

# Structure–Property Relationship in Polybutadiene–Polyamide Multiblock Copolymers

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## Synopsis

Two kinds of aromatic–aliphatic polyamide oligomers were newly prepared by the reactant pairs of 3,4'-oxydianiline–adipic acid and 3,4'-oxydianiline–azelaic acid. These oligomers were then condensed separately with  $\alpha$ ,  $\omega$ -polybutadienedicarboxylic acid giving two series of polybutadiene–polyamide multiblock copolymers. Properties of four series of polybutadiene–polyamide multiblock copolymers, whose polyamide blocks consisted of not only newly prepared polyamides but also previously synthesized aromatic polyamides derived from 4,4'-oxydianiline–isophthalic acid and 3,4'-oxydianiline–isophthalic acid, were investigated on the view point of structure-property relationship. A larger extent of the  $T_g$  depression of polybutadiene phase, and higher tensile strength and modulus were observed in the block copolymers having aromatic polyamides compared with those having aliphatic ones.

## INTRODUCTION

During the course of our investigation on the synthesis of polybutadiene–aromatic polyamide multiblock copolymers,<sup>1,2</sup> a novel and efficient methodology to prepare structurally well-regulated multiblock copolymers was established through direct polycondensation using triphenyl phosphite and pyridine as the condensing agent. These block copolymers thus prepared were cast into ductile and elastomeric films, whose properties are affected by the pseudocrosslinked structure between the aromatic polyamide blocks.

Our research interest was then directed to the relationships between structure and properties of polybutadiene–polyamide multiblock copolymers. In this article, properties such as solubility behavior and thermal and mechanical properties of polybutadiene–polyamide multiblock copolymers, where aliphatic polyamides as well as aromatic ones are incorporated into the multiblock copolymers, are discussed in detail.

## EXPERIMENTAL

### Materials

$\alpha$ , $\omega$ -Polybutadienedicarboxylic acid (LPB–diacid) was obtained from Goodrich Co. as “Hycar CTB.” The number average molecular weight was determined to be 5200 by titration. Its micro-structure was *cis*-1,4- 22.1%; *trans*-1,4-, 53.4%; and 1,2-vinyl, 24.5%.

Adipic acid, azelaic acid, and isophthalic acid were purified by recrystallization from water, aqueous ethanol, and water, respectively. 3,4'-Oxydianiline (3,4'-ODA), obtained from Teijin Ltd., Japan, and 4,4'-oxydianiline (4,4'-ODA) were recrystallized from dichloromethane-hexane and tetrahydrofuran (THF), respectively. Triphenyl phosphite, pyridine, *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylacetamide (DMAc) were purified by distillation. Other inorganic reagents were used as received.

### Synthesis of Multiblock Copolymers

**Block Copolymer VIII.** A mixture of 1.50 g (7.50 mmol) of 3,4'-ODA, 1.02 g (7.00 mmol) of adipic acid, 4.67 g (15 mmol) of triphenyl phosphite, and 2.06 g (15 mmol) of triethylamine hydrochloride in 3.0 mL of pyridine and 20 mL of NMP was heated with stirring at 100°C for 1.5 h under nitrogen. To the reaction solution, 2.60 g (0.5 mmol) of LPB-diacid in 12.5 mL of pyridine was added, and the mixture was stirred at 100°C for another 3 h. The polymer was isolated by pouring the reaction mixture into 1000 mL of methanol. The product was purified by reprecipitation from DMAc-methanol system, followed by successive washings with methanol and hexane. The yield of the polymer was 3.95 g (81%), and the inherent viscosity in DMAc was 0.52 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The IR spectrum (film) exhibited absorptions at 3300 cm<sup>-1</sup> (N—H), 2980 cm<sup>-1</sup> (C—H), 1660 cm<sup>-1</sup> (C=O), and 965 and 910 cm<sup>-1</sup> (C=C).

