

Synthesis and Properties of Aromatic Polyamides and Polyamide–Smectic Oligomer Graft Copolymer

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ABSTRACT: Two series of polyamides **1** and **2**, composed of succinic acid and aromatic diamines, were synthesized in the absence and in the presence of *p*-aminobenzoic acid (ABA) by a direct polycondensation using a phosphorylation polyamidation. Diamines used were 1,3-phenylenediamine, 1,4-phenylenediamine, 4-aminodiphenyl ether, 4,4'-diaminodiphenyl sulfide, and 4-aminodiphenyl sulfone. Polyamides **1** and **2** have 0.10–0.54 dl g⁻¹ and 0.38–0.76 dl g⁻¹ of $[\eta]$ and 2.1–23.6% and 8.2–23.5% of crystallinity, respectively. Polyamide **2**-smectic oligomer graft copolyamide, polyamide **3c**, was also prepared from the polycondensation of dicarboxyl terminated smectic macromonomer (MacMHB) and 4-aminodiphenyl ether in the presence of ABA. Polyamide **3c** exhibits a mesophase over the temperature range from 98.1 to 122.2°C, whereas polyamides **1** and **2** exhibit no melting process. The thermal degradation of polyamides **1** and **2** began at temperature range of 272–345°C and 356–417°C, respectively. On the other hand, polyamide **3c** degrades at 332°C through a two-step one.

KEY WORDS Phosphorylation Polycondensation / Aromatic Polyamides / Smectic Macromonomer / Graft Copolymer / Degree of Crystallinity / Thermal Properties /

Wholly aromatic polyamides are characterized as heat resistant, high strength, and high modulus materials. The relevant limitation of the materials resides in their low processability such as high melting point, low solubility in common organic solvents, and low compatibility with other polymers.^{1–4} A variety of concepts have been described to improve these disadvantages of rod-like polyamides, using proper methods such as copolymerization,^{2,5} *in situ* direct polycondensation,⁶ and introduction of the small substituents into the aromatic nucleus of polymer backbone.^{5,7} Recently, synthesis of block and graft copoly-

mers containing liquid-crystalline segments was found to be a useful method for the preparation of tailored liquid crystalline polymers (LCP).^{8–13} In the course of a study of LCP,^{14–16} our interest focused on how the properties of non-thermotropically aromatic polyamide containing poly(*p*-benzamide) (PBA) segment with a rod-like character can be changed by introducing the liquid crystalline oligomer in the side chain. In previous paper we reported on the synthesis and the characterization of graft copolymers, polyamides **4a–e**, comprised polyamides **2a–e** and nematic oligomers obtained from the macro-

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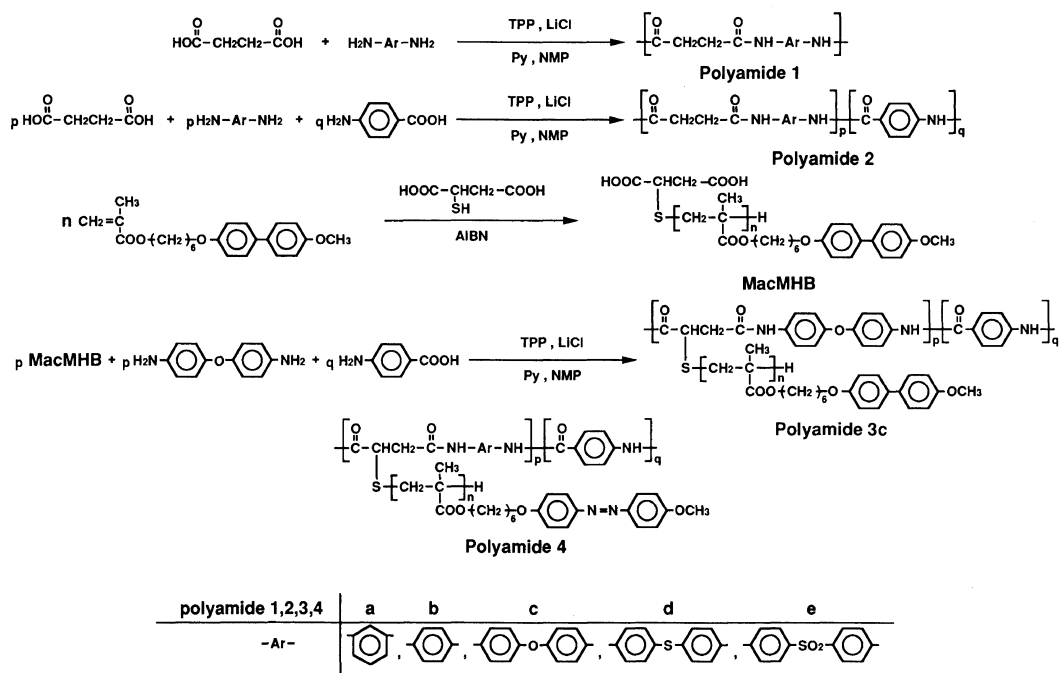


