Synthesis and Properties of Multiblock Copolymers Based on Polyoxyethylene and Polyamides by Diisocyanate Method

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Synopsis

Polyoxyethylene–polyamide multiblock copolymers were successfully synthesized from α, ω-polyoxyethylene–dicarboxylic acid (POE–diacid), a mixture of two dicarboxylic acids, and an aromatic diisocyanate by two synthetic routes, i.e., one-step and two-step method. In the two-step method, α, ω-diisocyanate-terminated polyamide oligomers, preformed from a mixture of isophthalic acid (IPA) and azelaic acid (AZA) with 4,4'-methylenedi(phenyl isocyanate) (MDI), were reacted with POE–diacid to form multiblock copolymers. In the one-step method, the reaction components, MDI, IPA, AZA, and POE diacid, were reacted all together. These polymerizations were carried out in the presence of 3-methyl-1-phenyl-2-phospholene 1-oxide as a catalyst in tetramethylene sulfone, giving multiblock copolymers with inherent viscosities of 0.5–1.1 dL/g. They were soluble in amide-type solvents, and transparent, ductile, and elastomeric films could be cast from their N,N-dimethylacetamide solutions. The tensile strength and modulus of the films thus prepared decreased with an increase in the polyoxyethylene content, whereas the elongation at break increased. The tensile strength/elongation at break/tensile modulus of the multiblock copolymer films ranged from 47 MPa/160%/1.1 GPa to 15 MPa/880%/12 MPa.

INTRODUCTION

Recently there has been an increasing interest in thermoplastic elastomers, which are generally block copolymers consisting of soft blocks with low glass transition temperature (T_g) and of hard blocks with high melting temperature (T_m) or high T_g.[1] Some of the block copolymers composed of polyethers and polyamides have already been commercialized as thermoplastic elastomers.[1] A number of synthetic routes for polyether–polyamide block copolymers have been known,[2–8] and we have also reported the synthesis of polyether–aramid multiblock copolymers by the direct polycondensation.[9,10]

We have further developed another promising method for the synthesis of polyoxyethylene–polyamide multiblock copolymers by the reaction of α, ω-polyoxyethylene–dicarboxylic acids and α, ω-diisocyanate-terminated polyamide oligomers, which were prepared *in situ* from a mixture of two dicarboxylic acids and an excess of diisocyanate.[11] The films of these multiblock copolymers thus prepared had ductile and elastomeric properties which were caused by pseudocrosslinked structure between the polyamide blocks.

In this article, we report a detailed study on the synthesis of polyoxyethylene–polyamide multiblock copolymers by two synthetic routes, i.e., one-step and two-step method. The properties of the multiblock copolymers, such as solubility, thermal behavior, and mechanical properties, are also described.

EXPERIMENTAL

Materials

Two α,ω-polyoxyethylene–dicarboxylic acids (POE–diacids) (**2a** and **2b**) were obtained from Kawaken Fine Chemicals Corp., Japan. Their number average molecular weights were determined to be 3900 and 7400 by titration. 4,4′-Methylenedi(phenyl isocyanate) (MDI) was obtained commercially and purified by vacuum distillation before use. Isophthalic acid and azelaic acid were purified by recrystallization from aqueous ethanol and water, respectively. Tetramethylene sulfone (sulfolane) and N,N-dimethylacetamide (DMAc) were purified by distillation over calcium hydride. 3-Methyl-1-phenyl-2-pholene 1-oxide was prepared according to the reported procedure.[12]

Synthesis of Block Copolymers

Block Copolymer 3b(I). In a flask, 0.3987 g (2.4 mmol) of isophthalic acid, 0.4517 g (2.4 mmol) of azelaic acid, 0.7800 g (0.2 mmol) of POE-diacid **2a**, and 2.4 mg of 3-methyl-1-phenyl-2-pholene 1-oxide were placed, and dissolved in 13 mL of sulfolane with stirring at 200°C under nitrogen. To the solution, 1.2513 g (5.0 mmol) of MDI in 5 mL of sulfolane was added dropwise over a period of 5 min, and the mixture was stirred at 200°C for another 2 h. The polymer was isolated by pouring the reaction mixture into 500 mL of methanol. The product was purified by reprecipitation from DMAc with methanol, followed by thorough washing with hot methanol and drying at 60°C in vacuo. The yield of the polymer was 2.24 g (91%), and the inherent viscosity in DMAc was 0.76 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The film was prepared by casting from a 20% DMAc solution (by weight) on a glass plate. The glass plate was heated at 80°C for 20 h in air, and then the film was peeled off, followed by vacuum drying at 80°C for 20 h. The infrared (IR) spectrum (film) exhibited absorptions at 3300 cm^{-1} (N—H), 1655 cm^{-1} (C=O), and 1100 cm^{-1} (C—O—C).

