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Synthesis and Properties of Multiblock Copolymers Based on Polybutadiene and Aromatic Polyamides

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ABSTRACT: Polybutadiene–aramid multiblock copolymers having structural regularity were synthesized by direct polycondensation using triphenyl phosphite and pyridine as the condensing agent. Three synthetic methods were applied, i.e., the two-pot, the one-pot, two-step, and the one-step methods. In the two-pot method, amine-terminated telechelic aromatic polyamide (aramid) oligomers were reacted with α,ω-dicarboxylatopolybutadiene (LPB-diacid) to form multiblock copolymers. Aramid oligomers prepared from bis(4-aminophenyl) ether (ODA) and isophthalic acid (IPA) were subjected to reaction with LPB-diacid in the one-pot, two-step method. In the one-step method, the reaction components, ODA, IPA, and LPB-diacid, were reacted together. These polymerizations at a total oligomer or monomer concentration of 100–200 g·L^{-1} in a mixture of pyridine and *N*-methyl-2-pyrrolidone gave multiblock copolymers having inherent viscosities of 0.2–0.8 dL·g^{-1}. They are soluble in *N*,*N*-dimethylacetamide (DMAc), and transparent, ductile, and elastomeric films were obtained by casting from the DMAc solution. The films of the multiblock copolymers prepared by three different methods exhibited almost the same morphologies by transmission electron microscopy. In the copolymers, tensile strength and modulus of the films decrease with an increase in the polybutadiene content, whereas elongation at break increases.

Introduction

Liquid α,ω-dicarboxylatopolybutadiene (LPB-diacid) is a class of telechelic polymer with carboxyl groups in both terminal positions and is suitable for the preparation of various block copolymers; however, only a few studies such as block copolymers with poly(oxyethylene)[1] and with amide–imide oligomer[2] were reported.

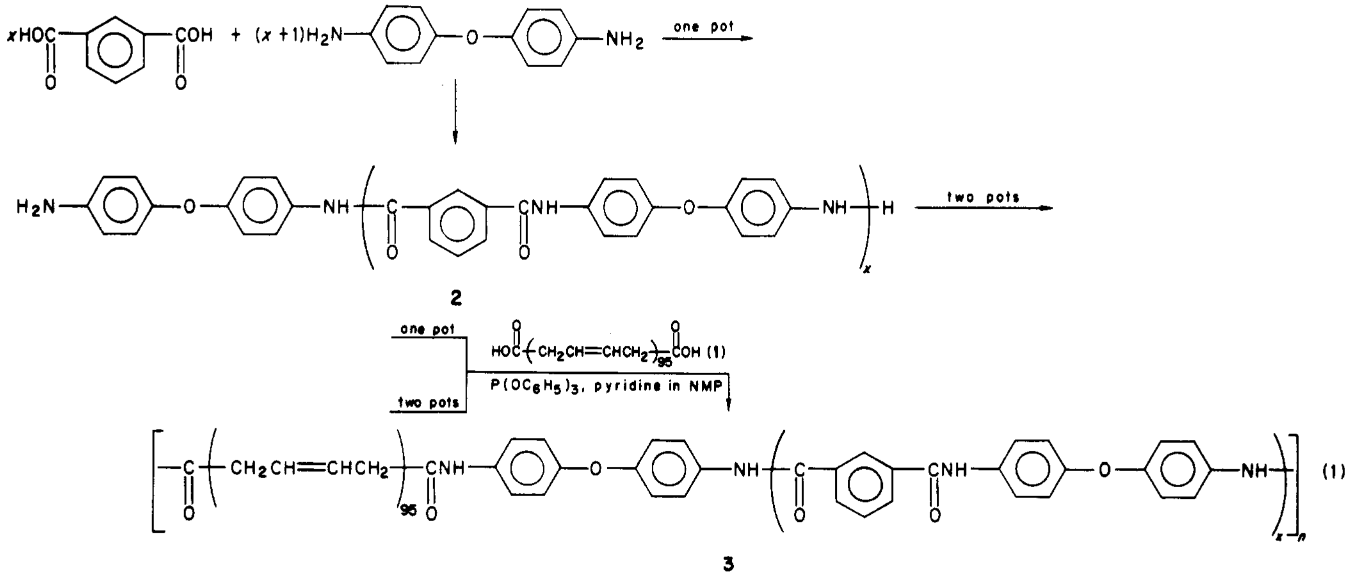
In our previous papers, syntheses of polyether–amides[3] and multiblock copolymers based on polyethers and aromatic polyamides (aramid)[4] by direct polycondensation using triphenyl phosphite and pyridine as the condensing agent[5] were described. It was found that the films of the polyether–aramid multiblock copolymers had ductile and elastomeric properties which are caused by pseudo-cross-linked structure between aramid blocks.[4] In this article, we report a successful synthesis of polybutadiene–aramid multiblock copolymers of high molecular weight from combinations of LPB-diacid and amino-terminated telechelic aramid oligomers.

