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Aromatic thermotropic liquid crystalline polymers from 1,3-bis[4-(4-aminophenoxy)-α,α-dimethylbenzyl]benzene

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Polymers were synthesized with 1,3-bis[4-(4-aminophenoxy)-α,α-dimethylbenzyl]benzene by polycondensation of pyromellitic dianhydride (PMDA), phthaloyl chlorides and trimellic anhydride chloride (TAC). Their possible use as aromatic thermotropic liquid crystalline polymers was investigated. The polyamide from terephthaloyl chloride (TPC), and the copolyamideimide from PMDA and TPC, showed thermotropic liquid crystalline properties according to the results of differential scanning calorimetry and observations from polarization microscopy. However, neither the polyamide from isophthaloyl chloride nor the polyamideimide from TAC exhibited liquid crystalline properties. © 1997 Elsevier Science Ltd.

(Keywords: liquid crystalline polymer; polyimide; polyamideimide)

INTRODUCTION

The aromatic polyimide and polyamide obtained from 1,3-bis[4-(4-aminophenoxy)-α,α-dimethylbenzyl]benzene (BAC diamine) are currently receiving considerable attention because of their liquid crystalline properties. In particular, the polyimide[1] from BAC diamine and pyromellitic dianhydride (PMDA) has excellent melt flowability and outstanding mechanical and thermal properties. It has been designated PI-LC, and several studies carried out on it. Yamaguchi *et al.*[2] and Fay *et al.*[3] investigated the liquid crystallinity of the structural isomer polyimide of PI-LC, and reported that only PI-LC showed liquid crystalline properties among their studied polyimides. Asanuma *et al.*[4] used PI-LC as an improver of melt flowability of other thermoplastic polymers such as PES (polyethersulfone), PEEK (polyether etherhetone) and AURUM, and reported its excellent melt flowability. Tamai *et al.*[5] investigated the mechanical and thermal properties of PI-LC, and reported that tensile strength, tensile modulus and elongation of PI-LC injection-moulded parts were 137 MPa, 4.7 GPa and 5.2%, respectively.

However, little is known about the other polymers obtained from BAC diamine; therefore, in this article, we investigate the basic properties of several polyamides and polyamideimides obtained from BAC diamine.

EXPERIMENTAL

Starting materials

1-Chloro-4-nitrobenzene, phthalic anhydride, terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), 2-propyl alcohol and methanol are products of Mitsui Toatsu Chemicals, Inc. 1,3-Bis(4-hydroxy-α,α-dimethylbenzyl)benzene was obtained from Mitsui Petrochemical Industries, Inc. and used as received. Benzoyl chloride and *N*,*N*-dimethylformamide (DMF) were obtained from Wako Junyaku Kogyo Co., Ltd. Methyl ethyl ketone (MEK), 3-methylphenol, γ-picoline, acetic anhydride and potassium carbonate were obtained from the Kanto Chemicals Co., Inc. Propylene oxide was obtained from the Tokyo Kasei Kogyo Co., Ltd. *N*-Methyl-2-pyrrolidinone (NMP) was obtained from the Mitsubishi Kasei Kogyo Co., Ltd. Pyromellitic dianhydride (PMDA) was obtained from Daicel Chemical Industries, Ltd. and used as received. Trimellitic anhydride chloride (TAC) was obtained from the Aldrich Chemical Co., Inc. and used as received. Five per cent palladium/active carbon used as a hydrogenation catalyst was obtained from Nihon-Engelhaldt Co., Ltd.