Figure 1. Structure of various polyamides.

monomer technique as shown in Figure 1.¹⁶ The present paper describes a characteristics of parent polyamides 1, 2, and a new polyamide 3c bearing smectic oligomer in the side chain.

EXPERIMENTAL

Materials

Thiomatic acid (TMA), methacryloyl chloride, *p*-aminobenzoic acid (ABA), 1,3-phenylenediamine, 1,4-phenylenediamine, 4-aminodiphenyl ether, 4,4'-diaminodiphenyl sulfide, 4-aminodiphenyl sulfone, triphenyl phosphite (TPP), and succinic acid (SA) were commercially obtained and purified by distillation or recrystallization. Pyridine (Py) and *N*-methyl-2-pyrrolidone (NMP) were freshly redistilled before use. 4-(6-Methacryloyloxyhexyloxy)-4'-methoxybiphenyl (MHB) was prepared from the direct acylation of 4-(6-hydroxyhexyloxy)-4'-methoxybiphenyl with methacryloyl chloride, K 63.1 S_A 76.2 I (lit.¹⁷: K 62 S 69 I).

Synthesis of Polyamides 1, 2

Into a 100 ml three-necked round bottomed flask equipped with a magnetic stirrer, drying tube, and N₂ inlet tube, were placed 10 mmol of SA, 10 mmol of aromatic diamine, 25 mmol of TPP, 12.6 mmol of LiCl in 6 ml of Py and 24 ml of NMP. After the solution was stirred at 100°C under nitrogen for 6 h, the reaction mixture was poured into a large amount of methanol to precipitate polyamide 1. The collected solid was stirred in 50 ml of hot ethanol for 10 min and the supernatant was discarded while hot. The small molecules were completely removed by repeating this procedure three times. Polyamide 2 was prepared by the same method mentioned above, using 3 mmol of SA, 3 mmol of diamine and 15 mmol of ABA. The intrinsic viscosity [η] of polyamides 1 and 2 was determined in H₂SO₄ at 30°C with an Ubbelohde viscometer.

Synthesis of ω -Hydro-poly[1-(4-methoxybiphenyloxyhexyloxycarbonyl)-1-methylene]thiomalic Acid (MacMHB)

Twenty milliliters of tetrahydrofuran (THF) solution containing 5.00 g (13.6 mmol) of MHB, 0.305 g (2.04 mmol) of TMA, and 0.022 g (0.14 mmol) of AIBN in a glass tube was degassed by the freeze-thaw technique using a dry-ice/methanol bath and sealed *in vacuo*. After polymerization at 50°C for 10 h, the contents of the tube were poured into a large amount of petroleum ether to precipitate MacMHB. MacMHB was purified by fractionation using a THF–petroleum ether solvent system: yield 4.63 g (87.2%). The THF solution of MacMHB was neutralized with 0.01 mol⁻¹ of aqueous potassium hydroxide using phenolphthalein as an indicator, and from the value of neutralization its molecular weight was calculated to be 4350. The molecular weight was also estimated to be $M_n = 4200$ with a polydispersity $M_w/M_n = 1.33$ by means of GPC measurement using a polystyrene standard.