The polyether–aramid multiblock copolymers having well-defined structures could be obtained by the polymerization of α,ω-dicarboxylatopoly(oxyethylene) oligomers with isolated amine-terminated aramid oligomers.[4] This two-pot method, however, is sometimes troublesome in the experimental procedure. If [A]–[B] multiblock copolymer (not random) can be obtained by the simple addition of carboxyl-terminated [B] oligomer to amine-terminated [A] oligomer solution prepared in situ, this one-pot, two-step method should be more convenient than the two-pot method. Therefore, the standard two-pot method as well as the one-pot, two-step method where amine-terminated aramid oligomers are not isolated were examined in the synthesis of polybutadiene–aramid multiblock copolymers (eq 1). The most convenient one-step method where all

Table I
Preparation of Amine-Terminated Aramid Oligomers 2

aramid oligomer	$\bar{M}_n$[a]	$\bar{x}$	η_{inh},[b] dL·g^{-1}
2b	960	2	0.11
2c	1200	3	0.13
2d	4100	12	0.18
2e	5100	15	0.29

[a] Calculated from eq 2. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C.



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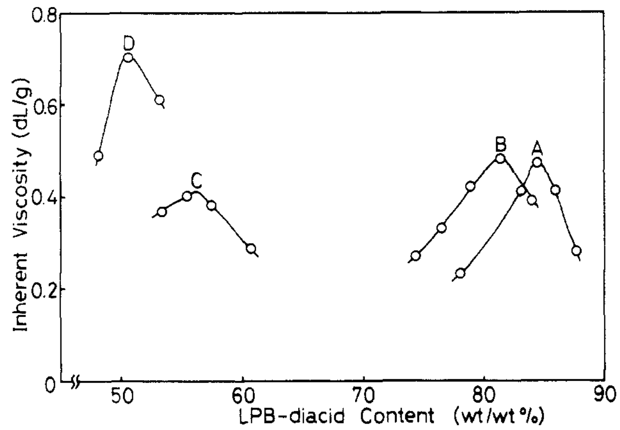

Figure 1. Influence of block ratio on inherent viscosity of the polybutadiene–aramid multiblock copolymers formed in the polycondensation of LPB-diacid with aramid oligomer **2a** (A), **2b** (B), **2c** (C), and **2d** (D).

the reaction components are reacted together was also investigated for comparison.

Results and Discussion

Synthesis of Polybutadiene–Aramid Multiblock Copolymers by Two-Pot Method. In order to prepare polybutadiene–aramid multiblock copolymers having high structural regularity, it was necessary to prepare both carboxyl-terminated telechelic polybutadiene blocks and amine-terminated telechelic aramid blocks. The former oligomer used commercially available LPB-diacid, whose number-average molecular weight ($\bar{M}_n$) calculated by end-group analysis was 5200 (average degree of polymerization is 95), and its microstructure is as follows: *cis*-1,4-, 22.1%; *trans*-1,4-, 53.4%; and 1,2-vinyl-, 24.5%. The smallest aramid oligomer, **2a**, was synthesized from *m*-phenylenediamine and isophthaloyl chloride. Four kinds of aramid oligomers, **2b–e**, having various $\bar{M}_n$ values (Table I) were prepared from calculated excess amount of bis(4-aminophenyl) ether (ODA) and isophthalic acid (IPA) by direct condensation using triphenyl phosphite and pyridine as the condensing agent. All these aramid oligomers are soluble in amide-type solvents.

