

Synthesis and properties of new multiblock copolymers based on poly(oxytetramethylene) and polyamides by diisocyanate method

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New poly(ether-urethane-amide) multiblock copolymers based on poly(oxytetramethylene) (POTM) and polyamides were synthesized via the diisocyanate route by two synthetic methods, i.e. one-step and two-step methods. These polymerizations afforded multiblock copolymers having inherent viscosities of 0.61–1.10 dl g⁻¹. They were soluble in amide-type solvents, and transparent, ductile and elastic films were obtained by casting from *N,N*-dimethylacetamide solutions. An unusual behaviour of glass transition temperature depression for the POTM phase was observed in the multiblock copolymers. In the copolymers, the tensile strength and modulus of the films decrease with increase in the POTM content, whereas elongation at break increases.

(Keywords: polyamide-polyether; multiblock copolymers; diisocyanate method; solubility; thermal behaviour; tensile properties)

INTRODUCTION

α,ω -Dihydroxypoly(oxytetramethylene) (POTM-diol) is a commercially available useful telechelic oligomer with hydroxy terminal groups, and has been widely utilized as a soft block component for commercial poly(ether-urethane) materials as well as poly(ether-ester) and poly(ether-ester-amide) thermoplastic elastomers^{1–3}. However, relatively few studies have been reported on the poly(oxytetramethylene) (POTM) based block copolymers other than poly(ether-urethanes) and poly(ether-esters). For example, Mumcu and coworkers⁴ reported the synthesis of copoly(ether-amide) block copolymers by the melt polycondensation of lauryllactam, dodecanedioic acid and POTM-diol. Onder and his group⁵ demonstrated the preparation and characterization of block copolymers of poly(ester-amide) and poly(ether-ester-amide) series by the solution polycondensation of diisocyanate, dicarboxylic acid and diacid-terminated polyester and polyether oligomers.

Recently we reported the synthesis and properties of polyoxyethylene-polyamide multiblock copolymers by the reaction of poly(oxyethylene) dicarboxylic acid and α,ω -diisocyanate-terminated polyamide oligomers, which were preformed from a mixture of two dicarboxylic acids and an excess of diisocyanate^{6,7}. Our next efforts were directed towards the preparation of new, simple polyether-polyamide multiblock copolymers via the diisocyanate route starting from commercially available POTM-diol.

In this paper, we report a straightforward synthesis of POTM-polyamide multiblock copolymers of high molecular weights from combinations of POTM-diol and α,ω -diisocyanate-terminated polyamide oligomers derived from 4,4'-methylenebis(phenyl isocyanate) (MDI) and a mixture of isophthalic acid (IPA) and azelaic acid (AZA). The synthetic procedure, referred to as a two-step method, is effective for the synthesis of multiblock copolymers having high structural regularity, compared with the one-step method, where all of the reaction components are reacted together. The properties of the resulting multiblock copolymers such as solubility, thermal behaviour and mechanical properties are also discussed in detail.

EXPERIMENTAL

Materials

POTM-diols having number-average molecular weights of 1000, 2000 and 2900 were obtained from Du Pont Co., and were dried at 80°C under vacuum before use. MDI and dibutyltin dilaurate were obtained commercially and purified by vacuum distillation. IPA and AZA were purified by recrystallization from aqueous methanol and water, respectively. Tetramethylene-sulphone (sulpholane) and *N,N*-dimethylacetamide (DMAc) were purified by distillation over calcium hydride. 3-Methyl-1-phenyl-2-phospholene 1-oxide was prepared according to the reported procedure⁸.

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Measurements

I.r. spectra were recorded on a Hitachi EP-G3 spectrophotometer. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) of the polymers were determined with a Waters 150C gel permeation chromatograph (g.p.c.) apparatus at 140°C, *N,N*-dimethylformamide (DMF) being used as an eluent and polystyrene as calibration standard. Thermogravimetry (t.g.) and differential scanning calorimetry (d.s.c.) were performed with a Shimadzu TGA-30M thermal analyser, and a Daini Seikosha SSC-580 differential scanning calorimeter, respectively. Dynamic thermo-mechanical analysis (d.m.a.) was performed 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⁻¹. 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⁻¹. Measurements were performed at room temperature with film specimens (0.1 mm thick, 1.0 cm wide and 5.0 cm gauge length) and an average of five individual determinations was taken.

