NOTES

Polyamide-Smectic Oligomer Graft Copolymers as Compatibilizers for Polymer Alloys

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Interest has been devoted to preparing graft and block copolymers for stabilizing the interphase of polymer blends because different polymers are generally non-compatible. Some graft and block copolymers containing the liquid crystalline segments have been synthesized so far.^{1–7} In the previous paper,⁸ the authors reported on the smectic oligomer graft copolyamide, PA-3B, obtained using a macromonomer technique (Figure 1). The introduction of smectic oligomer (MacMHB) with a definite molecular weight ($M_n=4200$) into a parent polyamide PA-2 results in improved solubility in common organic solvents. The present paper describes a series of graft copolyamides (PA-3A–D) having MacMHB of different molecular weights ($M_n=2300$ –4600) to obtain basic information on compatibilizers for polymer blends of *m*-aramid and succinic acid polyester containing the biphenyl moiety, SAPE.

EXPERIMENTAL

Synthesis of Macromonomer, MacMHB-A–D

A series of MacMHB with different molecular weights was synthesized by radical polymerization of 4-(6-methacryloyloxyhexyl-

oxy)-4'-methoxybiphenyl [MHB: K 63.1 S_A 76.2 I] initiated with 2,2'-azobisisobutyronitrile (AIBN) in the presence of thiomalic acid (TMA) in tetrahydrofuran at 60°C, by changing the molar ratio of MHB:TMA:AIBN. MacMHB was purified by reprecipitation from a tetrahydrofuran–petroleum ether solvent system and characterized by the method in the previous paper.⁸

Synthesis of Graft Copolyamides, PA-3A–D

PA-3A–D was synthesized by phosphorylation polyamidation of 4-aminodiphenyl ether (ADPE) and MacMHB in the presence of 4-aminobenzoic acid (ABA) with the molar ratio of 1:1:5 for ADPE:MacMHB:ABA according to the procedure described previously.⁸

Synthesis of Liquid Crystalline Succinic Acid Polyester, SAPE

4,4'-Bis(6-hydroxyhexyloxy)biphenol [K 97.5 S 175.7 I] was polycondensated with succinic acid in the presence of a catalytic amount of *p*-toluenesulfonic acid in 1,2-dichloroethane using a Soxhlet extractor. Liquid crystalline succinic acid polyester, SAPE, shows phase transition temperature of K 123.3 S 131.0 I

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Figure 1. Structures of various polymers.

and has an intrinsic viscosity $[\eta] = 0.50 \text{ dl g}^{-1}$ (1.0 g dl^{-1} in *N*-methyl-2-pyrrolidone).⁹

Preparation of Films

20 ml of *N*-methyl-2-pyrrolidone solution containing a known amount of *m*-aramid (supplied by Tsukuba Research Laboratory, Nippon Oil & Fat Co., Ltd.), SAPE, and PA-3 were cast on a mercury bath with 6.0 cm diameter. The solvent was evaporated by irradiation with an infrared lamp and ternary blends (alloy II) of films were obtained. Binary blends (alloy I) of *m*-aramid and SAPE were also prepared. The films were completely dried *in vacuo* at 80°C for 5 h. The films were annealed at 130°C at 100 kgf cm^{-2} pressure for 1 h with a Tester test press apparatus, followed by cutting into rectangular strips 2 mm wide, 20 mm long and 0.06–0.08 mm thick.

Measurements

Tensile testing was performed with a Seiko

TMA/SS 120c using a thin polymer blend film of rectangular strip. The elongation rate was kept at 0.1 mm min^{-1} at ambient temperature.

RESULTS AND DISCUSSION

Preparation and Characterization of MacMHB-A-D

Four kinds of dicarboxyl-terminated macromonomers (MacMHB-A–D) with different molecular weights from $M_n = 4600$ to $M_n = 2300$ were prepared by the radical polymerization of MHB initiated with AIBN in the presence of TMA as a chain transfer agent in tetrahydrofuran at 60°C, by changing the ratio of MHB:TMA:AIBN from 1:0.10:0.01 to 1:0.60:0.01. MacMHB-A–D exhibited a monotropic liquid crystalline mesophase with a focal conic texture. The isotropization temperature (T_i) of MacMHB-A–D decreased gradually from 123°C to 114°C with

Table I. Preparation and characterization of MacMHB with various molecular weights

MacMHB	MBH	:	TMA	:	AIBN	Mol. wt.			Phase transition temperature ^a		2θ	d
						Titration, M_n	GPC		T_m	T_i		
							M_n	M_w/M_n				
											degree	Å
A	1	:	0.10	:	0.01	4900	4600	1.41	115	123	3.44	25.7
B ^b	1	:	0.15	:	0.01	4350	4200	1.33	112	119	3.42	25.8
C	1	:	0.30	:	0.01	3000	2900	1.24	113	117	3.42	25.8
D	1	:	0.60	:	0.01	2300	2300	1.17	105	114	3.37	26.2

