

EXPERIMENTAL

Materials

POE-diacids were supplied by Kawaken Fine Chemicals Corp. Bis(4-aminophenyl) ether (ODA) and isophthalic acid (IPA) were purified by recrystallization from tetrahydrofuran and water, 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 Amine-Terminated Telechelic Aramid Oligomers

Aramid Oligomer IIa. A mixture of 10.00 g (0.05 mol) of ODA, 6.20 g (0.0375 mol) of IPA, 27 ml of triphenyl phosphite, 5 g of lithium chloride, and 2.5 g of calcium chloride in 50 ml of pyridine and 100 ml of NMP was heated with stirring at 100°C for 3 h under nitrogen. The reaction mixture was poured into 4 l of methanol, and the precipitate was collected. The product was purified by three reprecipitations from the DMAc-methanol system, followed by thorough washing with hot ethanol, and dried at 30°C *in vacuo*. The yield was 12.9 g (87%). Inherent viscosity of the aramid oligomer in DMAc was 0.11 dl g⁻¹ at 30°C. The infrared (IR) spectrum (KBr) exhibited absorptions at 3270 cm⁻¹ (N-H), 1645 cm⁻¹ (C=O), and 1230 cm⁻¹ (C-O-C).

Other aramid oligomers IIb and IIc were prepared by analogous procedures.

Synthesis of Multi-Block Copolymers

Block Copolymer E75A5. A mixture of 1.36 g (0.4 mmol) of Ib, 0.80 g (0.4 mmol) of IIa, 0.3 ml (1.1 mmol) of triphenyl phosphite, 0.5 g of lithium chloride, and 0.25 g of calcium chloride in 5 ml of pyridine and 10 ml of NMP was stirred at 100°C for 3 h under nitrogen. The resultant polymer was isolated by pouring the reaction solution into 500 ml of methanol. The product was purified as described for aramid oligomers. The polymer weighed 1.84 g

(86%) and had an inherent viscosity of 0.64 dl g⁻¹ in DMAc. The IR spectrum (film) showed absorptions at 3300 cm⁻¹ (N-H), 1660 cm⁻¹ (C=O), and 1225 and 1100 cm⁻¹ (C-O-C).

All other block copolymers were synthesized by the same procedure.

Measurements

IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-30M and TGA-30M, respectively. Tensile properties such as strength and elongation were determined from stress-strain curves obtained with a Toyo Baldwin Tensilon UTM-III at an elongation rate of 20% min⁻¹. Measurements were performed at room temperature with film specimens (1.0 cm wide, 5.0 cm long, and about 0.1 mm thick) and average of at least five individual determinations was taken.

RESULTS AND DISCUSSION

Synthesis of Amine-Terminated Telechelic Aramid Oligomers

To obtain condensation block copolymers having high structural regularity, it is necessary to synthesize both block species with terminal functional groups prior to polycondensation. In the present study, amine-terminated telechelic aramid block species were prepared and subsequently condensed with an equimolar amount of commercially available, carboxyl-terminated telechelic polyether blocks, POE-diacids, to give polyether-aramid multi-block copolymers.

Table I shows the molecular weight (M_n) determined by titration, the degree of polymerization (\bar{x}), and the inherent viscosity of POE-diacids Ia-c employed.

For the aramid components, a combination of ODA and IPA was selected to obtain aramid oligomers having high solubility in

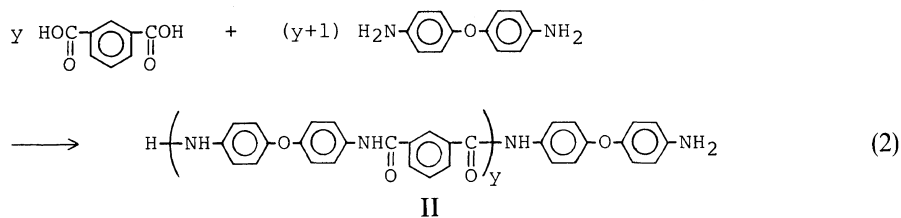
Table I. Characterization of POE-diacids

POE-diacid	M_n^a	\bar{x}	η_{inh}^b dl g ⁻¹
Ia	1000	20	0.05
Ib	3400	75	0.10
Ic	7600	170	0.17

^a Determined by titration.