Synthesis of Polyamide 3c

Into a 100 ml three-necked round bottomed flask equipped with a magnetic stirrer, drying tube, and N₂ inlet tube, were placed 3.00 mmol of MacMHB (calculated from the value of titration for terminated dicarboxyl groups), 15.00 mmol of ABA, 3.00 mmol of 4-aminodiphenyl ether, 26.25 mmol of TPP, and 12.60 mmol of LiCl in 6 ml of Py and 24 ml of NMP. After the solution was stirred at 100°C under nitrogen for 8 h, the reaction mixture was poured into a large amount of methanol to precipitate polyamide 3c. Polyamide 3c was purified by removing low molecular weight compounds by use of a Soxhlet extractor with ethanol as solvent for 20 h.

Measurements

FT-IR measurements were carried out with a JASCO FT/IR 8900 + M20 spectrometer with DSC FP-80. GPC analysis was conducted in



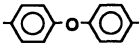
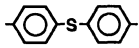
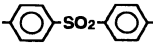
THF solution with TSK gel G(4+3+2)H_{XL}, using a TOSOH HPLC-8020 apparatus. The degree of crystallinity (X) was measured on powder samples by wide angle X-ray diffraction of Mac Science Co. type MXP 18V using Cu- K_α radiation. The scattering intensity was registered at 2° min⁻¹ for values of 2θ ranging from 5° to 70°. Small angle X-ray diffraction data were obtained by a Rigaku RINT-2500. Phase transition temperature was determined by DSC using a Rigaku Thermoflex apparatus DSC-8230B. Sample quantity was 10 mg with 10°C min⁻¹ of heating and cooling rate. Pyrolysis was carried out with a Rigaku TG-DSC instrument standard type CN8076E1. Polarized optical microscopy (POM) of thin samples, which sandwiched between two glass slides (spacing: 12 μ m), was performed using an Olympus microscope BH-2 with a heating stage attached to a temperature controller.

RESULTS AND DISCUSSION

Synthesis and Properties of Parent Polyamides 1, 2

Recently, a direct polycondensation reaction using TPP and LiCl was found to be a useful method for the preparation of aromatic polyamides by combination of diamines and dicarboxylic diacids.^{18–20} We applied the phosphorylation polyamidation to the preparation of polyamide 1 using TPP–LiCl–Py system. Diamines used were 1,3-phenylenediamine, 1,4-phenylenediamine, 4-aminodiphenyl ether, 4,4'-diaminodiphenyl sulfide, and 4-aminodiphenyl sulfone. Since PBA is known as fibers with high strength, high modulus, and heat resistance, we also prepared polyamide 2 with the molar ratio 1 : 1 : 5 for SA : diamine : ABA in feed using TPP–LiCl–Py system in providing a rigidity to polyamide 1. The results of polycondensation are summarized in Tables I and II. The polycondensation proceeded heterogeneously in NMP to give polyamides 1 and 2 with 0.10–0.54 dl g⁻¹ and 0.38–0.76 dl g⁻¹ of $[\eta]$, respectively. It was found that

Table I. Yields, intrinsic viscosities $[\eta]$, crystallinities (X), and elemental analysis of polyamide **1**^a