Monomer synthesis

A 5000 ml five-necked round bottom flask containing 807.5 g (5.13 mol) of 1-chloro-4-nitrobenzene, 414.6 g (3.00 mol) of potassium carbonate, 150 ml of toluene and 2500 g of DMF was fitted with a mechanical stirrer, a condenser with a Dean–Stark trap, a nitrogen pad and a thermometer. The mixture was heated to reflux with stirring, and the residued mixture was removed. After removal, the azeotropic mixture was cooled down to around 130°C, and then 866.2 g (2.50 mol) of 1,3-bis(4-hydroxy-α,α-dimethylbenzyl)benzene was added. After heating this mixture at 140–150°C for 10 h under a nitrogen atmosphere, it was cooled down to 90°C and filtered under hot conditions. The filtrate obtained was cooled to ambient temperature and poured into 1300 ml

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of water. The yellow precipitate obtained was filtered out and washed with 2-propyl alcohol, followed by drying at 60°C. The yield of 1,3-bis[4-(4-nitrophenoxy)-α,α-dimethylbenzyl]benzene was 1458.1 g (99.0%).

Elemental analysis. Calculated for $C_{36}H_{32}N_2O_6$: C 73.45%, H 5.48%, N 4.76%. Found: C 73.27%, H 5.62%, N 4.80%.

A closed vessel equipped with a thermometer and a stirrer was charged with the 1,3-bis[4-(4-nitrophenoxy)-α,α-dimethybenzyl]benzene obtained, 9.42 g of 5% palladium/active carbon catalyst and 1458 ml of 2-propyl alcohol. At 60–65°C, after stirring the mixture for 8 h, 102.11 (4.55 mol) of hydrogen was introduced and absorbed by the mixture. The catalyst was filtered off under hot conditions. After cooling to ambient temperature, the precipitated powder was filtered and washed with 2-propyl alcohol. The yield of BAC diamine was 400.4 g (94.7%); m.p. 103.5–105.5°C.

Elemental analysis. Calculated for $C_{36}H_{36}N_2O_2$: C 81.79%, H 6.86%, N 5.30%. Found: C 81.58%, H 6.97%, N 5.48%.

Polymer synthesis

Synthesis of polyimide. A mixture of 528.7 g (1.00 mol) of BAC diamine, 216.8 g (0.994 mol) of PMDA, 1.78 g (0.012 mol) of phthalic anhydride, 140 g (0.15 mol) of γ-picoline in 6000 g of 3-methylphenol was stirred at 150°C for 4 h, and, after cooling, the reaction mixture was poured into MEK. The precipitated polymer was collected by filtration, followed by thorough washing with MEK and dried at 250°C in an inert oven. The yield was 679.5 g (95.5%). I.r. (KBr, cm^{-1}): 1780, 1720 (–CO–), 1240 (–O–) and 720 (imide ring).

Synthesis of polyamide. A typical procedure for polyamide synthesis is as follows. A mixture of 528.7 g (1.00 mol) of BAC diamine, 201.8 g (0.994 mol) of TPC, 1.69 g (0.012 mol) of benzoyl chloride, 137.3 g (2.36 mol) of propylene oxide in 6000 g of NMP was stirred at ambient temperature for 4 h. Then the reaction mixture was poured into methanol. The precipitated polymer was collected by filtration, followed by thorough washing with methanol and dried at 220°C in an inert oven. The yield was 652.3 g (98.8%). I.r. (KBr, cm^{-1}): 3300 (N–H), 1650 (–CO–) and 1240 (–O–).

Polyamide from BAC diamine and IPC was prepared by the method described above.

Synthesis of polyamideimide. A mixture of 528.7 g (1.00 mol) of BAC diamine, 209.3 g (0.994 mol) of TAC, 1.69 g (0.012 mol) of benzoyl chloride and 69.7 g (1.20 mol) of propylene oxide in 1700 g of NMP was stirred at ambient temperature for 4 h. To this was added 204 g (2.00 mol) of acetic anhydride, 11.6 g (0.125 mol) of γ-picoline and 4300 g of NMP. This mixture was then heated at 65–70°C for 3 h under a nitrogen atmosphere. After cooling, the reaction mixture was poured into methanol. The precipitated polymer was collected by filtration, followed by thorough washing with methanol, and dried at 180°C for 6 h in an inert oven. The yield was 699 g (99.0%). I.r. (KBr, cm^{-1}): 3380 (N–N), 1780, 1720 (–CO–), 1240 (–O–) and 720 (imide ring).