^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

amide-type solvents. Amine-terminated telechelic aramid blocks IIa–c were prepared by the direct condensation using triphenyl phosphite and pyridine as the condensing agent (eq 2).



apparent. At peaks of the composition–inherent viscosity curves, there must be equivalent numbers of end groups present in the two oligomers.⁵ Therefore,

$$M_n(\text{aramid}) = M_n(\text{POE}) \times \frac{W(\text{aramid})}{W(\text{POE})} \quad (3)$$

where W and M_n are the weight and number average molecular weight, respectively, of the two blocks. From both Figure 1 and eq 3 with substituting 3400 for M_n (POE), the molecular weights of amine-terminated aramid oligomers IIa, IIb, and IIc are estimated to be 2000, 3300, and 5400, respectively. Table II shows the molecular weight (M_n), the degree of polymerization (\bar{y}), the inherent viscosity, and the elemental analysis of the aramid oligomers.

Synthesis of Polyether-Aramid Multi-Block Copolymers

The direct polycondensation of POE-diacids

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 used in this work are of relatively high molecular weights, end group analysis by titration and elemental analysis may not be sufficiently accurate to determine the optimum ratio of the coreactant species. A series of experiments was then designed for this purpose. The results of the polycondensation between POE-diacid Ib and amine-terminated aramid oligomer IIa–c 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

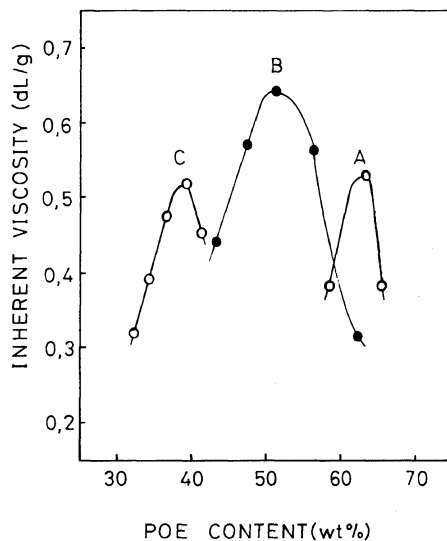


Figure 1. Influence of block ratio on inherent viscosity of the polyether-aramid multi-block copolymers formed in the polycondensation of POE-diacid Ib with aramid oligomer IIa (A), IIb (B), and IIc (C).

Table II. Characterization of amine-terminated telechelic aramid oligomers

Aramid oligomer	M_n^a	\bar{y}	η_{inh}^b dl g ⁻¹	Elemental analysis					
				Calcd/%			Found/%		
				C	H	N	C	H	N
IIa	2000	5	0.11	72.61	4.54	9.41	72.49	4.16	8.98
IIb	3300	9	0.17	72.66	4.40	8.99	72.47	4.33	8.68
IIc	5400	16	0.24	72.69	4.33	8.75	72.43	4.22	8.33

^a Calculated from eq 3.

^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

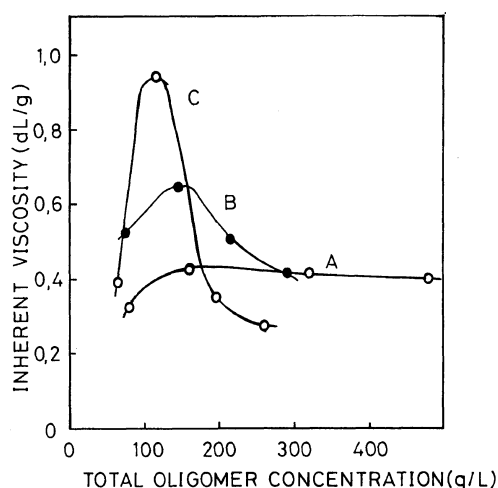


Figure 2. Influence of total oligomer concentration on inherent viscosity of polyether-aramid multi-block copolymers formed in the polycondensation of aramid oligomer IIa with POE-diacid Ia (A), Ib (B), and Ic (C).