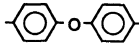
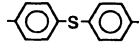
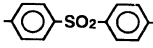
Polyamide 1	Ar in diamine	Yield %	$[\eta]^b$ dl g ⁻¹	X^c %	Formula	Elemental analysis			
						C	H	N	
						%	%	%	
1a		78.1	0.17	6.5	(C ₁₀ H ₁₀ N ₂ O ₂) _n	Calcd Found	63.15 61.50	5.30 5.31	14.73 13.54
1b		88.9	0.25	23.6	(C ₁₀ H ₁₀ N ₂ O ₂) _n	Calcd Found	63.15 60.75	5.30 5.35	14.73 13.61
1c		89.9	0.54	12.2	(C ₁₆ H ₁₄ N ₂ O ₃) _n	Calcd Found	68.08 66.81	5.00 5.03	9.92 9.37
1d		93.5	0.53	8.2	(C ₁₆ H ₁₄ N ₂ O ₂ S) _n	Calcd Found	64.41 63.35	4.73 4.85	9.39 8.89
1e		69.6	0.10	2.1	(C ₁₆ H ₁₄ N ₂ O ₄ S) _n	Calcd Found	58.17 56.22	4.27 4.38	8.48 7.78

^a SA, 10.0 mmol; H₂N-Ar-NH₂, 10.0 mmol; TPP, 25 mmol; LiCl, 12.6 mmol; Py, 6 ml; NMP, 24 ml, 100°C, 6 h, under N₂.

^b Measured at a concentration of 1.0 g dl⁻¹ in H₂SO₄ at 30°C.

^c Crystallinity determined by X-ray diffraction analysis.

Table II. Yields, intrinsic viscosities $[\eta]$, crystallinities (X), and elemental analysis of polyamide **2**^a

Polyamide 1	Ar in diamine	Yield %	$[\eta]^b$ dl g ⁻¹	X^c %	Formula	Elemental analysis			
						C	H	N	
						%	%	%	
2a		92.1	0.76	5.7	(C ₄₅ H ₃₅ N ₇ O ₇) _n	Calcd Found	68.78 67.97	4.49 4.65	12.48 11.71
2b		95.6	0.76	10.6	(C ₄₅ H ₃₅ N ₇ O ₇) _n	Calcd Found	68.78 67.92	4.49 4.70	12.48 11.64
2c		97.4	0.74	5.1	(C ₅₁ H ₃₉ N ₇ O ₈) _n	Calcd Found	69.77 69.70	4.48 4.69	11.17 10.58
2d		96.3	0.66	4.2	(C ₅₁ H ₃₉ N ₇ O ₇ S) _n	Calcd Found	68.52 68.03	4.40 4.56	10.97 10.39
2e		99.4	0.38	3.6	(C ₅₁ H ₃₉ N ₇ O ₉ S) _n	Calcd Found	66.15 65.97	4.25 4.47	10.59 10.05

^a SA, 3.0 mmol; H₂N-Ar-NH₂, 3.0 mmol; ABA, 15 mmol; LiCl, 12.6 mmol; TPP, 26 mmol; Py, 6 ml; NMP, 20 ml, 100°C, 6 h, under N₂.

^b Measured at a concentration of 1.0 g dl⁻¹ in H₂SO₄ at 30°C.

^c Crystallinity determined by X-ray diffraction analysis.

the addition of ABA resulted in an increase in yield and $[\eta]$ of polyamide, because ABA is a high reactive for the polycondensation. The structure of polyamides **1** and **2** shown in Figure 1 was identified by IR spectroscopy and elemental analysis. The characteristic absorptions of N–H stretch at around 3340 cm^{-1} and C=O stretch at around 1660 cm^{-1} of amide linkage support the formation of polyamide in all cases. The IR spectra of these polyamides coincide with those of corresponding to the polyamides obtained separately by polycondensation of succinic acid dichloride and diamines. This means that little phosphorus compound derived from catalyst system is contained in polyamides obtained here. It is well known that the hydrogen bonded N–H bond broadens, shifts to higher frequency, and decreases in intensity as the temperature is raised because the strength of the hydrogen bonds decreases.²¹ Figure 2 shows the decrease in intensity at around 3500 cm^{-1} in FT-IR spectra of polyamide **2a** as a function of temperature in the range of 50 to 175°C , including the N–H stretch relative intensity is characteristic of hydrogen bond formation.²² It was, therefore, found that polyamide **2a** exhibits thermal behavior analogous to flexible chain polyamides.²¹ From the elemental analyses of polyamides, the C-contents and the N-contents were found to be lower than the calculated ones for the proposed structure and