In general, high polymer formation is favored by an equimolar balance of the coreactants; an excess of either of the coreactants results in chain termination. In view of the fact that the aramid block species **2** used in this work are of relatively high molecular weights, end-group analysis by titration and elemental analysis may not be sufficiently accurate to enable the determination of the optimum ratio of the coreactant species. The results of the polycondensation between LPB-diacid **1** and amine-terminated aramid oligomers **2b–e** conducted with a number of different block ratios are shown in Figure 1, where the extreme sensitivity of the copolymer inherent viscosity to the ratio of the coreacting blocks is apparent. At the peak of the composition–inherent viscosity curves, there must be an equivalent number of end groups present in the two oligomers.[6] Therefore

$$\bar{M}_n(\text{aramid}) = \bar{M}_n(\text{LPB-diacid})\frac{W(\text{aramid})}{W(\text{LPB-diacid})} \quad (2)$$

where W and $\bar{M}_n$ are the weight- and number-average molecular weights of the two blocks, respectively. From both Figure 1 and eq 2 by substituting 5200 for $\bar{M}_n$(LPB-diacid), molecular weights of the amine-terminated aramid oligomers **2b–e** are estimated to be 960, 1200, 4100, and 5100, respectively. Table I shows the molecular weight ($\bar{M}_n$), the degree of polymerization ($\bar{x}$), and the inherent viscosity of the aramid oligomers.

Table II
Preparation of Polybutadiene–Aramid Multiblock Copolymers 3

method of preparation[a]	aramid oligomer	block polymer		
		code	yield, %	η_{inh},[b] dL·g^{-1}
II	**2a**	**3a**(II)	85	0.70[c]
II	**2b**	**3b**(II)	40	0.47
II	**2c**	**3c**(II)	53	0.48
II	**2d**	**3d**(II)	84	0.40
II	**2e**	**3e**(II)	96	0.70
I/II	**2b**	**3b**(I/II)	66	0.24
I/II	**2c**	**3c**(I/II)	55	0.31
I/II	**2d**	**3d**(I/II)	90	0.61
I/II	**2e**	**3e**(I/II)	75	0.60
I	**2b**	**3b**(I)	85	0.22
I	**2c**	**3c**(I)	76	0.28
I	**2d**	**3d**(I)	83	0.72
I	**2e**	**3e**(I)	89	0.80

[a] II, two-pot method; I/II, one-pot, two-step method; and I, one-step method. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Measured in benzene.

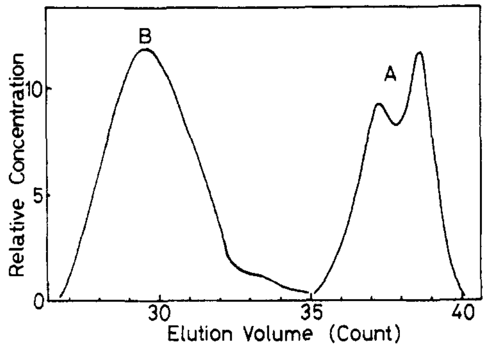

Figure 2. Gel permeation chromatograms of LPB-diacid (A) and multiblock copolymer **3a**(II) (B).

The direct polycondensation of LPB-diacid **1** with amine-terminated aramid oligomers **2a–e** giving polybutadiene–aramid multiblock copolymers **3** was carried out in *N*-methyl-2-pyrrolidone (NMP) by using triphenyl phosphite and pyridine as the condensing agent (eq 1). The multiblock copolymers of the **3**(II) series (**3** by two-pot method) having inherent viscosities of 0.4–0.7 dL·g^{-1} were obtained readily, suggesting that these block copolymers are sufficiently high molecular weight materials (Table II).

Gel permeation chromatograms (GPC) of LPB-diacid and block copolymer **3a**(II) eluted by tetrahydrofuran (THF) are shown in Figure 2. In the case of the block copolymer, $\bar{M}_n$ and $\bar{M}_w$ values are 57 000 and 109 000, respectively, for standard polystyrene, and therefore the ratio of $\bar{M}_w/\bar{M}_n$ is 1.92. From these results, **3**(II) series copolymers were confirmed as the multiblock copolymers whose $\bar{M}_n$ was estimated to be about several times higher than that of starting LPB-diacid.