ANAL. Calcd for (C<sub>689</sub>H<sub>787</sub>N<sub>32</sub>O<sub>47</sub>)<sub>n</sub>: C, 79.72%; H, 8.56%; N, 4.32%. Found: C, 79.41%; H, 8.81%; N, 4.75%.

Multiblock copolymers of the VII and VIII series as well as those of the V and VI series were prepared by analogous procedures.

### Measurements

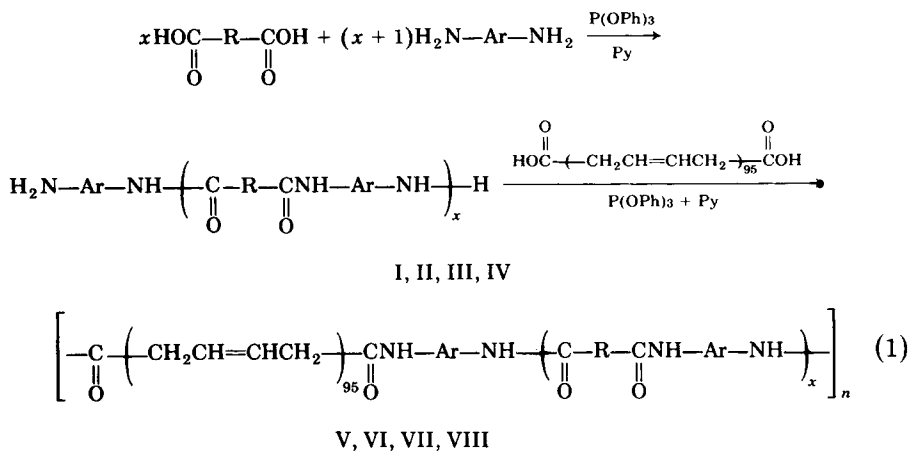
Infrared (IR) spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential scanning calorimetry (DSC) was performed with a Daini Seikosha SSC-560 differential scanning calorimeter. Transmission electron microscopy was observed with a Hitachi HLT-12 electron microscope. Tensile properties were determined from stress-strain curves obtained with a Toyo Baldwin Tensilon UTM-III at an elongation rate of 33%/min. Measurements were performed at room temperature with film specimens (1.0 cm wide, 3.0 cm long, and about 0.1 mm thick) and the average of at least five individual determinations was taken.

## RESULTS AND DISCUSSION

### Synthesis of Polybutadiene-Polyamide Multiblock Copolymers

Polybutadiene-polyamide multiblock copolymers having aromatic-aliphatic polyamide blocks were newly synthesized according to eq. (1) by the one-pot two-step method reported previously.<sup>1,2</sup> Thus, in the first step, amine-terminated polyamide oligomers III and IV were prepared from calculated

excess of 3,4'-ODA and adipic and azelaic acid, respectively, in the presence of triphenyl phosphite and pyridine in NMP. After that, LPB-diacid was added to the stirred solutions and reacted under similar conditions for the polyamide oligomer preparation, affording polybutadiene-polyamide multiblock copolymers VII and VIII. LPB-diacid used had a number average molecular weight of 5200 determined by end group analysis, and the average degree of polymerization was 95.





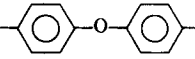
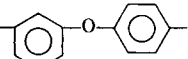
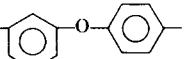
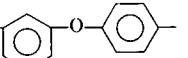
	I, V	II, VI	III, VII	IV, VIII
R			$-(\text{CH}_2)_4-$	$-(\text{CH}_2)_7-$
Ar				

Table I shows the results of the synthesis of multiblock copolymers VII and VIII as well as block copolymers V and VI having aromatic polyamide blocks derived from the reactant pairs of 4,4'-ODA-isophthalic acid and 3,4'-ODA-isophthalic acid, respectively.<sup>1,2</sup> Molecular weights of the polyamide blocks were varied from 1000 to 9000, which means that the content of polybutadiene block was from about 80 to 30% in the multiblock copolymers. The present one-pot two-step method could be applicable to prepare multiblock copolymers VII and VIII, having inherent viscosities of 0.2–0.7 dL/g from aliphatic polyamide oligomers.