ANAL. Calcd for $(C_{704}H_{862}N_{50}O_{136.5})_n$: C, 69.26%; H, 7.12%; N, 5.74%. Found: C, 69.00%; H, 7.18%, N, 5.76%.

Other multiblock copolymers of **3(I)** series were synthesized by the same one-step procedure. Multiblock copolymers of **3(II)** series were prepared by the two-step method according to the previously reported procedure.[11]

Measurements

IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential scanning calorimetry (DSC) was performed with a Daini Seikosha SSC-580 differential scanning calorimeter, and the midpoint temperature on the DSC curve was defined as the glass transition temperature of the polymer. Ther-

mogravimetry (TG) was performed with a Shimadzu thermal analyzer TGA-30M. Molecular weights of the polymers were determined with a Waters 150C gel permeation chromatograph at 140°C, N,N-dimethylformamide (DMF) being used as eluent and polystyrene as calibration standard. Tensile properties, such as strength, elongation at break, and initial modulus were determined from stress–strain curves obtained with a Toyo Baldwin Tensilon UTM-III at an elongation rate of 20%/min. Measurements were performed at room temperature with film specimens (about 0.1 mm thick, 1.0 cm wide, and 5.0 cm long) and an average of five individual determination was taken. Dynamic mechanical measurements (DMA) were made with film specimens on a Toyo Baldwin Rheovibron DDV-II at 11 Hz in the temperature range from −100 to 250°C at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

Synthesis of Multiblock Copolymers

Polyoxyethylene (POE)–polyamide multiblock copolymers were synthesized according to Scheme 1 by the one-step method, as well as by the two-step method reported previously.[11] Two POE–diacids having number average molecular weights of 3900 (**2a**) and 7400 (**2b**) were used in this study. For the block copolymer synthesis, the contents of POE block were varied from 17 to 78 wt %. To accelerate the polyamide formation, 3-methyl-1-phenyl-2-phospholene 1-oxide was used as the catalyst[13]:
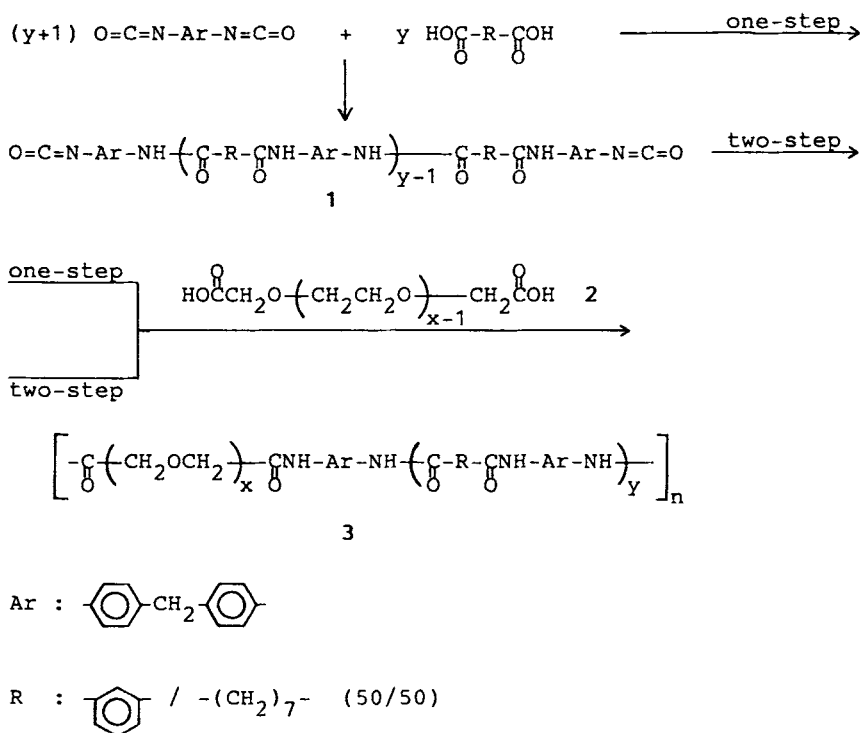
Scheme 1

The results of the synthesis of multiblock copolymers of **3(I)** series by the one-step method, and of multiblock copolymers of **3(II)** series by the two-step method, are summarized in Table I. The present one-step method gave the **3(I)** series block copolymers having inherent viscosities of 0.5–0.8 dL/g, and the two-step method afforded the **3(II)** series block copolymers with viscosity values of 0.5–1.1 dL/g.