Synthesis of multiblock copolymers

Copolymer 3ab(II) by two-step method. A mixture of 0.3821 g (2.3 mmol) of IPA, 0.4329 g (2.3 mmol) of AZA and 2.4 mg (0.0125 mmol) of 3-methyl-1-phenyl-2-phospholene 1-oxide in 10 ml of sulpholane was heated with stirring at 200°C under nitrogen. To the solution, 1.2513 g (5.0 mmol) of MDI in 5 ml of sulpholane was added dropwise over a period of 5 min with stirring. After 20 min, a solution of 0.8000 g (0.4 mmol) of POTM-diol and 6.3 mg (0.01 mmol) of dibutyltin dilaurate in 6 ml of methylene chloride was added dropwise, and then the methylene chloride was distilled out. The mixture was stirred for another 2 h at 200°C. 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 under vacuum. The polymer weighed 2.32 g (95%) and had an inherent viscosity of 0.72 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ in DMAc 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 infra-red (i.r.) spectrum (film) exhibited absorptions at 3300 cm⁻¹ (N-H), 1730 cm⁻¹ (urethane C=O), 1655 cm⁻¹ (amide C=O) and 1110 cm⁻¹ (C-O-C). Analysis calculated for (C_{148.9}H_{189.4}N₁₀O_{21.4})_n: C, 72.65; H, 7.75; N, 5.69%. Found: C, 72.31; H, 8.06; N, 5.52%.

Other multiblock copolymers of the 3(II) series were prepared by an analogous two-step procedure.

Copolymer 3ad(I) by one-step method. A mixture of 0.2990 g (1.8 mmol) of IPA, 0.3388 g (1.8 mmol) of AZA, 2.800 g (1.4 mmol) of POTM-diol, 6.3 mg (0.01 mmol) of dibutyltin dilaurate and 2.4 mg (0.0125 mmol) of 3-methyl-1-phenyl-2-phospholene 1-oxide in 20 ml of sulpholane was heated with stirring at 200°C under nitrogen. To the solution, a solution of 1.2513 g (5.0 mmol) of MDI in 5 ml of sulpholane was added dropwise, and the mixture was stirred for another 2 h at 200°C. The

polymer was isolated and purified by the same procedure as that described above. The yield of the polymer was 4.10 g (95%) and the inherent viscosity was 1.04 dl g⁻¹ in DMAc. The i.r. spectrum (film) showed absorptions at 3300 cm⁻¹ (N-H), 1730 cm⁻¹ (urethane C=O), 1655 cm⁻¹ (amide C=O) and 1110 cm⁻¹ (C-O-C). Analysis calculated for (C_{249.6}H_{400.4}N₁₀O_{47.1})_n: C, 69.80; H, 9.40; N, 3.26%. Found: C, 69.11; H, 9.21; N, 3.27%.

Other block copolymers of the 3(I) series were prepared by an analogous one-step procedure.

RESULTS AND DISCUSSION

Synthesis and characterization

POTM-polyamide multiblock copolymers were synthesized according to *Scheme 1* by the one-step and two-step methods. Three POTM-diols having \bar{M}_n of 2000 (2a), 1000 (2b) and 2900 (2c) were used in this study, and the average degrees of polycondensation (*x*) were 27.5, 13.5 and 40, respectively.

In the two-step procedure, the solution of α,ω -diisocyanate-terminated polyamide oligomers 1a-1h having \bar{M}_n of 8300, 4100, 2000, 1100, 630, 530, 5500 and 1600 were prepared by the reaction of calculated excess of MDI with a mixture of IPA and AZA in sulpholane in the presence of 3-methyl-1-phenyl-2-phospholene 1-oxide as a condensation catalyst. To accelerate the solubilization of the polyamide oligomers in sulpholane, a mixture of two dicarboxylic acids was used. After that, POTM-diol 2 was added to the solution just prepared, and the reaction was continued in the presence of dibutyltin dilaurate as a urethane-forming catalyst, affording POTM-polyamide multiblock copolymers 3(II), whose POTM and polyamide blocks were connected with urethane linkages. As shown in *Table 1*, the multiblock copolymers of the 3(II) series having inherent viscosities of 0.61-1.10 dl g⁻¹ were obtained readily. Two pairs of block copolymers 3cb(II) and 3fb(II), and 3gc(II) and 3hc(II), derived from POTM 2b and 2c, were prepared to investigate the effect of the POTM block length on the thermal and mechanical properties.