Ia–c with amine-terminated aramide oligomers IIa–c giving polyether-aramid multi-block copolymers III was carried out in NMP using triphenyl phosphite and pyridine as the condensing agent (eq 1). The resultant multi-block copolymers are coded as ExAy, where the symbols x and y denote, respectively, the average degree of polymerization of a POE-diacid and that of an aramid oligomer.

To obtain the block copolymers with high molecular weights, the effects of oligomer concentration in the reaction mixture was investigated in detail. As shown in Figure 2, the total oligomer concentration, that is, the total

Table III. Synthesis of polyether-aramid multi-block copolymers

Oligomers		POE content ^a wt%	Block copolymer	
POE-diacid	Aramid		Code	η_{inh}^b dl g ⁻¹
Ia	IIa	33	E20A5	0.42
Ia	IIb	23	E20A6	0.44
Ia	IIc	16	E20A16	0.50
Ib	IIa	63	E75A5	0.64
Ib	IIb	51	E75A9	0.65
Ib	IIc	39	E75A16	0.52
Ic	IIa	79	E170A5	0.93
Ic	IIb	70	E170A9	0.90
Ic	IIc	58	E170A16	0.81

^a $W(\text{POE})/[W(\text{POE}) + W(\text{aramid})]$ in feed.

^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

amount of the POE-diacid and the aramid oligomer in a mixture of pyridine and NMP, greatly influenced the inherent viscosity of the polymers. For all the polymerizations, 100–200 g l⁻¹ oligomer concentration was found to be optimum and the inherent viscosity values reached as high as 0.9 dl g⁻¹.

Under these polymerization conditions, various types of multi-block copolymers with inherent viscosities of 0.4–0.9 dl g⁻¹ were obtained readily, suggesting that the block copolymers are sufficiently high molecular weight materials (Table III).

The structure of the resulting polymers was confirmed by IR spectroscopy and elemental

Table IV. Elemental analysis of polyether-aramid multi-block copolymers

Block copolymer	Calcd/%			Found/%		
	C	H	N	C	H	N
E20A9	68.35	5.29	6.77	67.19	5.36	6.38
E75A5	61.16	7.23	3.35	59.36	7.04	2.79
E75A9	63.40	6.65	4.35	61.76	6.57	3.88
E75A16	65.63	6.08	5.33	64.17	5.85	4.80
E170A5	58.27	8.04	1.88	59.51	7.71	2.35

analysis (Table IV). In the IR spectra, characteristic amide absorptions at 3300 cm^{-1} (N-H) and 1660 cm^{-1} (C=O), aromatic absorptions at 1600 and 1490 cm^{-1} due to aramid linkages, and two ether absorptions at 1230 and 1100 cm^{-1} appeared, whereas a strong carbonyl absorption at 1740 cm^{-1} due to the carboxylic acid function of the starting POE-diacids disappeared. The IR spectra are almost identical with those of the polyether-aramides reported previously.²

Properties of Polyether-Aramid Multi-Block Copolymers

The multi-block copolymers ExAy are readily soluble in DMAc, but insoluble in other organic solvents including NMP, pyridine, *m*-cresol, formic acid, tetrahydrofuran, acetone, methanol, chloroform, benzene, and water. This solubility behavior is fairly comparable to that of the aramid oligomers, in contrast to the good solubility nature of the POE-diacids in a wide range of solvents. Transparent, ductile, and elastomeric films could be cast from DMAc solutions.

Moisture regain of these block copolymers in the form of films in 60% relative humidity at 25°C was determined to be in the range of 5–6%. These values are compared with those of 8.5 and 1.4% for the parent POE homopolymer (M_n , 20000) and poly(4,4'-oxydi-*p*-phenylene isophthalamide) (aramid homopolymer II_d, η_{inh} : 2.01 dl g^{-1} in DMAc), respectively.