The structure of the resulting polymers was confirmed by IR spectroscopy and elemental analysis. In the IR spectra of the copolymers, characteristic amide absorptions at 3300 cm^{-1} (N—H) and 1655 cm^{-1} (C=O), and an ether absorption at 1100 cm^{-1} were observed. The elemental analysis is in good agreement with the calculated values (Table II). The observed POE contents of the block copolymers, which were calculated from the nitrogen content in the elemental analysis, are also shown in Table I. The observed POE contents agreed quite well with those calculated from the reactants in feed.

The gel permeation chromatograms (GPC) of block copolymers **3b(I)**, **3b(II)**, and POE-diacid (**2a**), eluted by DMF, are shown in Figure 1. In the case of the block copolymers, number average molecular weight (M_n) and weight average molecular weight values (M_w) are 42,000 and 117,000 for **3b(I)**, and 35,000 and 108,000 for **3b(II)**, respectively, relative to standard polystyrene.

TABLE I
Synthesis of Polyoxyethylene-Polyamide Multiblock Copolymers

Method of preparation	$\overline{Mn}$ of POE diacid	$\overline{Mn}$ of polyamide[a] oligomer	Code	POE content (wt %) Calcd[b]	Found[c]	Yield (%)	η inh[d] (dL/g)
I	3900	16800	**3a(I)**	17	20	81	0.56
I	3900	8300	**3b(I)**	29	32	91	0.76
I	3900	3200	**3c(I)**	51	53	87	0.53
I	3900	2000	**3d(I)**	63	66	93	0.74
I	3900	1000	**3e(I)**	78	75	84	0.54
I	7400	16800	**3f(I)**	31	30	93	0.79
I	7400	8300	**3g(I)**	49	43	100	0.69
I	7400	4100	**3h(I)**	64	61	98	0.51
I	7400	2300	**3i(I)**	77	74	100	0.54
II	3900	16800	**3a(II)**	17	23	89	0.84
II	3900	8300	**3b(II)**	29	32	94	0.92
II	3900	3200	**3c(II)**	51	55	84	0.56
II	3900	2000	**3d(II)**	63	62	87	0.54
II	3900	1000	**3e(II)**	78	76	90	0.51
II	7400	16800	**3f(II)**	31	27	97	1.17
II	7400	8300	**3g(II)**	49	47	97	0.59
II	7400	4100	**3h(II)**	64	64	98	0.51
II	7400	2300	**3i(II)**	77	78	86	0.53

[a] Calculated from feed ratio of the monomers.
[b] Weight (POE diacid)/[weight (POE diacid) + weight (polyamide)] in the feed.
[c] Calculated from the elemental analysis (nitrogen content).
[d] Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

TABLE II
Elemental Analysis of Polyoxyethylene-Polyamide Multiblock Copolymers

Block copolymer	Calcd (%)			Found (%)		
	C	H	N	C	H	N
3b(I)	69.40	7.10	5.81	69.00	7.18	5.76
3b(II)	69.40	7.10	5.81	69.36	7.16	5.83
3e(I)	59.20	8.41	2.02	58.93	8.54	2.30
3e(II)	59.20	8.41	2.02	59.22	8.49	2.21
3f(I)	69.49	7.11	5.78	68.87	6.85	5.90
3f(II)	69.49	7.11	5.78	69.64	6.81	6.06
3h(I)	62.20	8.07	3.04	62.30	8.00	3.34
3h(II)	62.20	8.07	3.04	62.30	7.81	3.15

From these data, these copolymers were confirmed to be multiblock copolymers whose M_n was estimated to be several times higher than that of the starting POE–diacid.

These results indicate that the present diisocyanate method, either one-step or two-step, is highly effective for the synthesis of the POE–polyamide multiblock copolymers.