Synthesis of copolyamideimide. A typical procedure of copolyamideimide synthesis is as follows. A mixture of 528.7 g (1.00 mol) of BAC diamine, 108.4 g (0.497 mol) of PMDA and 1700 g of NMP was stirred at ambient temperature under a nitrogen atmosphere for 2 h. To this was added 100.9 g (0.497 mol) of TPC, 1.78 g (0.012 mol) of phthalic anhydride, 69.7 g (1.20 mol) of propylene oxide and 1700 g of NMP. After stirring at ambient temperature for 12 h, 204 g (2.0 mol) of acetic anhydride, 11.6 g (0.125 mol) of γ-picoline and 2600 g of NMP were added. This mixture was heated at 65–70°C for 3 h under a nitrogen atmosphere. After cooling, the reaction mixture was poured into methanol. The precipitated polymer was collected by filtration, followed by thorough washing with methanol, and dried at 200°C for 6 h in an inert oven. The yield was 692 g (98.0%). I.r. (KBr, cm^{-1}): 3370 (N–H), 1780, 1720, 1650 (–CO–), 1240 (–O–) and 720 (imide ring).

Copolyamideimides having different amounts of PMDA and TPC were prepared by a similar method.

MEASUREMENTS

Inherent viscosities (η) of the polymers were obtained at a concentration of 0.5% in a solvent (*p*-chlorophenol/phenol, 9/1 (w/w)) at 35°C. The thermal properties of the polymers were investigated using d.s.c. (Shimadzu 40 type calorimeter) and thermogravimetric analysis (t.g.a.; Shimadzu 40 type analyser). Thermal transitions of the polymers were monitored by d.s.c. with a 10°C min^{-1} heating rate. The glass transition temperature (T_g) of the polymers was taken at the inflection point of the ΔT *versus* temperature curve (d.s.c.). The endothermic transition temperature (T_1, T_2) value was taken at the endothermic peak temperature from the d.s.c. curve. The thermo-oxidative stability of the samples were estimated by the 5% weight reduction temperature in air (T_{d5}), using t.g.a. with a 10°C min^{-1} heating rate. Photomicroscopic observations were made with a Nikon Optiphoto-Pol, together with the use of a LINKAM TH-600RMS hot stage model equipped with a temperature controller, by setting a polymer sample between crossed polarizers at a 10°C min^{-1} heating rate.

RESULTS AND DISCUSSION

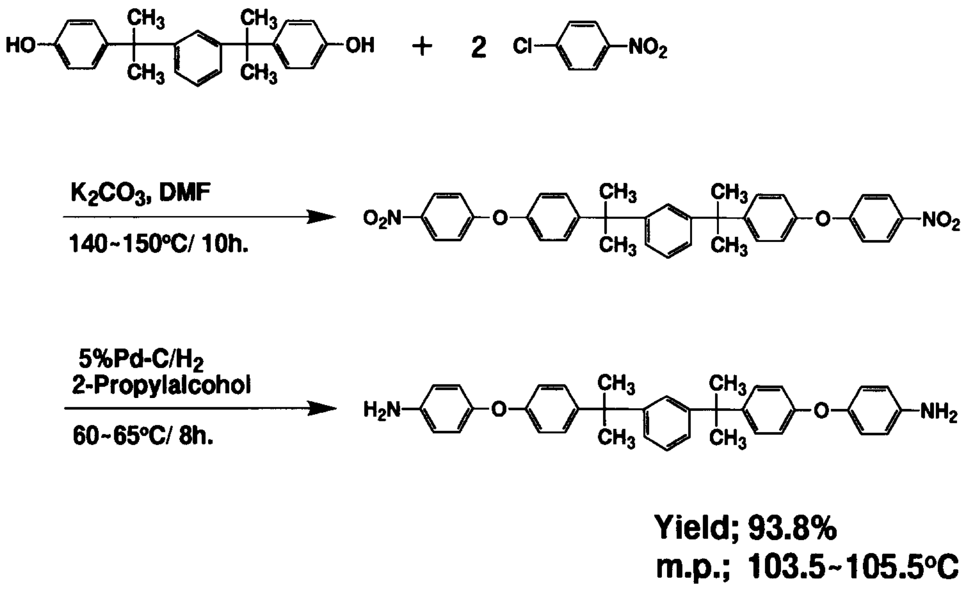
The synthesitic procedure for BAC diamine is shown in *Scheme 1.*