The structure of multiblock copolymers obtained were confirmed by IR and elemental analysis. In the IR spectra of the copolymers, characteristic amide absorptions at  $3300 \text{ cm}^{-1}$  (N—H) and  $1660 \text{ cm}^{-1}$  (C=O), and olefinic absorptions at  $956$  and  $910 \text{ cm}^{-1}$  (C=C) were observed. The elemental analysis is in fairly good agreement with the calculated values.

TABLE I  
Synthesis of Polybutadiene-Polyamide Multiblock Copolymers

Polyamide block			Block copolymer			
Code	Diacid/diamine <sup>a</sup> (mol/mol)	$\bar{M}_n$	Code	Polybutadiene content <sup>b</sup> (%)	Yield (%)	$\eta_{inh}^c$ (dL/g)
Ia	3/4	1200	Va	81	86	0.31
Ib	7/8	2500	Vb	68	90	0.39
Ic	12/13	4100	Vc	57	90	0.61
Id	15/16	5100	Vd	50	85	0.60
Ie	26/27	8800	Ve	37	90	0.78
IIa	3/4	1200	VIa	81	93	0.23
IIb	7/8	2500	VIb	68	86	0.32
IIc	12/13	4100	VIc	57	84	0.39
IId	15/16	5100	VIId	50	83	0.40
IIe	26/27	8800	VIe	37	86	0.43
IIIa	3/4	1100	VIIa	82	90	0.23
IIIb	8/9	2700	VIIb	66	83	0.39
IIIc	14/15	4500	VIIc	54	81	0.52
IIIe	27/28	8600	VIIe	38	85	0.71
IVa	2/3	900	VIIIa	85	95	0.19
IVb	5/6	2000	VIIIb	72	90	0.23
IVc	9/10	3400	VIIIc	60	89	0.37
IVd	14/15	5100	VIIIId	50	84	0.48
IVe	25/26	9000	VIIIe	37	81	0.69

<sup>a</sup>Monomers in the feed.

<sup>b</sup>Weight (LPB-diacid)/[weight(LPB-diacid) + weight(polyamide)] in the feed.

<sup>c</sup>Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

### Solubility Behavior of Multiblock Copolymers

The qualitative solubility of multiblock copolymers Vc, VIc, VIIc, and VIIIc, in organic solvents is shown in Table II. Block copolymer V was soluble only in DMAc, which was a good solvent for the corresponding polyamide homopolymer. Despite the fact that the other polyamide homopolymers are also soluble in rather limited solvents, block copolymers VI, VII, and VIII showed a wider range of solubility which slightly varied with changing the

TABLE II  
Solubility of Polybutadiene-Polyamide Multiblock Copolymers<sup>a</sup>

Solvent	LPB- diacid	Polyamide homopolymer				Block copolymer			
		I	II	III	IV	Vc	VIc	VIIc	VIIIc
<i>N,N</i> -Dimethylacetamide	-	+	+	+	+	+	+	+	+
Pyridine	+	-	+	-	-	-	+	+	+
Tetrahydrofuran	+	-	-	-	-	-	+	+	+
Chloroform	+	-	-	-	-	-	-	-	±
Methanol	-	-	-	-	-	-	-	-	-

<sup>a</sup>Solubility: +, soluble; ±, swelling; and -, insoluble.

polybutadiene content in the multiblock copolymers. Thus, the copolymers with higher polybutadiene content were more readily soluble in pyridine and THF. Transparent, ductile, and elastomeric films were obtained by casting mainly from the DMAc solutions.