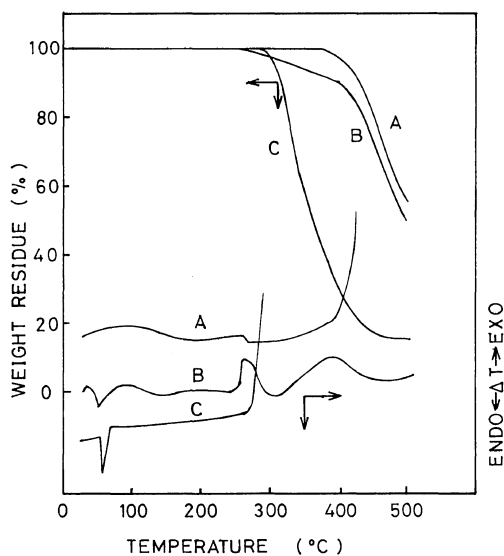


Figure 3. DTA and TG curves in nitrogen for (A) aramid homopolymer, (B) multi-block copolymer E170A16, and (C) POE homopolymer: DTA heating rate, $20^\circ\text{C min}^{-1}$; TG heating rate, 5°C min^{-1} .

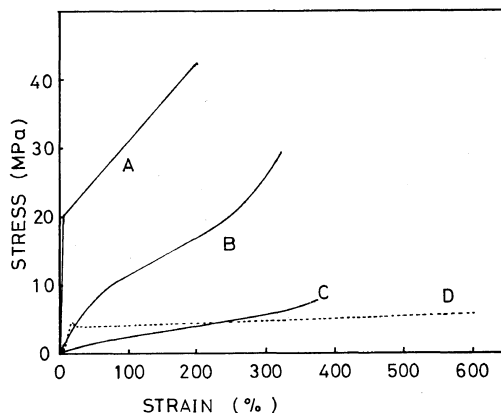


Figure 4. Stress-strain curves for polyether-aramid multi-block copolymer E75A16 (A), E75A9 (B), E75A5 (C), and E170A5 (D).

The thermal behavior of the polyether-aramid multi-block copolymers was evaluated by DTA and TG. Typical DTA and TG curves for the representative multi-block copolymer, E170A16, as well as for the parent POE homopolymer and aramid homopolymer II_d, are shown in Figure 3.

On the DTA curves in nitrogen, all the

Table V. Tensile properties of cast films of polyether-aramid multi-block copolymers

Block copolymer		Tensile strength MPa	Elongation at break %	Tensile modulus MPa	Elastic recovery %
Code	POE content %				
E75A16	39	42	200	500	58
E75A9	51	29	320	470	86
E75A5	63	6.9	370	6	100
E170A9	70	7.1	580	42	53
E170A5	79	5.6	600	28	59
Aramid IId	—	68	4	1700	—

^a Measured by 100% extension of film specimens and relaxation.

multi-block copolymers exhibited two strong exothermic peaks at around 270 and 410°C due to the decomposition of oxyethylene units and aramid linkages, respectively. In addition, a characteristic endothermic peak, probably due to the melting of POE crystallites, was observed in the range of 51–56°C for the E170Ay series block copolymers having increased POE block length. These melting temperatures are in good agreement with that of the POE homopolymer (59°C). Aramid homopolymer IId showed glass transition temperature at 270°C, but similar transition in these block copolymers could not be detected because of the appearance of a strong exothermic peak due to decomposition of the POE blocks in the same region. The TG curves of the multi-block copolymers were fairly similar in shape to those of the aramid homopolymer, though the block copolymers began to lose weight above 270°C in nitrogen.

Stress-strain curves of the polyether-aramid multi-block copolymer films are shown in Figure 4 and the tensile properties are summarized in Table V. Since these block copolymers are ductile and elastomeric, their tensile properties differ significantly from those of aramid homopolymer IId. The rigid structure of the aramid blocks is apparently retained in

the block copolymers to produce strong elastomeric pseudo-crosslinked materials. A typical example is a snappy elastomer of E75A5 which displays a tensile strength of 6.9 MPa with 370% elongation and 100% elastic recovery. In the E75Ay block copolymer series, tensile strength and modulus fall steeply with increasing POE concentrations, whereas elongation at break increases rather gradually. Similar structure-property effects have been observed with other block copolymer systems based on POE and polycarbonate.^{6–8}

Morphology and other behavior of these polyether-aramid multi-block copolymers will be published in the near future.

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