BAC diamine was synthesized from 1,3-bis(4-hydroxy-α,α-dimethylbenzyl)benzene and 1-chloro-4-nitrobenzene followed by reduction. The yield of BAC diamine based on 1,3-bis(4-hydroxy-α,α-dimethylbenzyl)benzene was 93.8%.

The chemical structures of the monomers used for polymerization and their abbreviations are given in *Figure 1.*

Polyimide, polyamides and polyamideimide from TAC were synthesized by the previously mentioned method[5] in our laboratory. Copolyamideimides were synthesized from BAC diamine, PMDA and TPC according to *Scheme 2.* In this case, propylene oxide was selected as a hydrochloride catcher, because chloropropyl alcohol, which is a reaction product from hydrochloride and propylene oxide, is easily removed from the obtained copolyamideimide. The monomer compositions of the synthesized polymers and their sample codes are listed in *Table 1.*

The properties of the synthesized polymers are summarized in *Table 2.* η values of these polymers were controlled to around 1.0 dl g^{-1}, and polymer chain ends



Scheme 1

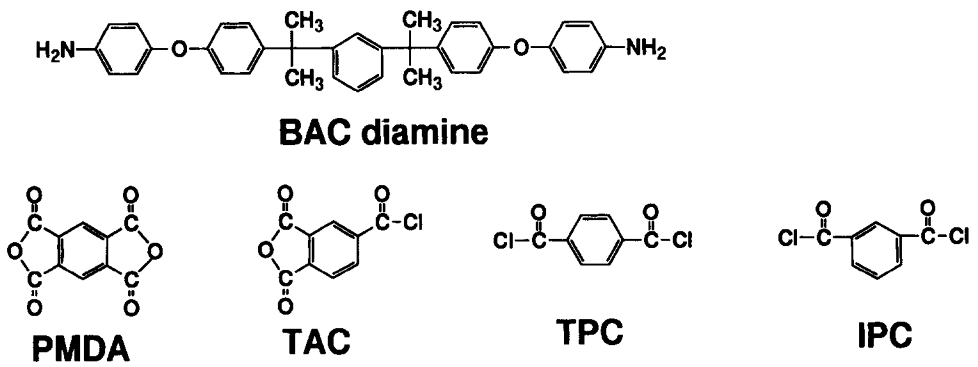


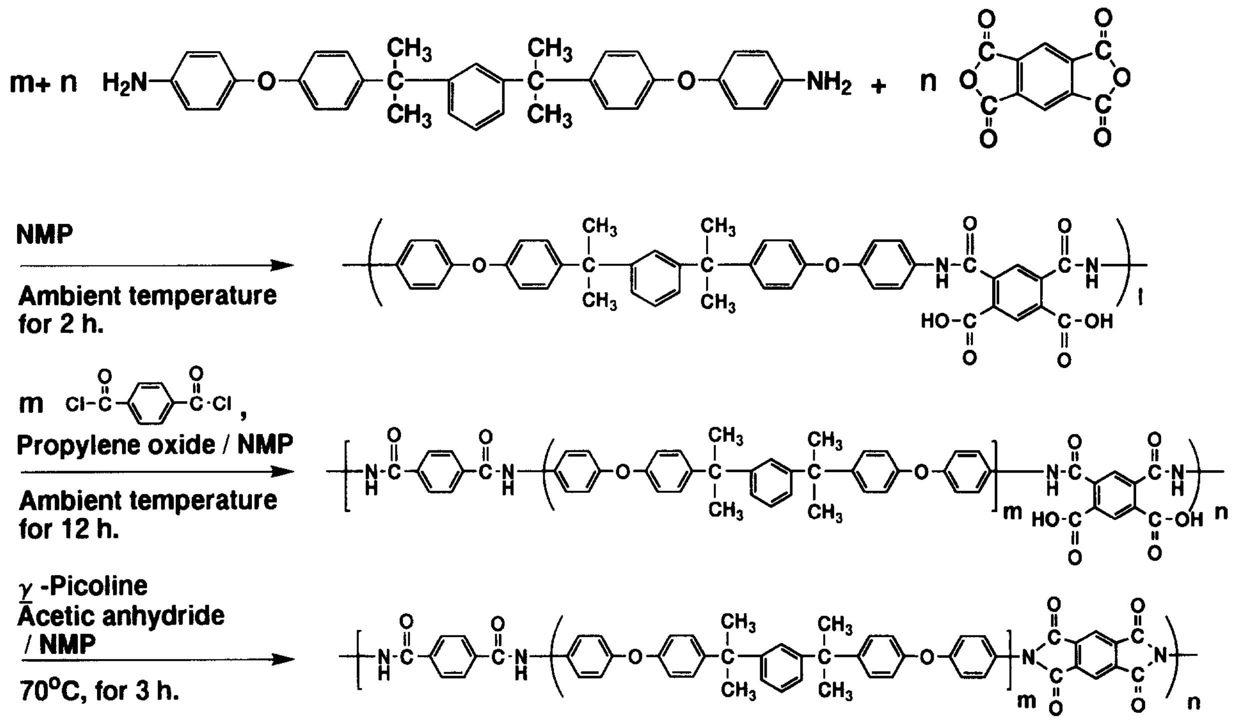
Figure 1 Chemical structures of monomers used for polymer synthesis