The one-step procedure, where the reaction components, POTM-diol, MDI, IPA and AZA, were reacted all together in sulpholane in the presence of 3-methyl-1-phenyl-2-phospholene 1-oxide and dibutyltin dilaurate,

Scheme 1

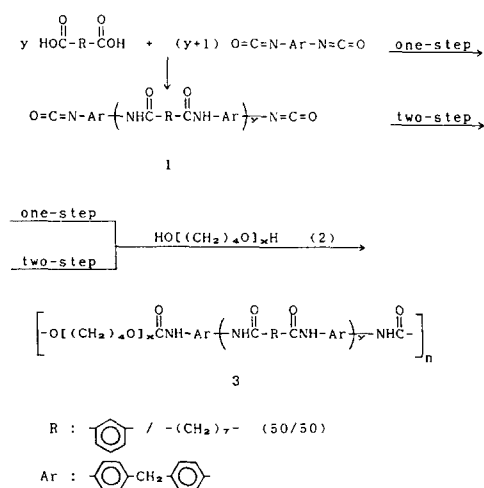


Table 1 Synthesis of POTM-polyamide multiblock copolymers

Method of synthesis	POTM-diol		Polyamide oligomer				Block copolymer				
	Code	\bar{M}_n	Code	γ	\bar{M}_n^b	η_{inh}^c (dl g ⁻¹)	POTM content (%)		Yield (%)	η_{inh}^c (dl g ⁻¹)	
							Calcd ^d	Obsd ^e			
I	2a	2000	1a	24	-	-	3aa(I)	19	18	96	0.67
I	2a	2000	1b	12	-	-	3ab(I)	33	31	100	0.95
I	2a	2000	1c	6	-	-	3ac(I)	50	47	91	0.72
I	2a	2000	1d	3	-	-	3ad(I)	65	63	97	1.09
I	2a	2000	1e	2	-	-	3ae(I)	76	71	93	0.96
II	2a	2000	1a	24	8300	0.41	3aa(II)	19	20	92	0.96
II	2a	2000	1b	12	4100	0.29	3ab(II)	33	35	95	0.72
II	2a	2000	1c	6	2000	0.18	3ac(II)	50	52	93	0.81
II	2a	2000	1d	3	1100	0.13	3ad(II)	65	63	95	1.04
II	2a	2000	1e	2	630	0.10	3ae(II)	76	75	90	0.76
II	2b	1000	1c	6	2000	0.18	3bc(II)	33	31	99	0.82
II	2b	1000	1f	2	530	0.09	3bf(II)	65	66	100	0.61
II	2c	2900	1g	16	5500	0.32	3cg(II)	33	32	94	1.07
II	2c	2900	1h	5	1600	0.15	3ch(II)	65	68	98	1.10

^a I, one step method; II, two-step method

^b Calculated from the reactants in the feed

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

^d Weight (POTM-diol)/[weight(POTM-diol) + weight(polyamide)] in the feed

^e Calculated from the elemental analysis (nitrogen content)

gave **3(I)**-series block copolymers with inherent viscosities of 0.67–1.09 dl g⁻¹.

The structure of the resulting copolymers was confirmed to be the proposed block copolymers by means of i.r. spectroscopy and elemental analysis. In the i.r. spectra of the block copolymers, characteristic amide absorptions at 3300 cm⁻¹ (N-H) and 1655 cm⁻¹ (C=O), urethane carbonyl absorption at 1730 cm⁻¹ and an ether absorption at 1100 cm⁻¹ were observed. The elemental analysis values were in fairly good agreement with the calculated values (Table 2). The observed POTM contents of the block copolymers, calculated from the nitrogen content in the elemental analysis, are also shown in Table 1. The observed POTM contents agreed well with those calculated from the reactants in the feed.

Figure 1 shows the g.p.c. curves of the block copolymers **3ab(II)** and **3ad(II)**, and POTM-diol eluted by DMF. In the case of the block copolymers, \bar{M}_n and \bar{M}_w values are 28 700 and 89 000 for **3ab(II)**, and 25 600 and 110 000 for **3ad(II)**, respectively, relative to standard polystyrene. From these results, these copolymers were undoubtedly multiblock copolymers, whose average degree of polycondensation (n) was estimated to be 4–8.

Thus, the present diisocyanate method, either one-step or two-step procedures, was straightforward for the preparation of POTM-polyamide multiblock copolymers from POTM-diol.