### Thermal Behavior of Multiblock Copolymers

Thermal behavior of polyamide phase in the multiblock copolymers was determined by differential thermal analysis (DTA). In the case of block

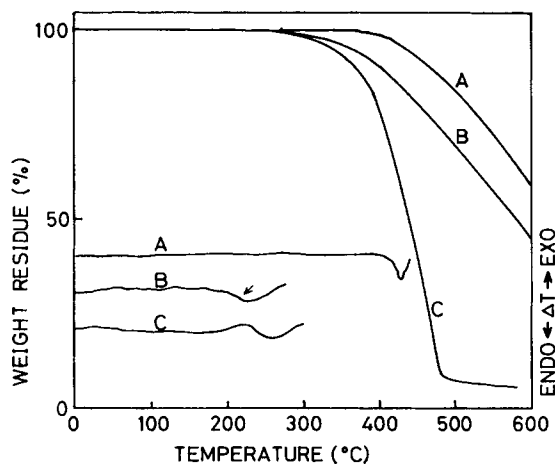


Fig. 1. DTA and TG curves in nitrogen at a heating rate of  $10^{\circ}\text{C}/\text{min}$  for polyamide homopolymer II (A), block copolymer VIc (B), and LPB-diacid (C).

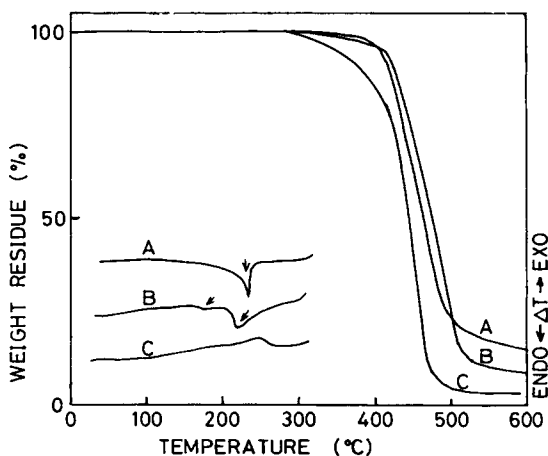


Fig. 2. DTA and TG curves in nitrogen at a heating rate of  $10^{\circ}\text{C}/\text{min}$  for polyamide homopolymer III (A), block copolymer VIIc (B), and LPB-diacid (C).

TABLE III  
Glass Transition Temperatures ( $T_g$ ) and Melting Temperatures ( $T_m$ ) of Polyamide Phase of Polybutadiene-Polyamide Multiblock Copolymers<sup>a</sup>

Block copolymer	Polybutadiene content (%)	$T_g$ (°C)	$T_m$ (°C)
VIa	81	187	—
VIb	68	205	—
VIc	57	207	—
VId	50	211	—
VIe	37	215	—
Polyamide homopolymer II	0	240	—
VIIa	82	149	191
VIIb	66	—	198
VIIc	54	—	200
VIIe	38	153	207
Polyamide homopolymer III	0	160	225

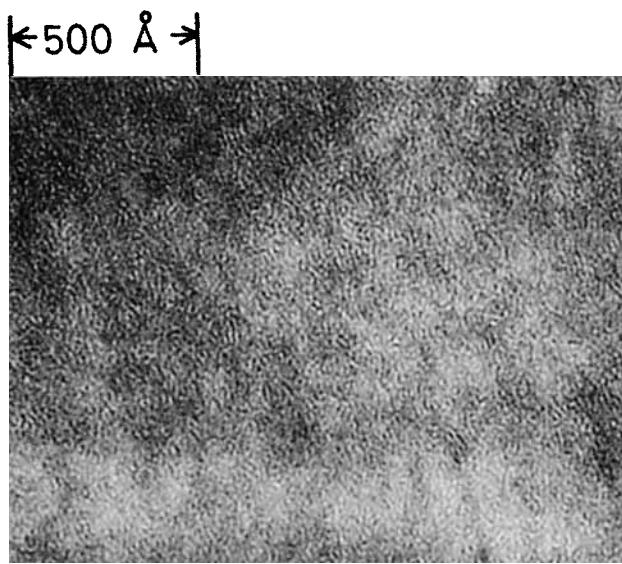
<sup>a</sup> Determined by DTA in air at a heating rate of 10°C/min.