^a T_m and T_i represent temperatures of melting process, and isotropic melt, respectively. ^b Data in ref 8.

decreasing M_n . MacMHB-A—D showed a small angle X-ray diffraction (SAX) peak at around $2\theta = 3.4^\circ$ corresponding to an interplanar spacing of $d = 26 \text{ \AA}$, which was assigned to the layer spacing in a smectic mesophase. Characteristics of a series of MacMHB-A—D are summarized in Table I, along with data for MacMHB-B from previous paper.⁸

Preparation and Characterization of Graft Copolyamides, PA-3A—D

Phosphorylation polyamidation^{10–12} was conducted for the synthesis of PA-3A—D with the molar ratio of 1:1:5 for ADPE: MacMHB-A—D:ABA in feed. The results of polycondensation are summarized in Table II, along with data for PA-3B described previously.⁸ IR spectra of PA-3A—D showed specific absorptions of N—H stretch in $3330\text{--}3350 \text{ cm}^{-1}$ and C=O stretch of amide linkage in $1650\text{--}1660 \text{ cm}^{-1}$ as well as C=O stretch of ester in $1720\text{--}1730 \text{ cm}^{-1}$. PA-3A—D is thus the sum of absorption of the polyamide segment and grafting MacMHB parts. From GPC measurement, the chromatogram of PA-3B, for instance, indicated a unimodal peak of $M_n = 6000$, which did not show the starting MacMHB-B ($M_n = 4200$) as described previously.⁸ It was also found that PA-3A was thermally degraded through a two step mechanism whereas PA-3A decomposed randomly as mentioned below. These results demonstrate the formation of graft copoly-

mer made up of polyamide backbone and grafting MacMHB parts.

From elemental analysis, the molar ratio of poly(*p*-benzamide)(PBA) segment in PA-3 increased from $q = 0.91$ to $q = 0.98$ with decreasing M_n of the starting MacMHB. The $[\eta]$ of PA-3 increased with the content of PBA segment.

The degree of crystallinity (X) decreased with increasing content of PBA segment, because a rod-like character of PBA segment prevented the MacMHB molecules in PA-3 from smectic orienting.

PA-3A and PA-3B showed a SAX peak at $2\theta = 3.43^\circ$ corresponding to an interplanar spacing of $d = 25.7 \text{ \AA}$. This indicates that the smectic phase of the grafted MacMHB remains even in PA-3A and PA-3B.

PA-3A and PA-3B with $q \leq 0.94$ were soluble in various solvents such as *N*-methyl-2-pyrrolidone, hexamethylphosphoramide, methyl sulfoxide, and even in tetrahydrofuran, while neither solubility nor swelling was observed in common organic solvents other than sulfuric acid for PA-3C and PA-3D with $q \geq 0.97$.

Thermal Properties

PA-3A as well as PA-3B⁸ showed a mesophase, whereas no other graft copolyamides exhibited a melting process. In the case of PA-3A, the melting process indicated by two endothermic peaks at 120°C (melting point)

Figure 2. TG curves of PA-1 (a), PA-2 (b), and PA-3A (c).

and 128°C (T_i) is followed by decomposition beginning at 339°C. It is considered that PA-3A and PA-3B form the microphase-separated biphasic structure. The thermal stability of PA-3A as a typical instance was studied by TG-DTA measurements in air as shown in Figure 2, together with that of PA-1 and PA-2. PA-1 and PA-2 seem to decompose through random fission of the polyamide backbone, whereas PA-3A degrades *via* a two-step mechanism including the decomposition of the grafting MacMHB parts and polyamide backbone. The thermal properties of PA-3 are summarized in Table II.

Compatibilizing Ability

Prior to testing the compatibilizing ability of PA-3, the mechanical properties of the binary blends (alloy I) of *m*-aramid and SAPE were examined. Tensile strength (σ), tensile modulus (E), and ultimate elongation (ϵ) *versus* weight ratio of two components for alloy I are shown in Figures 3, 4, and 5 (dotted line), respectively. Tensile strength and ultimate elongation of *m*-aramid fall by blending with SAPE, while the tensile modulus of alloy I with the weight ratio of *m*-aramid:SAPE=80:20 raises slightly more than that of *m*-aramid itself. Hence, ternary blends (alloy II) were prepared by adding 10 wt% of PA-3A—D as compatibilizer to alloy I with the weight ratio of *m*-aramid:SAPE=80:20. The stress-strain

Table II. Preparation and characterization of PA-3^a

PA-3	MacMHB	ADPE	ABA	TPP	Yield	Elemental analysis				$[\eta]^c$	$p : q^b$	T_m^e	T_i^e	T_{dec}^f
						C	H	N						
A	A : 0.15	0.15	0.75	1.34	75.1	73.36	7.50	0.86	0.09 : 0.91	0.09	0.09	110	124	339
B	B : 0.24	0.24	1.20	2.04	77.5	72.96	7.26	1.12	0.06 : 0.94	0.12	0.12	106	120	344
C	C : 0.32	0.32	1.60	2.78	84.2	71.85	6.89	2.72	0.03 : 0.97	0.19	0.19	—	—	328
D	D : 0.42	0.42	2.10	3.45	83.4	71.17	6.59	3.36	0.02 : 0.98	0.25	0.25	—	—	327