were terminated by using phthalic anhydride or benzoyl chloride as end-cappers. In the case of polymers having a pyromellitic imide unit (PI, PAI2a, PAI2b, PAI2c), the polymer chain end was terminated by phthalic anhydride. In the case of polymers having no pyromellitic imide unit (PA1, PA2, PAI1), the polymer chain end was terminated by benzoyl chloride.

The T_{d5} value is the 5% weight reduction temperature in air; a higher value indicates better thermo-oxidative stability of the polymer. PAI2a, PAI2b and PAI2c have a pyromellitic imide unit and a terephthaloyl amide unit in a repeating structural unit, and the terephthaloyl amide unit content increases in the order PAI2a, PAI2b and PAI2c, as summarized in *Table 1*. This result indicates that the thermo-oxidative stability is improved by decreasing the content of the terephthaloyl amide unit in a repeating structural unit of copolyamideimide.

The thermal transitions of polymers were monitored by d.s.c. between 100 and 340°C with a heating rate of $10°\mathrm{C\,min}^{-1}$. Glass transition temperatures (T_g) of polymers were detected between 177 and 191°C; however, glass transitions were not clearly detected for PI, PA1 and PAI2. The comparison of the T_g values of polyamideimides (PAI1, PAI2b, PAI2c) shows that the T_g values of copolyamideimides (PAI2b, PAI2c) having a pyromellitic imide unit and a terephthaloyl amide unit are higher than that of PAI1 having no pyromellitic imide unit in a repeating structure.