Synthesis of Polybutadiene–Aramid Multiblock Copolymers by One-Pot Methods. Although the two-pot method had a benefit that the method afforded multiblock copolymers possessing high structural regularity, the actual experiment included several steps: isolation and purification of amine-terminated aramid oligomers **2** and subsequent reaction with LPB-diacid **1**. In order to improve these troublesome procedures, the one-pot, two-step method for preparation of polybutadiene–aramid multiblock copolymers **3**(I/II) was examined, where aramid oligomers **2** were not isolated. The solution of amine-terminated aramid oligomers **2** was obtained by the reaction of IPA

Table III
Elemental Analysis of 3(II) Series of Polybutadiene–Aramid Multiblock Copolymers

block copolymer	calcd, % for $n = \infty$ C	H	N	calcd, % for $n = 5$ C	H	N	found, % C	H	N
3b	85.88	10.03	1.51	85.48	9.86	1.76	80.99	8.88	3.32
3c	85.40	9.82	1.76	84.94	9.62	2.04	80.58	8.67	3.56
3d	81.42	8.08	3.87	80.71	7.77	4.27	78.78	7.94	4.28
3e	80.58	7.71	4.32	79.87	7.40	4.71	77.79	7.55	4.40

Table IV
Solubility of 3(II) Series of Polybutadiene–Aramid Multiblock Copolymers[a]

solv	LPB-diacid	block copolymer 3a	3b	3c	3d	3e	aramid homopolymer
N,N-dimethylacetamide	−	+	++	++	++	++	++
pyridine	++	++	++	±	±	±	±
benzene	++	++	±	±	±	±	−
ethyl ether	++	+	±	−	−	−	−
ethyl acetate	++	±	−	−	−	−	−
hexane	+	−	−	−	−	−	−
methanol	−	−	−	−	−	−	−

[a] ++, soluble; +, partially soluble; ±, swelling; and −, insoluble.

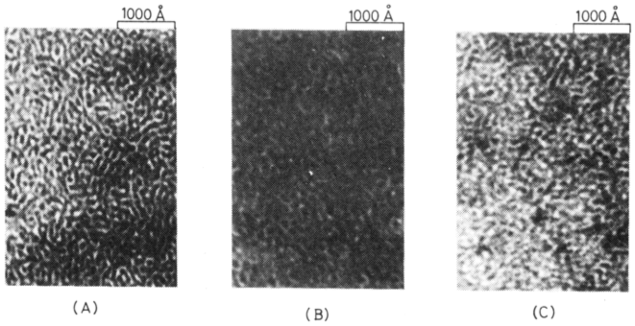

Figure 3. Transmission electron micrographs of multiblock copolymer **3e**(II) (A), **3e**(I/II) (B), and **3e**(I) (C).

and calculated excess of ODA in the presence of triphenyl phosphite and pyridine in NMP. After that, LPB-diacid **1** was added to the solution of **2** just prepared and reacted under the same polymerization conditions as those for the two-pot method. In the present method, the amounts of IPA and ODA were calculated to form the aramid oligomers having the desired $\bar{M}_n$ and the number of amine terminals which should be exactly the same number of carboxyl terminals of LPB-diacid **1**. As shown in Table II, multiblock copolymers **3**(I/II) (**3** by one-pot, two-step method) of high molecular weight were obtained readily.

Furthermore, this convenient one-pot, two-step method was extended to the simplest one-step method, in which the reaction components, ODA, IPA, and LPB-diacid, were reacted together by using triphenyl phosphite and pyridine as the condensing agent, giving **3**(I) series copolymers (**3** by one-step method) with almost the same inherent viscosity values.

Structure of Polybutadiene–Aramid Multiblock Copolymers. The structure of the resulting multiblock copolymers of **3**(II), **3**(I/II), and **3**(I) series was confirmed by means of IR spectroscopy, elemental analysis, and transmission electron microscopy.

In the IR spectra of the block copolymers, characteristic amide absorptions at 3300 (N—H) and 1655 (C=O) cm^{-1}, aromatic absorptions at 1610 and 1480 cm^{-1}, and olefinic absorptions at 965 and 910 cm^{-1} appeared, whereas a strong carbonyl absorption at 1710 cm^{-1} due to the carboxylic function of the starting LPB-diacid disappeared.

The results of elemental analysis of **3**(II) series copolymers are shown in Table III. If the degree of polymerization (n) is taken as 5 and both terminal positions have aramid oligomers, the calculated values of elemental analysis are in fairly good agreement with the observed values.