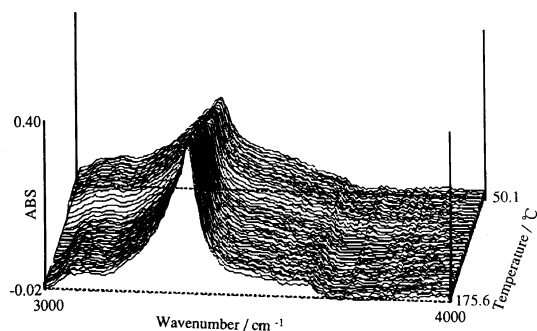


Figure 2. Infrared spectra of polyamide **2a** in the range $3000\text{--}4000\text{ cm}^{-1}$ recorded as a function of increasing temperature from 50.1 to 175.6°C .

the H-contents were higher than the calculated ones. This may be attributed to the hydrophilic nature of the amide group.²⁰ It was observed that the degree of crystallinity (X) of polyamides **2** was smaller than that of polyamides **1** except for polyamide **2e**. This means that the introduction of PBA segments into polyamide **1** prevents the molecules from orienting because of its rigidity.

Preparation of Polyamide **3c**

The dicarboxyl-terminated liquid crystalline macromonomer, MacMHB, was obtained by radical polymerization of MHB initiated by AIBN in the presence of TMA as a chain transfer agent. According to DSC (Figure 3) and POM (Figure 4), the mesophase of MacMHB showed a monotropic liquid crystalline mesophase with a focal conic texture. The small angle X-ray diffraction of MacMHB was taken at room temperature in the solid phase as shown in Figure 5. MacMHB shows the

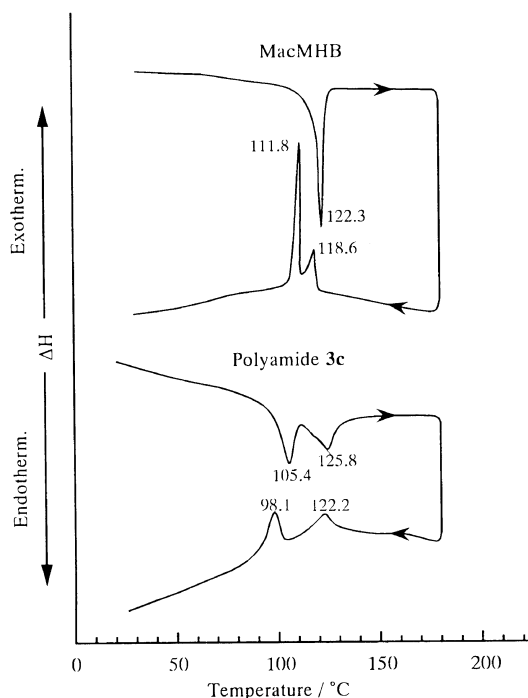


Figure 3. DSC thermograms of MacMHB and polyamide **3c**.

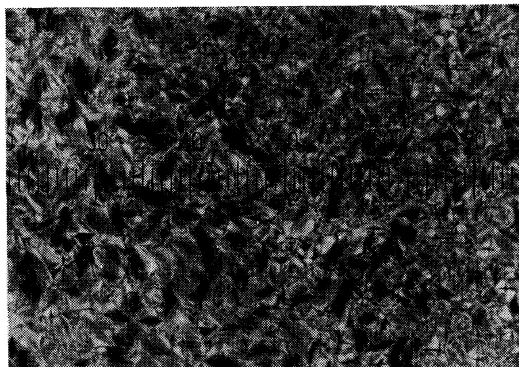


Figure 4. POM photograph of MacMHB at 119.0°C on cooling cycle, $\times 150$.