copolymer V, the glass transition temperature ( $T_g$ ) of the polyamide phase was not detected because of the overlapping of exothermic shift due to thermal decomposition of the polybutadiene block,<sup>1</sup> whereas the  $T_g$  of block copolymer VI was observed at around 200°C (Fig. 1). In the case of block copolymer VII, both melting point ( $T_m$ ) and  $T_g$  were recognized (Fig. 2). These  $T_m$  and  $T_g$  values of block copolymers VI and VII, as summarized in Table III, tended to decrease with increasing the polybutadiene content. The hot-press method was effectively applied for the fabrication of films for block copolymers VII and VIII having aromatic-aliphatic polyamide blocks below decomposition temperature of the polybutadiene phase.

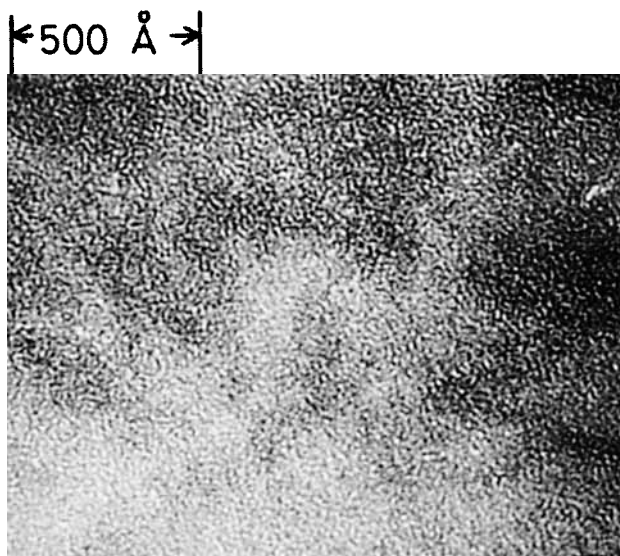
Figure 3 shows transmission electron micrographs of films of block copolymer VIIIId cast from DMAc and fabricated by the hot-press method, which imply that these films have almost the same microphase-separated structures.

Glass transition temperatures of the polybutadiene phase were then evaluated by differential scanning calorimetry (DSC) to investigate the influence of structure of polyamide blocks in the multiblock copolymers. The unusual depression of  $T_g$  values of the polybutadiene phase with increasing polyamide content has already been reported.<sup>1-3</sup>

Similar phenomena were observed again in block copolymers VII and VIII as shown in Table IV and Figure 4. The extent of  $T_g$  depression for these multiblock copolymers tended to be more gradual than that for copolymers V and VI. This is probably due to the less rigid nature of polyamide blocks III and IV compared with aromatic polyamides I and II. In the case of multiblock copolymer VIII, the extent of  $T_g$  depression for the cast films was almost the same as that for the hot-pressed films (Table IV). The fact suggests that these films have almost identical microphase-separated structures with each other as mentioned above.



(A)



(B)

Fig. 3. Transmission electron micrographs ( $50000\times$ ) of films of block copolymer VIIIId stained with osmium tetroxide: (A) cast film and (B) hot-pressed film.

TABLE IV  
Glass Transition Temperatures ( $T_g$ ) of Polybutadiene Phase for Films  
of Polybutadiene-Polyamide Multiblock Copolymers<sup>a</sup>

Block copolymers	Polybutadiene content (%)	$T_g$ (°C)	
		Cast film	Hot-pressed film
Polybutadiene homopolymer <sup>b</sup>	98	-73.5	—
VIIa	82	-75.0	—
VIIb	66	-74.8	—
VIIc	54	-76.0	—
VIIe	38	-78.1	—
VIIIc	60	-75.1	-75.2
VIIIId	50	-77.2	-76.8
VIIIe	37	-78.7	-78.1

<sup>a</sup>Determined by DSC in air at a heating rate of 20°C/min.

<sup>b</sup>Polymer derived from LPB-diacid and *p*-phenylenediamine.

