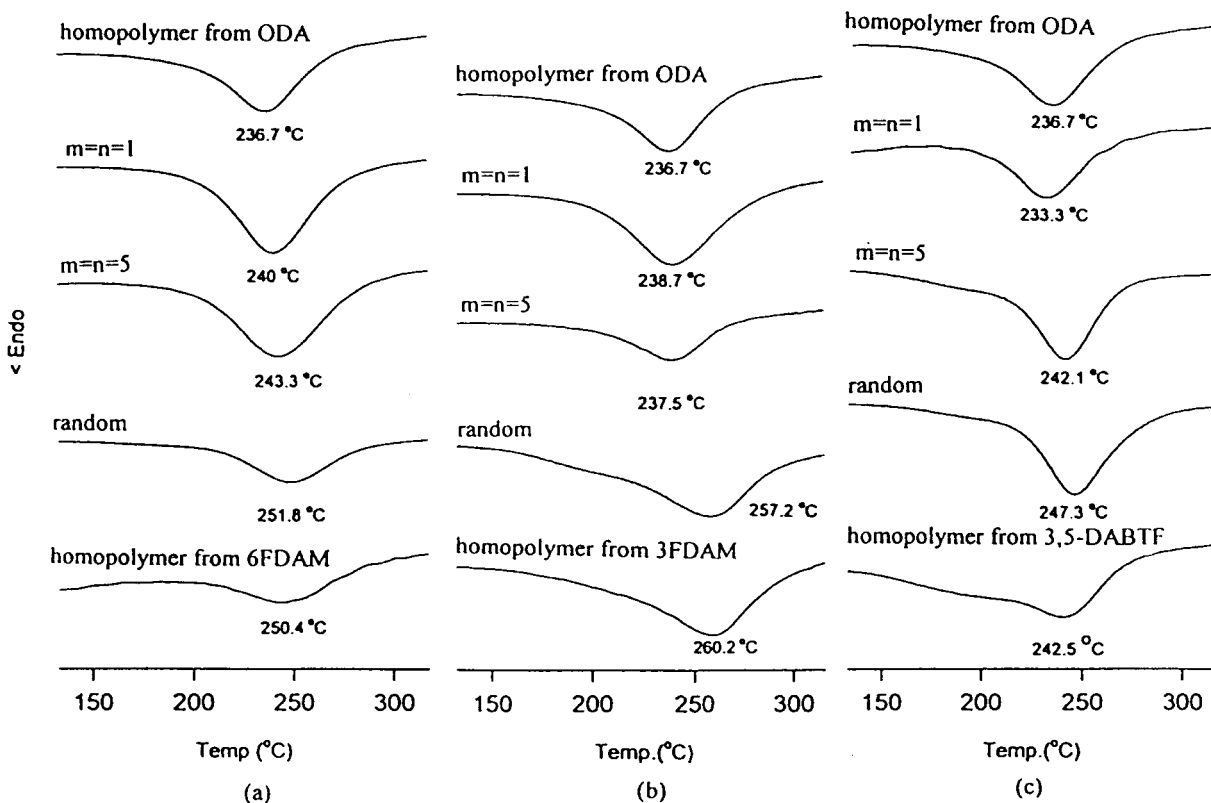
^a Distribution of ODA moiety.^b Distribution of fluoro-containing diamine moiety.^c Average sequence length of ODA moiety.^d Average sequence length of fluoro-containing diamine moiety.^e Cannot be calculated.

Fig. 3. DSC thermograms of copolyamic acid methyl esters synthesized from (a) ODA/6FDAM, (b) ODA/3FDAM and (c) ODA/3,5-DABTF.

Table 3
Imidization of polyamic acid methyl esters and the thermal properties of their corresponding polyimides

Polymer	Weight loss during imidization		T_d^a (°C)	Residue at 800°C	
	Found	Calculated			
<i>Homo-polymer</i>					
ODA	15.3	14.2	573	61.3	
6FDAM	13.4	11.0	525	54.5	
3FDAM	8.5	10.8	536	76.3	
3,5-DABTF	21.4	15.0	573	59.8	
<i>Copolymer</i>					
ODA/6FDAM	$m = n = 1$	14.2	12.4	546	58.1
	$m = n = 5$	13.0	12.4	544	59.7
	random	13.4	12.4	536	62.0
ODA/3FDAM	$m = n = 1$	14.0	12.3	546	66.4
	$m = n = 5$	14.1	12.3	547	64.5
	random	11.7	12.3	537	65.6
ODA/3,5-DABTF	$m = n = 1$	17.2	14.6	575	57.6
	$m = n = 5$	12.8	14.6	580	71.0
	random	14.9	14.6	577	64.6

^a 5% weight loss.

Table 4
Solubility^a of polyimides

Polymer	Solvent				
	H ₂ SO ₄	NMP	DMF	DMSO	THF
<i>Homo-polymer</i>					
ODA	s	i	i	i	i
6FDAM	s	i	i	i	i
3FDAM	s	s	s	s	s
3,5-DABTF	s	ps	i	i	i
<i>Copolymer</i>					
ODA/6FDAM	$m = n = 1$	s	i	i	i
	$m = n = 5$	s	i	i	i
	random	s	i	i	i
ODA/3FDAM	$m = n = 1$	s	ps	i	i
	$m = n = 5$	s	i	i	i
	random	s	i	i	i
ODA/3,5-DABTF	$m = n = 1$	s	ps	i	i
	$m = n = 5$	s	i	i	i
	random	s	ps	i	i

^a Measured at 25°C for 24 h; s = soluble; ps = partly soluble; i = insoluble.

3,5-DABTF were used as comonomers, and also increased overall with a decrease in the average sequence length.

4. Conclusions

Fluoro-containing copolyamic acid methyl esters with about 2, 3, and 5 of average sequence length were synthesized by direct copolycondensation. This chemical structure was well determined by ¹H-NMR. The degree of polymerization of the copolyamic acid methyl esters

was high enough for film casting. The maximum imidization temperature of copolyamic acid methyl esters with an average sequence length of around 3 approached that of homopolyamic acid methyl esters synthesized from fluoro-containing diamines, and was higher than that of homopolyamic acid methyl esters synthesized from ODA. Introduction of a bulky and flexible group to a Kapton[®]-based polyimide improved its solubility in organic solvents. This solubility increased as the average sequence length of the copolyimide decreased. The average sequence length did not affect the thermal properties of the copolyimide in this system.

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