Solubility Behavior of Multiblock Copolymers

Table III summarizes the qualitative solubility behavior of typical multiblock copolymers in organic solvents, as well as of the parent POE–diacid and the polyamide derived from MDI and a mixture of isophthalic acid and azelaic acid (50/50 molar ratio). These block copolymers were soluble in amide-type solvents such as DMF and DMAc, dimethyl sulfoxide, and m-cresol. Transparent, ductile, and elastomeric films were obtained by casting from their DMAc solutions.
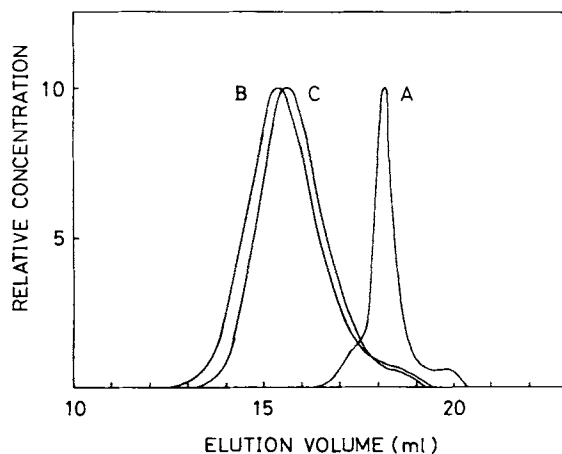

Fig. 1.   Gel permeation chromatograms of POE-diacid 2a (A), multiblock copolymer 3b(I) (B), and 3b(II) (C).

Solvent	POE-diacid	Polyamide	Block copolymer			
			3c(I)	3c(II)	3g(I)	3g(II)
N-Methyl-2-pyrrolidone	++	++	++	++	++	++
N,N-Dimethylacetamide	++	++	++	++	++	++
N,N-Dimethylformamide	++	++	++	++	++	++
Dimethyl sulfoxide	++	+	++	++	++	++
m-Cresol	++	++	++	++	++	++
Pyridine	++	—	+	—	±	±
Methanol	++	—	—	—	—	—

[a] Solubility: ++, soluble at room temperature; +, soluble on heating; ±, swelling; and —, insoluble.

Thermal Behavior of Multiblock Copolymers

The thermal behavior of the polyether–polyamide multiblock copolymers was evaluated by means of thermogravimetry (TG), differential scanning calorimetry (DSC), and dynamic mechanical measurements (DMA). Figure 2 shows typical TG curves in nitrogen for the representative multiblock copolymer 3c(II), as well as for the parent polyamide and POE–diacid. The TG curves of all the block copolymers lay between the curve of the polyamide and that of POE–diacid. The thermal decomposition temperature (10% weight loss temperature) of the multiblock copolymers decreased with an increase in POE content in the block copolymers from 430°C for the polyamide, reaching 300°C for POE–diacid.
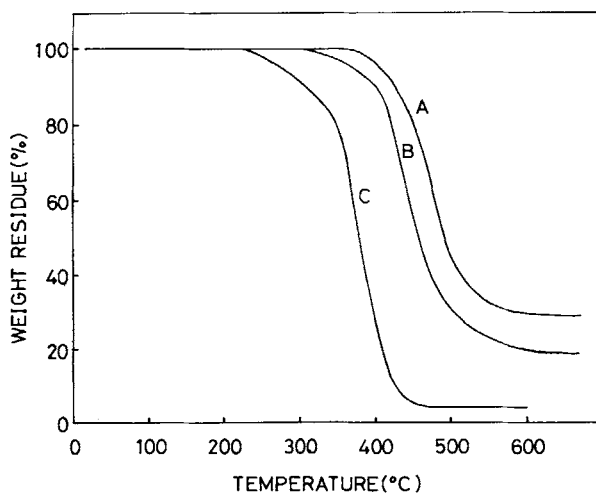

Fig. 2.   TG curves in nitrogen at a heating rate of 20°C/min for (A) parent polyamide, (B) multiblock copolymer 3c(II), and (C) POE-diacid 2a.

Figure 3 shows some examples of DSC thermograms of the **3(II)** series block copolymers and of the parent polyamide and POE–diacid. Table IV summarizes the results of DSC measurements for all the multiblock copolymers. A glass transition temperature (T_g) of POE phase was observed as an endothermic shift in the range of -27 to $-48°C$ for these multiblock copolymers, which is higher than that of POE–diacid **2a** ($T_g = -47°C$) or **2b** ($T_g = -50°C$). The T_g of the hard polyamide phase could not be detected in the DSC thermograms. The T_g of the soft POE phase became lower with increasing POE content in the block copolymers, and finally approached that of the POE–diacid. This suggests a certain degree of soft and hard segment mixing, and the larger the POE content the smaller the intermixing.