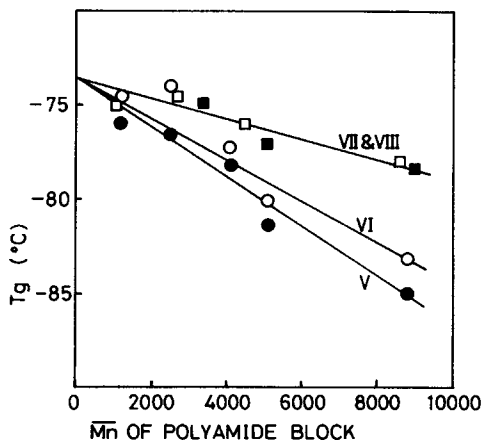


Fig. 4. Glass transition temperatures ( $T_g$ ) of polybutadiene phase as a function of molecular weight ( $\bar{M}_n$ ) of polyamide block for cast films of block copolymers V, VI, VII, and VIII.

### Tensile Properties of Multiblock Copolymers

Stress-strain curves of films of the representative block copolymers having polybutadiene content of 80 and 50% are shown in Figure 5, and tensile properties of films of all block copolymers are summarized in Table V. The films of the block copolymers are ductile and elastomeric, and the tensile strength and initial modulus decreased with increasing the polybutadiene content, whereas the elongation at break increased. The rigid structure of the polyamide block is apparently retained in the multiblock copolymers to produce a strong elastomeric pseudocrosslinked materials. In each case of both high and low polybutadiene content, the tensile strength decreased in the order of block copolymers V, VI, VII, and VIII, while the elongation at break increased in the same order. This suggests that the multiblock copolymers possessing more rigid aromatic polyamides show stronger pseudocrosslinking



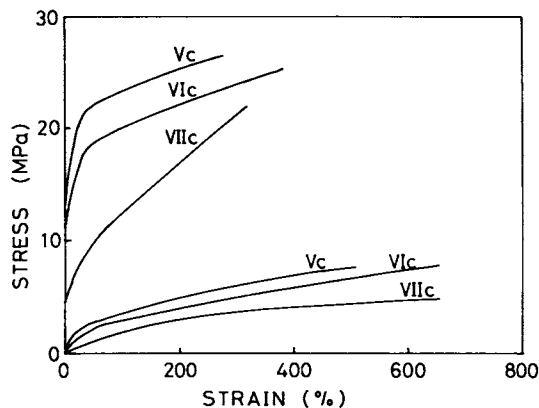


Fig. 5. Stress-strain curves for cast films of block copolymers V, VI, and VII.

between the polyamide blocks. In fact, higher elongation at break was observed in the block copolymers having weaker pseudocrosslinking. It was further recognized that the film of block copolymer VIIIc cast from DMAc was very similar in tensile properties to that fabricated by hot-press method (Table V).

Among these polybutadiene-polyamide block copolymers, 3,4'-ODA-adipic acid series block copolymer of low polybutadiene content VIIe gave flexible and tough films with the highest fracture energy, and therefore this block copolymer can be used as promising transparent and tough polyamide plastics.

TABLE V  
Tensile Properties of Cast Films of Polybutadiene-Polyamide Multiblock Copolymers

Block copolymer	Polybutadiene content (%)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (MPa)
Va	81	7	440	5
Vc	57	26	260	320
Vd	50	35	180	540
VIa	81	7	630	5
VIb	68	13	340	27
VIc	57	21	200	420
VIc	50	29	180	600
VIIa	82	2	200	2
VIIb	66	12	350	76
VIIc	54	20	290	190
VIIe	38	29	400	660
VIIIa	85	3	800	4
VIIIb	72	8	420	26
VIIIc	60	10	190	49
VIIIc		(14) <sup>a</sup>	(210) <sup>a</sup>	(23) <sup>a</sup>
VIIIc	50	22	330	220
VIIIe	37	23	210	460

<sup>a</sup>Tensile data given in parentheses are those of hot-pressed film.

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