^a LiCl: 12.6 mmol, Py: 6 ml, NMP: 24 ml, 100°C, 8 h, under N₂. ^b Calculated based on C content obtained by elemental analysis. ^c Measured at a concentration of 0.5 g dl⁻¹ in *N*-methyl-2-pyrrolidone at 30°C. From GPC molecular weights of PA-3A and PA-3B were $M_w/M_n=1.49$ and $M_w/M_n=6000$ with $M_w/M_n=1.40$, respectively. ^d Crystallinity determined by wide angle X-ray diffraction. ^e T_m and T_i represent melting and clearing points, respectively. ^f Temperature corresponding to 5% weight loss.

Figure 3. Tensile strength σ vs. SAPE content in alloy I (dotted line, SAPE/*m*-aramid) and alloy II (solid line, alloy I/PA-3B).

Figure 5. Ultimate elongation ϵ vs. SAPE content in alloy I (dotted line, SAPE/*m*-aramid) and alloy II (solid line, alloy I/PA-3B).

Figure 4. Tensile modulus E vs. SAPE content in alloy I (dotted line, SAPE/*m*-aramid) and alloy II (solid line, alloy I/PA-3B).

Figure 6. Stress-strain curves for a series of alloy II [alloy I (*m*-aramid : SAPE = 80 : 20) : PA-3 = 90 : 10], alloy I/PA-3A (a), alloy I/PA-3B (b), alloy I/PA-3C (c), and alloy I/PA-3D (d).

curves of a series of alloy II are shown in Figure 6. To see clearly the effects of M_n of MacMHB in PA-3 on the mechanical properties of alloy II, tensile strength and ultimate elongation versus M_n of MacMHB used for PA-3 are shown in Figure 7. PA-3B prepared from MacMHB with $M_n = 4200$ yielded the highest tensile strength and largest ultimate elongation of alloy II. This means that when *m*-aramid and SAPE are compatibilized by adding PA-3 as the third component, an appropriate mole-

cular weight of smectic MacMHB is needed because polyamide backbone and MacMHB part in PA-3 are expected to interact intermolecularly with *m*-aramid and SAPE, respectively. A series of alloy II was thus prepared by adding 10 wt% PA-3B to alloy I with different weight ratios of *m*-aramid and SAPE. Figures 3, 4, and 5 (solid line) show tensile strength, tensile modulus, and ultimate elongation versus the weight ratio of *m*-aramid and SAPE in alloy II. The mechanical properties

Figure 7. Effects of M_n of MacMHB in PA-3 on tensile strength σ and ultimate elongation ϵ of alloy II [alloy I (m -aramid : SAPE = 80 : 20) : PA-3A—D = 90 : 10].

of alloy I were enhanced by the addition of PA-3 as a compatibilizer. It is noteworthy that tensile strength and tensile modulus of alloy II with the weight ratio of alloy I (m -aramid : SAPE = 80 : 20) : PA-3B = 90 : 10 were higher than that of m -aramid.

The films of alloy I were turbid, whereas alloy II gave slightly transparent films. It is presumed that intermolecular hydrogen bonding interactions between m -aramid and poly-

amide backbone of PA-3 as well as that between the mesogenic groups of SAPE and grafted MacMHB parts of PA-3 play important roles in the enhancement of the mechanical properties of alloy II.

REFERENCES AND NOTES

1. C. Pugh and V. Perec, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **27**, 366 (1986).
2. Y. Chujo, H. Kobayashi, and Y. Yamashita, *Polym. J.*, **20**, 407 (1988).
3. A. Gottschalk and H.-W. Schmit, *Liq. Cryst.*, **5**, 1619 (1989).
4. M. Sato, T. Kobayashi, F. Komatsu, and N. Takeno, *Makromol. Chem., Rapid Commun.*, **12**, 269 (1991).
5. T. Heitz and O. W. Webster, *Makromol. Chem.*, **192**, 2463 (1991).
6. M. Hefft and J. Springer, *Makromol. Chem.*, **193**, 329 (1992).
7. K. Sugiyama, T. Oda, and Y. Yoshimitsu, *Polym. J.*, **25**, 769 (1993).
8. Y. Yoshimitsu, K. Sugiyama, S. Shiraishi, T. Oda, and T. Ohashi, *Polym. J.*, **26**, 551 (1994).
9. Preparation and characteristics of SAPE will be described in detail elsewhere.
10. F. Higashi, M. Goto, and H. Kakinoki, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1711 (1980).
11. C.-P. Yang, J.-M. Cheng, and S.-H. Hinta, *Makromol. Chem.*, **193**, 445 (1992).
12. C.-P. Yang and W.-T. Chen, *Makromol. Chem.*, **193**, 2323 (1992).