In more detail, multiblock copolymers **3f–3i**, based on POE–diacid **2b** with longer POE block length, exhibited a much lower T_g of $-37-$ $-48°C$, compared with block copolymers **3a–3e**, derived from **2a**, having a T_g of $-27--45°C$. It appears that in block copolymers **3f–3i**, hard segment solubilization in the soft POE segment is minimal. Furthermore, the **3(II)** series multiblock copolymers exhibited a higher degree of microphase separation and higher purity of the POE phase than the **3(I)** series block copolymers, as was evidenced by a much lower T_g in the **3(II)** series block copolymers. This suggests that the **3(II)** series block copolymers have higher structural regularity, while the **3(I)** series block copolymers are more randomly coupled block copolymers having some irregular structure.
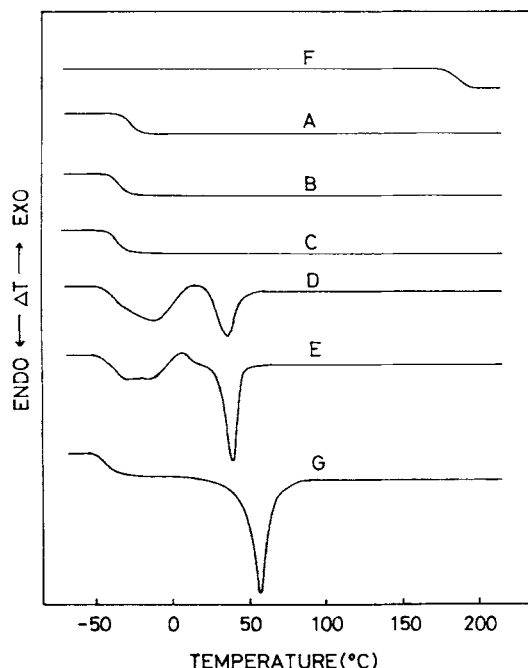

Fig. 3. DSC curves in nitrogen at a heating rate of 20°C/min for multiblock copolymer (A) **3a(II)**, (B) **3b(II)**, (C) **3c(II)**, (D) **3d(II)**, (E) **3e(II)**, (F) parent polyamide, and (G) POE diacid **2a**.

TABLE IV
Glass Transition Temperatures (T_g) and Melting Temperatures (T_m) of Polyoxyethylene Phase
of Polyoxyethylene–Polyamide Multiblock Copolymers[a]

Block copolymer	Polyoxyethylene content (wt %)	T_g (°C)		T_m (°C)	
		(II) series	**(I)** series	**(II)** series	**(I)** series
3a	17	−30	−27	—	—
3b	29	−37	−34	—	—
3c	51	−41	−36	—	—
3d	63	−40	−39	35	37
3e	76	−45	−42	41	42
POE diacid **2a**	100	−47	−47	58	58
3f	31	−37	−37	—	—
3g	47	−44	−41	—	—
3h	64	−47	−45	47	37
3i	77	−48	−45	50	48
POE diacid **2b**	100	−50	−50	65	65
Polyamide	0	184	184	—	—

[a] Determined by DSC in nitrogen at a heating rate of 20°C/min.

For the multiblock copolymers with higher POE content, the endothermic peak due to the melting temperature (T_m) of POE crystallites was observed in the range from 35 to 50°C. A much higher T_m of block copolymers **3h(II)** and **3i(II)** than that of the corresponding **3(I)** series block copolymers may also reflect higher structural regularity of the former block copolymers.

The dynamic mechanical storage modulus (E') and the dynamic loss modulus (E'') of the **3(II)** series multiblock copolymers and the parent polyamide are plotted as a function of temperature in Figure 4. The results indicate that a two-phase nature for the multiblock copolymers, especially for **3a(II)** and **3b(II)** having low POE content. Most block copolymers showed a low-temperature E'' peak near −50°C, which corresponds to the T_g of the soft POE phase. The parent polyamide had three peaks designated α, β, and γ from the high-temperature side in the E'' curve, and showed a low-temperature γ peak near −80°C, which overlapped with the low-temperature E'' peak of **3a(II)** and **3b(II)**. A high-temperature E'' peak relating to the T_g of the hard polyamide segment was detected to be 150 and 100°C for block copolymers **3a(II)** and **3b(II)**, respectively. These T_g values are compared with the T_g of 184°C for the parent polyamide, and were found to decrease with increasing POE content in the block copolymers. These results suggest that some solubilization of the soft POE segment occurs in the hard polyamide phase, i.e., the microphase separation between the polyamide and POE phases is less complete.