T_1 and T_2 values of *Table 2* show endothermic transition temperatures, which were taken at the endothermic peak temperatures from the d.s.c. curves of the polymers. T_1 values of the polymers were detected between 234 and 277°C, and T_2 values of the polymers were detected between 266 and 303°C. The polymers, except for PA2 and PAI1, showed two endothermic transition peaks in the d.s.c. curves, as shown in *Figure 2*. PA2 and PAI1 have neither a pyromellitic imide unit nor a terephthaloyl amide unit in their repeating structural units. However, the other polymers, except for PA2 and PAI1, have a pyromellitic imide unit and/or a terephthaloyl amide unit in their repeating structural units. Therefore it is assumed that the existence of a pyromellitic imide unit and/or a terephthaloyl amide unit in a repeating structural unit of a polymer is strongly related to the endothermic transition behaviour shown by the d.s.c. curve. In the case of the d.s.c. thermogram of PAI2b, two distinct endothermic peaks can be observed at 235°C (T_1) and 266°C (T_2). The other transition, corresponding to the glass transition, is observed at 191°C; however, the inflection degree of the glass transition is not so clear. Therefore, the crystal phase of PAI2b is assumed to be residual at up to 235°C (T_1), and the d.s.c. transition at T_1 can be attributed to the crystal-to-liquid crystal transition, since the specimen gains fluidity, showing the same high polarization as another thermotropic liquid crystalline polyimide



Scheme 2

Table 1 Monomer composition and sample codes

Sample codes	BAC diamine (mol%)	PMDA (mol%)	TAC (mol%)	TPC (mol%)	IPC (mol%)
PI	100	100	0	0	0
PA1	100	0	0	100	0
PA2	100	0	0	0	100
PAI1	100	0	100	0	0
PAI2a	100	70	0	30	0
PAI2b	100	50	0	50	0
PAI2c	100	30	0	70	0

reported by Inoue *et al.*[6]. T_2 is assumed to be the isotropization temperature of the liquid crystal.

Asanuma *et al.* and Fay *et al.* reported that the polyimide of BAC diamine and PMDA, that is, the polyimide in this article, showed a liquid crystalline phase at the temperature between two endothermic peaks observed by d.s.c. Observation of the liquid crystalline phase of the other polymers obtained from BAC diamine by polarizing microscopy was also carried out. *Figure 3* shows photographs of the phase transition of PAI2b obtained by polarizing the microscope. These four photographs show different phases of PAI2b on heating. The photograph obtained at 230°C shows a solid state. The photographs obtained at 232 and 275°C show the liquid crystalline phase. This temperature range between 232 and 275°C is nearly equal to the temperature between the two endothermic peaks (T_1, T_2) which were observed by d.s.c. The isotropic phase was observed by heating up to 278°C. The phase transition behaviour of PAI2b observed by polarizing microscopy was almost the same as that of the liquid crystalline polyimide reported by Asanuma *et al.*

The temperature ranges of the liquid crystalline phase of the other polymers observed by polarizing microscopy are summarized as T_p ranges in *Table 2*. The T_p ranges of the other polymers are also nearly equal to the

Table 2 Properties of polymers from BAC diamine

Sample codes	η $(\mathrm{dl\,g^{-1}})^a$	T_{d5} $(^\circ\mathrm{C})^b$	T_g $(^\circ\mathrm{C})^c$	T_1 $(^\circ\mathrm{C})^d$	T_2 $(^\circ\mathrm{C})^d$	T_p range $(^\circ\mathrm{C})^e$
PI	1.21	522	ND[f]	272	303	276–310
PA1	1.03	435	ND	277	286	248–300
PA2	1.10	442	180	ND	ND	NO[g]
PAI1	0.85	470	177	ND	ND	NO
PAI2a	1.15	486	ND	240	281	240–287
PAI2b	0.94	463	191	235	266	232–275
PAI2c	0.93	454	189	234	269	235–275

[a] Inherent viscosity measured at a concentration of 0.5% in a solvent (*p*-chlorophenol/phenol, 9/1 (w/w)) at 35°C