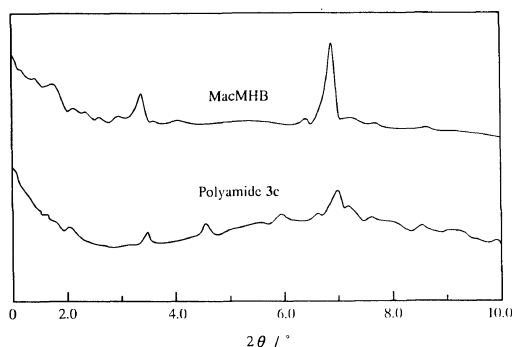


Figure 5. Small-angle X-ray diffraction patterns for MacMHB and polyamide 3c.

peak at $2\theta = 3.42^\circ$ corresponding to an interplanar spacing of $d = 25.81 \text{ \AA}$. This is assigned to the layer spacing in a smectic mesophase with phase transition as K 111.8 S 118.6 I.

We developed the phosphorylation polyamidation to the preparation of polyamide 3c with the molar ratio 1 : 1 : 5 for 4-aminodiphenyl ether : MacMHB : ABA in feed using TPP-LiCl-Py system as shown in Figure 1. The polycondensation proceeded in a homogeneous NMP solution to give polyamide 3c in 84% yield, while the condensation of SA, aromatic diamines, and ABA did heterogeneously to give the parent polyamides as mentioned above. Polyamide 3c was characterized using IR and GPC measurements. The IR spectrum of polyamide 3c is shown in Figure 6, together

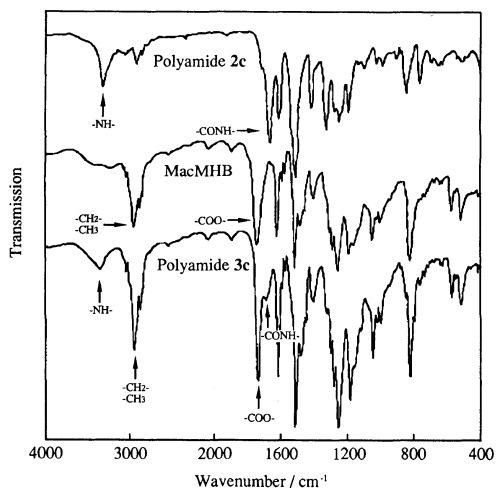


Figure 6. IR spectra of polyamide 2c, MacMHB, and polyamide 3c.

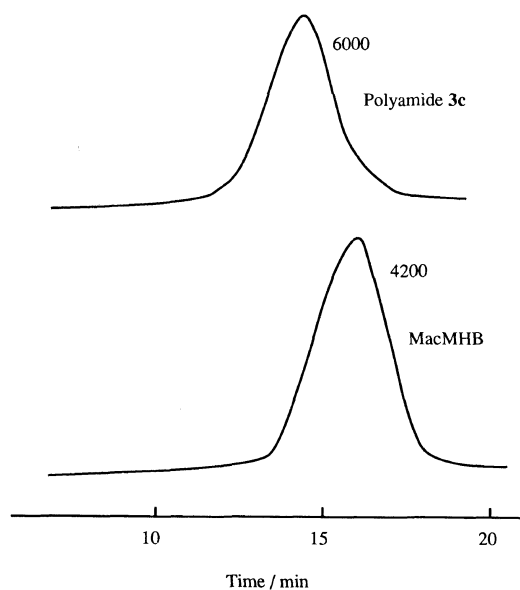


Figure 7. GPC chromatograms of polyamide 3c and MacMHB.