Tensile Properties of Multiblock Copolymers

The stress–strain curves for various multiblock copolymer films prepared from solution casting with DMAc are shown in Figure 5. Table V summarizes the tensile properties of films of all the block copolymers. A comparison of the
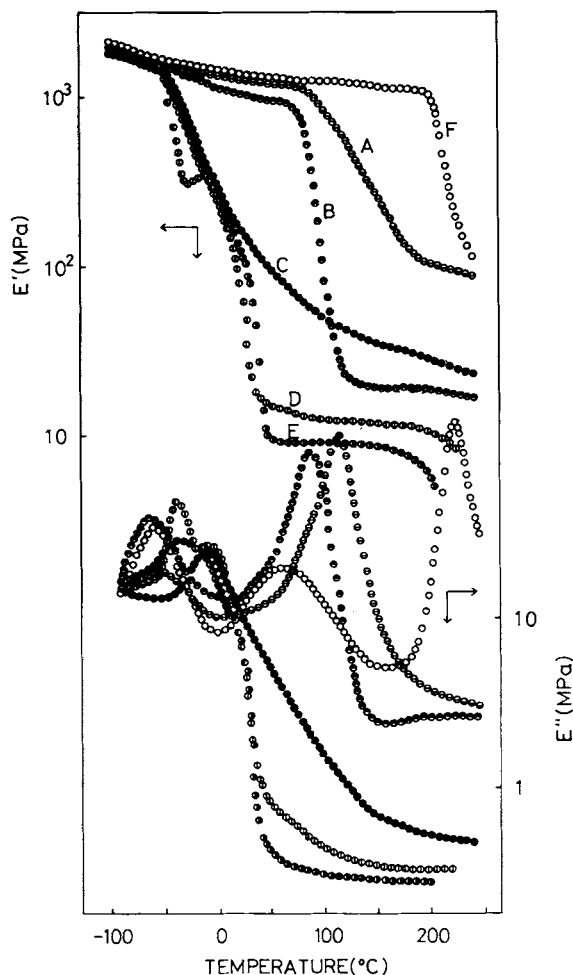
Fig. 4. Temperature dependence of the dynamic storage modulus E' and the dynamic loss modulus E'' measured at 11 Hz at a heating rate of 3°C/min of multiblock copolymer (A) **3a(II)**, (B) **3b(II)**, (C) **3c(II)**, (D) **3d(II)**, (E) **3e(II)**, and (F) parent polyamide.

curves in Figure 5 shows that by increasing the POE content at constant soft POE molecular weight, the tensile strength (T) and tensile modulus (M) decreased, while the elongation at break (E) increased. In case of the films of block copolymer **3a** having the lowest POE content, a yield point was observed between 5 and 10% elongation, which strongly indicates the more continuous nature of the polyamide phase. Thus, the tensile properties of the parent polyamide film could be greatly improved by the incorporation of POE unit into the block copolymer backbone, giving **3a** film with tough and ductile properties. At higher POE content, on the other hand, a more pronounced elastomeric character is evident for the multiblock copolymers, no doubt due to the more continuous nature of the POE phase. Over the composition range, the multiblock copolymer films were between a tough and ductile film having $T/E/M$ of 47
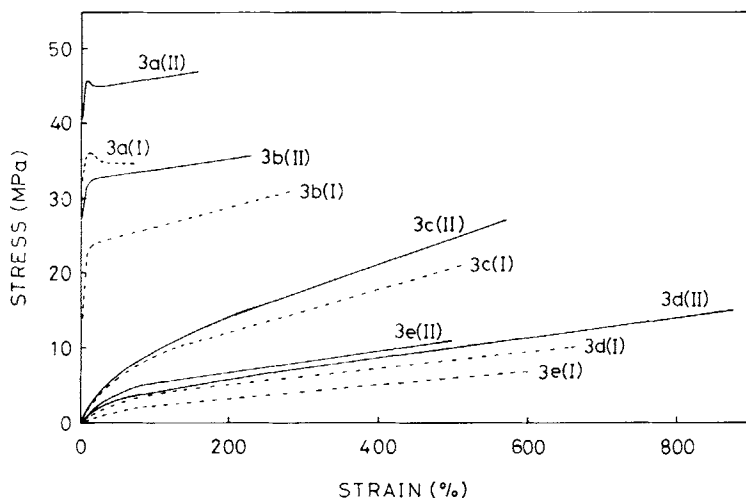
Fig. 5. Stress–strain curves for polyoxyethylene-polyamide multiblock copolymers **3a(I)**–**3e(I)** and **3a(II)–3e(II)**.