Figure 3 shows transmission electron micrographs of multiblock copolymers **3e**(II), **3e**(I/II), and **3e**(I), all of which are composed of the same LPB content. As can be seen from the figure, these three copolymers have almost the same microstructures. This suggests that polybutadiene–aramid multiblock copolymers having high structural regularity were obtained by both the two-pot method and the one-pot, two-step method, and by the one-step method as well.

In the two-pot method and the one-pot, two-step method, aramid oligomers were prepared prior to the reaction with LPB-diacid. The results that copolymer **3e**(I/II) has the same microstructure as **3e**(II) imply that the formation of the aramid oligomers in situ and subsquent polymerization with LPB-diacid proceeded according to our expectations in the one-pot, two-step method, giving multiblock copolymer **3e**(I/II) with high structural regularity.

It is quite interesting to note that the one-step method also afforded copolymer **3e**(I) with well-defined structure, contrary to the expectations of the formation of random block copolymer by such a method. Supposing in the one-step method the reaction between ODA and IPA was much faster than that between ODA and LPB-diacid, multiblock copolymer should be produced. The difference of both reaction rates could be explained by the low solubility of LPB-diacid in NMP. Since the LPB-diacid phase was separated from the NMP phase in which ODA and IPA as well as the condensing agents existed, it was considered that the formation of aramid oligomer smoothly proceeded in the NMP phase at the first stage of the reaction, and finally LPB-diacid reacted with aramid oligomer just formed giving copolymer **3e**(I).

Properties of Polybutadiene–Aramid Multiblock Copolymers. Qualitative solubility behavior of the multiblock copolymers **3** in organic solvents is shown in Table IV. The solubilities of copolymers **3b–e** containing less than 84 wt % of LPB units resemble that of the aramid homopolymer, whereas copolymer **3a** has solubility more comparable to that of LPB-diacid. Transparent, ductile, and elastomeric films of the multiblock copolymers could be cast from the *N,N*-dimethylacetamide (DMAc) solutions.

The thermal behavior of the polybutadiene–aramid multiblock copolymers was evaluated by differential

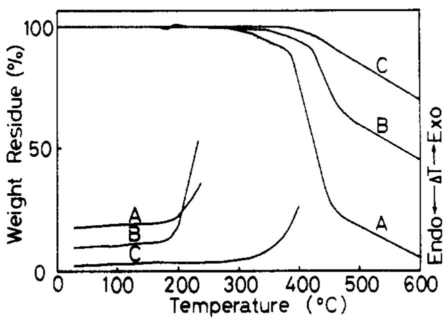

Figure 4. DTA and TG curves in air at a heating rate of 10 °C min^{-1} for polybutadiene homopolymer (A), copolymer **3e**(I/II) (B), and aramid homopolymer (C).

Table V
Glass Transition Temperatures (T_g) of Polybutadiene-Aramid Multiblock Copolymers

copolymer	T_g,[a] °C (II) series	(I/II) series	(I) series
3b	-73.5	-74.0	-74.0
3c	-73.5	-76.0	-74.0
3d	-77.5	-78.0	-76.0
3e	-79.0	-81.5	-79.5
PB[b]			-73.5

[a] Determined by DSC at a heating rate of 20 °C·min^{-1} in air. [b] Polybutadiene homopolymer prepared by chain extension of LPB-diacid through polycondensation with *p*-phenylenediamine. Inherent viscosity was 0.70 dL·g^{-1} measured at a concentration of 0.5 g·dL^{-1} in benzene at 30 °C.

thermal analysis (DTA) and thermogravimetry (TG). Typical DTA and TG curves for the representative multiblock copolymer, **3e**(I/II), as well as for the parent LPB-diacid and aramid homopolymer, are given in Figure 4. On the DTA curves in air, onset of exothermic reaction was observed for all the copolymers at around 200 °C. The exothermic reaction is probably due to the thermal polymerization of polybutadiene units through carbon-carbon double bonds, which gave cross-linked, insoluble materials. The TG curves showed that the cross-linked polymers began to lose weight above 350 °C in air.

Glass transition temperatures (T_g) of the polybutadiene component in the multiblock copolymers were further evaluated by differential scanning calorimetry (DSC). The results are summarized in Table V. For the individual series of copolymers, **3**(II), **3**(I/II), and **3**(I), the unusual phenomenon of depression of the low T_g was found for the polybutadiene component in the multiblock copolymers, which has been reported briefly.[7] The extent of T_g depression for **3**(I/II) series copolymers, as well as **3**(I), is almost comparable to that for standard **3**(II) series copolymers. Therefore, it may be concluded again that the microstructures of **3**(II), **3**(I/II), and **3**(I) series copolymers are almost the same.