[b] Temperature at which the sample lost 5% of its weight in air as measured by t.g.a. with a 10°C min^{-1} heating rate

[c] Glass transition temperature measured by d.s.c. with a 10°C min^{-1} heaating rate

[d] Endothermic transition measured by d.s.c. with a 10°C min^{-1} heating rate

[e] Temperature range of observation of polarization by polarizing microscopy with a 10°C min^{-1} heating rate

[f] Thermal transition by d.s.c. measurement was not clearly detectable

[g] Polarization was not clearly observed by polarizing microscopy

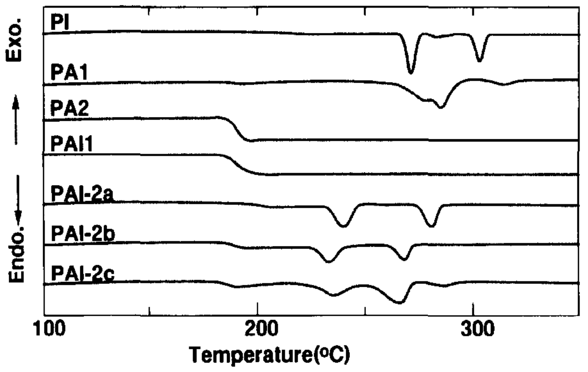


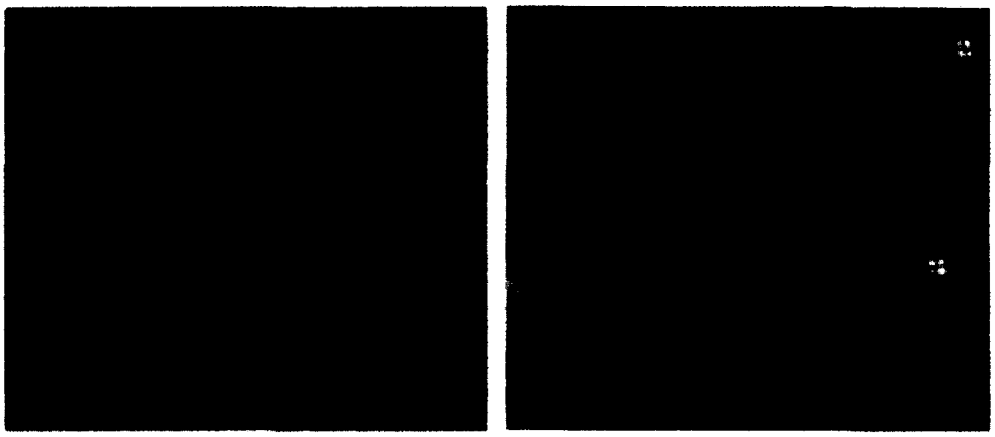
Figure 2 D.s.c. thermograms of polymers during the heating process

temperature between T_1 and T_2. In the case of PA2 and PAI1, a liquid crystalline phase was not observed. These two polymers also did not show two endothermic peaks on d.s.c. This result indicates that polymers having two endothermic peaks (T_1, T_2) by d.s.c. show a liquid crystalline phase at the temperature between T_1 and T_2. In the case of polymers synthesized from BAC diamine, it was found that polymers having a pyromellitic imide unit and/or a terephthaloyl amide unit in a repeating structural unit show thermotropic liquid crystalline properties.

Figure 4 shows the relationship between pyromellitic imide unit content in a repeating structure of copolyamide-imide and the temperature range of the liquid crystalline phase observed by polarizing microscopy. A pyromellitic imide unit content of 100% in a repeating structural unit of copolyamide-imide indicates polypyromellitic imide, namely PI, and a 0% content indicates polyphthaloylamide, namely PA1. *Figure 4* shows that copolyamide-imides obtained from PMDA, TPC and BAC diamine have a thermotropic liquid crystalline phase between 232 and 310°C, and copolyamideimides containing 50% pyromellitic imide unit in a repeating structural unit have the lowest temperature range of the liquid crystalline phase between 232 and 275°C. *Figure 4* also indicates that the temperature range of the liquid crystalline phase of copolyamideimide is controlled by selecting a suitable pyromellitic imide unit content in a repeating structural unit of copolyamideimide.