MPa/160%/1.1 GPa and a elastomeric film with $T/E/M$ of 15 MPa/880%/ 12 MPa.

The effect of soft POE block length at constant POE content on the tensile properties of the films did not always exhibit the same trend as the effect of POE content. An increase of the POE block length from 3900 to 7400 generally led to the films having slightly lower T, slightly higher M, and lower E.

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

Block copolymer	Polyoxyethylene content (wt %)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
3a(I)	17	35	80	720
3a(II)	17	47	160	1110
3b(I)	29	31	280	370
3b(II)	29	36	230	620
3c(I)	51	21	510	47
3c(II)	51	27	570	30
3d(I)	63	10	660	10
3d(II)	63	15	880	12
3e(I)	76	7.2	600	3.9
3e(II)	76	11	500	22
3f(I)	31	29	130	330
3f(II)	31	43	150	940
3g(I)	47	23	590	43
3g(II)	47	25	730	57
3h(I)	64	9.3	610	23
3h(II)	64	8.1	480	30
3i(I)	77	9.1	430	23
3i(II)	77	6.2	240	36
polyamide	0	73	15	2200

The method of preparation of the multiblock copolymers also had a strong influence on tensile properties of the films, i.e., the films of the **3(II)** series block copolymers generally exhibited higher T, higher E, and higher M, compared with the films of the **3(I)** series block copolymers. This suggests that block copolymers **3(II)** have higher structural regularity, compared with block copolymers **3(I)** having some irregularly coupled structures. Similar results were reported in polyoxyethylene–aramid multiblock copolymers.[10]

In conclusion, these polyoxyethylene–polyamide multiblock copolymers having low polyoxyethylene content can be used as transparent and tough polyamide plastics, whereas the multiblock copolymers having moderate to high polyoxyethylene content may be considered as new candidates for transparent thermoplastic elastomers.

References

1. N. R. Legge, G. Holden, and H. E. Schroeder, *Thermoplastic Elastomers,* Hanser, New York, 1987.
2. A. Noshay and J. E. McGrath, *Block Copolymers,* Academic, New York, 1977.
3. R. J. Zdrahala, E. M. Firer, and J. F. Fellers, *J. Polym. Sci. Polym. Chem. Ed.,* **15,** 689 (1977).
4. L. Castaldo, G. Maglio, and R. Palumbo, *J. Polym. Sci. Polym. Lett. Ed.,* **16,** 643 (1978).
5. M. Raab, B. Masar, J. Kolarik, and P. Cefelin, *Int. J. Polym. Mater.,* **7,** 219 (1979).
6. J. K. Rasmussen and H. K. Smith II, *J. Appl. Polym. Sci.,* **28,** 2473 (1983).
7. N. Ogata and N. Yui, *J. Macromol. Sci.-Chem.,* **A21,** 1097 (1984).
8. F. de Candia, V. Petrocelli, R. Russo, G. Maglio, and R. Palumbo, *Polymer,* **27,** 797 (1986).
9. Y. Imai, M. Kajiyama, S. Ogata, and M. Kakimoto, *Polym. J.,* **16,** 267 (1984).
10. Y. Imai, M. Kajiyama, S. Ogata, and M. Kakimoto, *Polym. J.,* **17,** 1173 (1985).
11. T. Otsuki, M. Kakimoto, and Y. Imai, *Makromol. Chem., Rapid, Commun.,* **8,** 637 (1987).
12. W. B. McCormak, *Organic Synthesis,* Coll. Vol. 5, Wiley, New York, 1973, p. 787.
13. K. B. Onder and P. S. Andrews, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.,* **21**(2), 132 (1980).