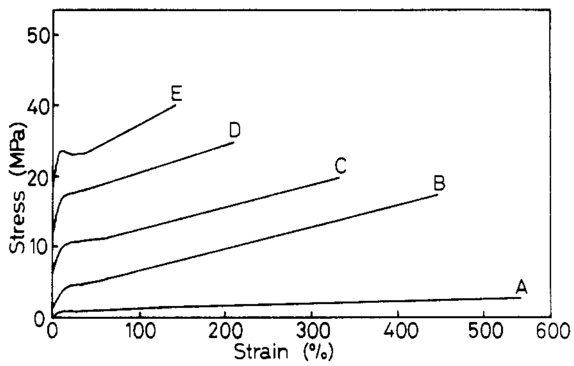

Figure 5. Stress-strain curves for **3**(II) series of polybutadiene-aramid multiblock copolymer **3a** (A), **3b** (B), **3c** (C), **3d** (D), and **3e** (E).

Stress-strain curves of the polybutadiene-aramid multiblock copolymer films which were cast from the DMAc solutions are shown in Figure 5, and the tensile properties are summarized in Table VI. When the properties of the block copolymers having the same LPB content are compared with each other, the tensile values appear to be comparable regardless of their methods of preparation. These block copolymers are ductile and elastomeric, and their tensile properties differ significantly from those of the aramid homopolymer. The rigid structure of the aramid blocks is apparently retained in the block copolymers to produce a strong elastomeric pseudo-cross-linked materials. A typical example is a snappy elastomer of **3c**(I/II) which displays a tensile strength of 7 MPa with 440% elongation and 88% elastic recovery. In these block copolymers, tensile strength and modulus fall steeply with increasing LPB content, whereas elongation at break increases rather gradually. Similar structure-property relationships have been reported in polyoxyethylene-aramid multiblock copolymers.[4]

Experimental Section

Materials. LPB-diacid was obtained from Goodrich Co. as Hycar CPB ($\bar{M}_n$ = 4800 and functionality = 2.01). Number-average molecular weight of LPB-diacid was determined to be 5200 by titration. IPA and ODA were purified by recrystallization from water and THF, respectively. Triphenyl phosphite, pyridine, NMP, and DMAc were purified by distillation. Other inorganic

Table VI
Tensile Properties of Polybutadiene-Aramid Multiblock Copolymer Films

block copolymer code	LPB content, wt %	tensile strength, MPa	elongation at break, %	initial modulus, MPa	elastic recovery,[a] %
3a(II)	94	0.3	610	5	76
3b(II)	84	16	380	57	66
3c(II)	81	17	370	73	53
3c(I/II)	81	7	440	5	88
3c(I)	81	7	370	5	92
3d(II)	56	20	220	310	
3d(I/II)	56	26	260	320	19
3d(I)	56	20	240	230	19
3e(II)	50	29	240	580	
3e(I/II)	50	35	180	540	
3e(I)	50	26	210	440	
aramid[b]	0	68	4	1700	

[a] Measured by extension of film specimens to two-thirds of elongation at break, and relaxation. [b] Aramid homopolymer prepared by polycondensation of ODA and IPA. Inherent viscosity was 0.80 dL·g^{-1} measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C.

reagents were used as received.

Synthesis of Amine-Terminated Telechelic Aramid Oligomers. Aramid Oligomer 2a, *N,N'*-Bis(3-aminophenyl)isophthalamide. To a solution of 21.63 g (0.20 mol) of *m*-phenylenediamine in 400 mL of dichloromethane was added 5.06 g (0.025 mol) of isophthaloyl chloride dissolved in 70 mL of dichloromethane. After the mixture was stirred at 25 °C for 10 min, the precipitate was filtered and washed with water. The precipitate was suspended in 1 L of water and the mixture was acidified with concentrated sulfuric acid. Insoluble material was filtered off to give a clear solution. Crude *N,N'*-bis(3-aminophenyl)isophthalamide was obtained by the addition of concentrated aqueous ammonia to the filtrate. Two recrystallizations from a methanol-water system afforded the pure product: yield 4.8 g (55%); mp 242–243 °C (lit.[8] mp 245 °C). The IR spectrum (KBr) exhibited absorptions at 3300 (N—H) and 1650 (C=O) cm^{-1}.