with those for polyamide 2c and MacMHB for comparison. The presence of the amide and ester groups in polyamide 3c was revealed by specific absorption of N-H stretch in $3330\text{--}3350 \text{ cm}^{-1}$, C=O stretch of ester in $1720\text{--}1730 \text{ cm}^{-1}$, and C=O stretch of amide linkage in $1650\text{--}1660 \text{ cm}^{-1}$. Polyamide 3c, therefore,

exhibits the sum of absorption of the polyamide segment and grafting MacMHB parts. The molecular weight of polyamide **3c** was measured by GPC with polystyrene standard, as shown in Figure 7. The chromatogram indicated 6000 of molecular weight M_n with $M_w/M_n=1.47$ for polyamide **3c**, which should not be the starting MacMHB (M_n : 4200). The results also support the composition of polyamides **3c** shown in Figure 1. The degree of crystallinity of polyamide **3c** ($X=7.8\%$) was found to be larger than that of its parent polyamide **2c** ($X=5.1\%$). In addition, the small angle X-ray diffraction of polyamide **3c** (Figure 5) shows the peak at $2\theta=3.51^\circ$ corresponding to an interplanar spacing of $d=25.15 \text{ \AA}$. This means that characteristic of MacMHB retains even in graft copolymer.

Thermal Properties of Polyamides 1 and 2

All of polyamides **1** and **2** exhibit no melting

process. Figures 8 and 9 depict the TG curves of polyamides **1** and **2** at a heating rate of $10^\circ\text{C min}^{-1}$ in air. For instance, polyamide **1a** began the thermal degradation at 272°C and maximum degradation occurs at 537°C , while polyamide **2a** having rigid rod-like segments showed reasonably higher degradation temperature at 401°C and 601°C for initial and maximum degradation temperature, respectively. Polyamides **1** and **2** seem to decompose through a two-step and a one-step mechanism, respectively. Such difference in the thermal stability may be attributed to the molecular weight and the structural effects. It is possibly speculated that polyamide **2** has higher molecular weight with narrower molecular weight distribution than polyamide **1**. The results are summarized in Table III. Comparing polyamide **1a** with polyamide **1b**, the former shows a rather low initial decomposition temperature. This is believed to be due to both

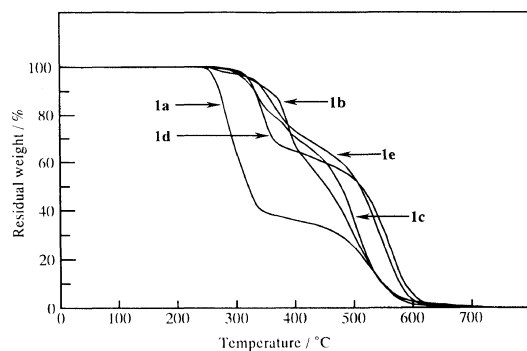


Figure 8. TG curves of polyamides **1a**–**1e**.

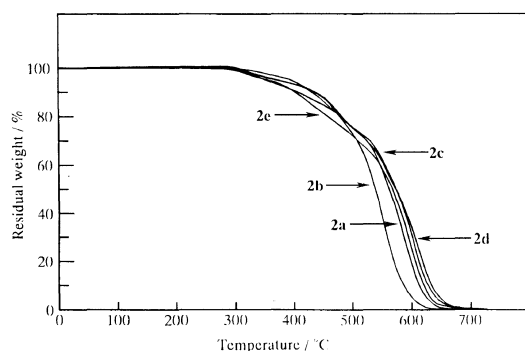


Figure 9. TG curves of polyamides **2a**–**2e**.