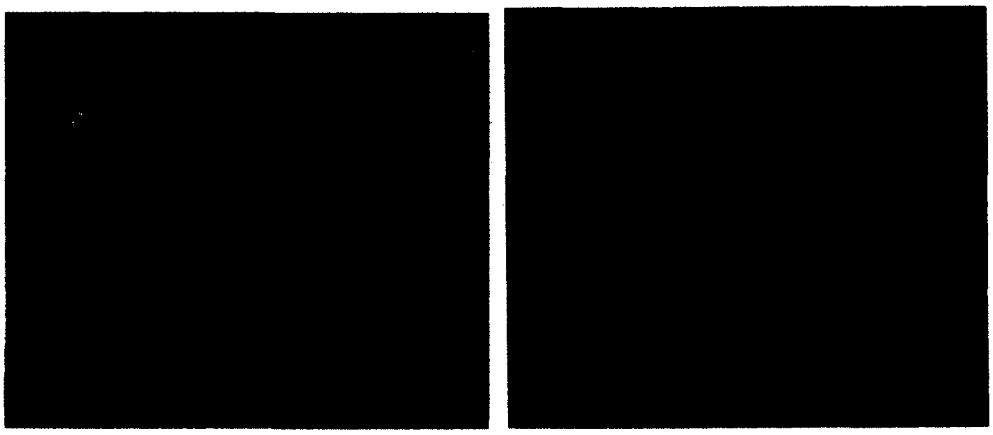
SUMMARY AND CONCLUSIONS

Polymers were synthesized with BAC diamine by polycondensation of PMDA, phthaloyl chlorides (TPC, IPC) and TAC. Their utility as aromatic thermotropic liquid crystalline polymers was investigated by using



Solid state :230℃

Final liquid crystalline phase :275℃



Initial liquid crystalline phase :232℃

Isotoropic melting state :278℃

Figure 3 Polarizing micrographs of copolyamideimide (PAI2b)

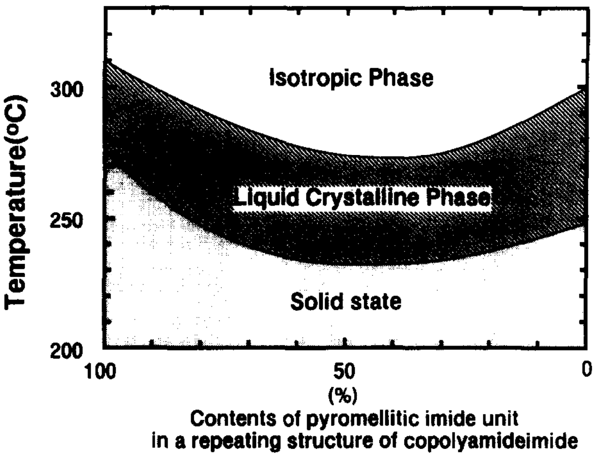


Figure 4 Temperature ranges of the liquid crystalline phase of copolyamideimides estimated by observation from polarizing microscopy

d.s.c. and polarizing microscopy. Polyamide synthesized from BAC diamine and TPC showed liquid crystalline properties; however, polyamide synthesized from BAC diamine and IPC did not show such properties. Copolyamideimide synthesized from BAC diamine, PMDA and TPC also showed liquid crystalline properties, but polyamideimide obtained from BAC diamine and TAC did not show liquid crystalline properties. These results suggest that the liquid crystallinity of these polymers is related to their chemical structure, such as the number of pyromellitic imide units and/or terephthaloyl amide units in a repeating structural unit.

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