Aramid Oligomer 2e. A mixture of 15.24 g (0.076 mol) of ODA, 11.63 g (0.07 mol) of IPA, 43.4 g (0.14 mol) of triphenyl phosphite, and 9.30 g of lithium chloride in 100 mL of pyridine and 133 mL of NMP was heated with stirring at 100 °C for 3 h under nitrogen. The reaction mixture was poured into 1 L of methanol, and the precipitate was collected. The product was purified by reprecipitation from a DMAc–methanol system, followed by thorough washing with hot methanol and drying at room temperature in vacuo. The yield was 22.90 g (89%). Inherent viscosity of the aramid oligomer in DMAc was 0.29 $dL \cdot g^{-1}$ at 30 °C. The IR spectrum (KBr) showed absorptions at 3270 (N—H), 1645 (C=O), and 1230 (C—O—C) cm^{-1}.

Other aramid oligomers **2b–2d**, were prepared by an analogous procedure.

Synthesis of Multiblock Copolymers. Copolymer 3e(II) by Two-Pot Method. A mixture of 2.54 g (0.5 mmol) of aramid oligomer **2e**, 2.60 g (0.5 mmol) of LPB-diacid, 3.10 g (10 mmol) of triphenyl phosphite, and 1.40 g of lithium chloride in 15 mL of pyridine and 20 mL of NMP was stirred at 100 °C for 3 h under nitrogen. The resulting polymer was isolated by pouring the viscous solution into 1 L of methanol. The product was purified by reprecipitation from a DMAc–methanol system, followed by thorough washing with methanol and hexane. The polymer weighed 4.20 g (92%) and had an inherent viscosity of 0.70 $dL \cdot g^{-1}$ in DMAc at 30 °C. The IR spectrum (film) showed absorptions at 3300 (N—H), 1650 (C=O), and 990, 965, and 910 (C=C) cm^{-1}.

Other multiblock copolymers, **3a**(II), **3b**(II), **3c**(II), and **3d**(II), were prepared by an analogous two-pot procedure.

Copolymer 3e(I/II) by One-Pot, Two-Step Method. A mixture of 1.58 g (7.89 mmol) of ODA, 1.23 g (7.39 mmol) of IPA, 6.20 g (20 mmol) of triphenyl phosphite, 0.33 g of lithium chloride, and 1.01 g of calcium chloride in 3.5 mL of pyridine and 20 mL of NMP was heated with stirring at 100 °C for 2 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 for another 3 h at the same temperature. The polymer was isolated by pouring the reaction mixture into 1 L of methanol. The product was purified as described in the preceding experiment. The yield of the polymer was 3.84 g (75%), and the inherent viscosity in DMAc was 0.60 $dL \cdot g^{-1}$.

Other multiblock copolymers, **3b**(I/II), **3c**(I/II), and **3d**(I/II), were prepared by an analogous one-pot, two-step procedure.

Copolymer 3e(I) by One-Step Method. A mixture of 1.58 g (7.89 mmol) of ODA, 1.23 g (7.39 mmol) of IPA, 2.60 g (0.5 mmol) of LPB-diacid, 6.20 g (20 mmol) of triphenyl phosphite, 0.33 g of lithium chloride, and 1.01 g of calcium chloride in 50 mL of pyridine and 20 mL of NMP was heated with stirring at 100 °C for 3 h under nitrogen. The polymer was isolated and purified as described above. The product weighed 4.56 g (89%) and had an inherent viscosity of 0.80 $dL \cdot g^{-1}$ in DMAc.

Other multiblock copolymers, **3b**(I), **3c**(I), and **3d**(I), were obtained by an analogous one-step procedure.

Measurements. IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. DTA and TG were performed with Shimazu DTA-30M and TGA-30M thermal analyzers, respectively. DSC was performed with a Daini Seikosha SSC-560 differential scanning calorimeter. Molecular weights of the polymers were determined with a Toyo Soda HLC-802 gel permeation chromatograph and a UVIGRAPH LC-1 UV detector, THF being used as eluent and polystyrene as calibration standards. Transmission electron microscopy was observed with a Hitachi HLI-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^{-1}. Measurements were performed at room temperature with film specimens (1.0 cm wide, 3.0 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was taken.

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