Table III. Thermal properties of polyamides **1, 2**

Polyamide 1,2	Ar in diamine	Decomposition temperature/ $^\circ\text{C}$	
		Initial	Maximum
1a		272	537
1b		345	500
1c		318	517
1d		325	577
1e		330	555
2a		401	601
2b		407	557
2c		417	616
2d		356	623
2e		369	610

lower intrinsic viscosity **1a** than that of **1b** in addition to the structural effect. As a conclusion, polyamides **1** and **2** decompose thermally through a random fission of the polymer backbone before their melting occurs. The introduction of PBA as hard segments results in an increase in thermal stability of polyamide.



Figure 10. POM photograph of polyamide **3c** at 121.5°C on cooling cycle, $\times 150$.

Thermal Properties of Polyamide **3c**

Thermal properties of polyamide **3c** was also studied by DSC between 20 and 200°C as shown in Figure 3. The melting process of polyamide **3c** indicated by two endothermic peaks at 105.4°C (melting point) and 125.8°C (isotropization transition) is followed by decomposition begun at 332°C. POM of polyamide **3c** reveals a birefringence as shown in Figure 10. Taking into account the result of X-ray diffraction for polyamide **3c** (Figure 5), the mesophase was identified as a smectic phase

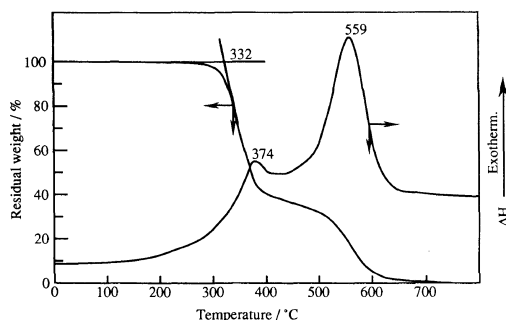


Figure 11. TG-DTA curves of polyamide **3c**.

Table IV. Characteristic of polyamide **3**

	Mol. weight		X %	Phase transition temperature		Decomposition	
	M_n	M_w		$T_m/^\circ\text{C}$	$T_i/^\circ\text{C}$	$T_{int}/^\circ\text{C}$	$T_{max}/^\circ\text{C}$
MacMHB	4200	5600	27.3	112.0	118.6	—	—
Polyamide 3c	6000	8800	7.8	98.1	122.2	332	559
Polyamide 4c ^a	7900	10000	3.9	88.8	133.9	319	554

^a Reference 16.

Table V. Solubility of polyamides **1** and **2**^a

Solvent	1a	1b	1c	1d	1e	2a	2b	2c	2d	2e
NMP	○	×	×	○	○	×	×	×	×	△
HMPA	△	○	○	○	×	×	×	×	×	×
DMSO	○	×	×	×	○	×	×	×	×	△
DMAc	○	×	×	×	○	×	×	×	×	×
DMAc/LiCl 10% w/v	○	△	○	○	○	△	○	△	△	○
H ₂ SO ₄	○	○	○	○	○	○	○	○	○	○

^a Approximately 5% (w/v) of concentration: ○, soluble at room temperature; △, soluble at 60°C; ×, insoluble at 60°C.

with $d=25.15\text{ \AA}$. It is considered that polyamide **3c** form the microphase-separated biphasic structure because a rigid polyamide main-chain still remains in smectic phase. The thermal stability of polyamide **3c** was studied by TG-DTA measurements in air as shown in Figure 11. Polyamide **3c** degrades via a two-step mechanism including the decomposition of the oligomeric side chains at temperature near 370°C and polyamide backbones at 559°C . Characteristic of polyamide **3c** was listed in Table IV.

Solubility Test

From the solubility test of polyamides **1** and **2**, neither solubility nor swelling was observed in common organic solvents other than 10% w/v of *N,N*-dimethylacetamide (DMAc)/LiCl and sulfuric acid without any lyotropic behavior³ as shown in Table V. Polyamide **3c** having smectic oligomers in the side chain, however, is soluble in a variety of solvents such as NMP, hexamethylphosphoramide (HMPA), methyl sulfoxide (DMSO), DMAc, and even in THF and dichloromethane.¹⁶

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