Properties

Solubility behaviour. The qualitative solubility behaviour of the multiblock copolymers in organic solvents, as well as of the parent POTM-diol and the polyamide derived from MDI and a mixture of IPA and AZA (50/50 molar ratio), was examined. All the block copolymers of the whole POTM composition ranges, irrespective of the synthetic methods, dissolved quite readily in amide-type

Table 2 Elemental analysis of POTM-polyamide multiblock copolymers

Block copolymer	Calcd (%)			Found (%)		
	C	H	N	C	H	N
3aa(I)	74.05	7.13	6.74	74.00	7.43	6.86
3aa(II)	74.05	7.13	6.74	73.49	7.36	6.69
3ac(I)	70.84	8.55	4.34	70.80	8.85	4.56
3ac(II)	70.84	8.55	4.34	70.00	8.81	4.13
3ae(I)	68.20	9.72	2.37	68.44	9.91	2.69
3ae(II)	68.20	9.72	2.37	67.61	9.99	2.37

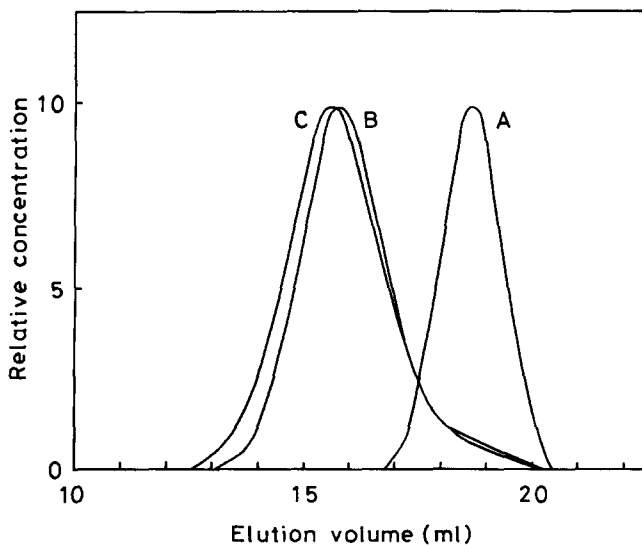


Figure 1 G.p.c. curves of POTM-diol **2a** (A) and multiblock copolymers **3ab(II)** (B) and **3ad(II)** (C)

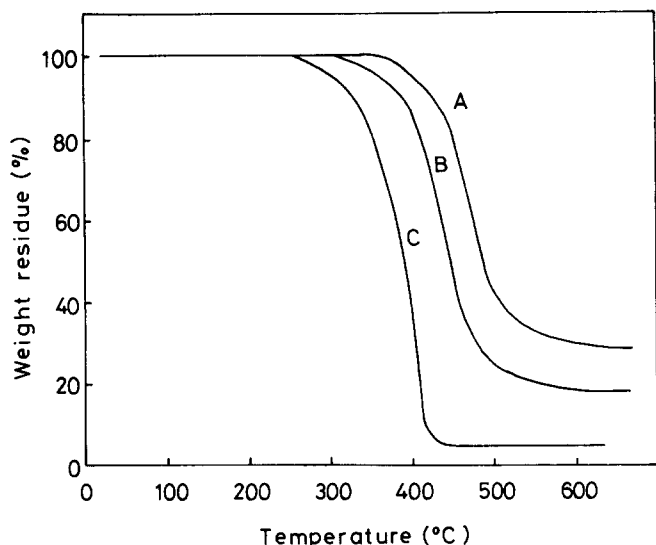


Figure 2 T.g. curves in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$ for the parent polyamide (A), multiblock copolymer **3ac(II)** (B) and POTM-diol **2a** (C)

solvents such as DMF and DMAc, dimethyl sulphoxide and *m*-cresol, which are good solvents for both POTM-diol and the parent polyamide. These block copolymers gave transparent, ductile and elastic films by casting from the DMAc solutions.

Thermal behaviour. The thermal behaviour of the multiblock copolymers was evaluated by means of t.g., d.s.c. and d.m.a. *Figure 2* shows typical t.g. curves in nitrogen for the representative multiblock copolymers of the **3(II)** series, as well as for the parent POTM-diol and the polyamide. The t.g. curves of all the block copolymers lie between the curves of the polyamide and that of POTM-diol. The thermal decomposition temperature (10% weight-loss temperature) of the multiblock copolymers decreased with increase in the POTM content in the block copolymers, from 430°C for the polyamide, reaching to 330°C for POTM-diol.

Figure 3 shows the d.s.c. curves of the **3(II)** series of block copolymers, as well as of the parent polyamide and POTM-diol. The dynamic mechanical storage modulus (E') and the dissipation factor ($\tan \delta$) of the **3(II)** series multiblock copolymers and the parent polyamide plotted as a function of temperature are given in *Figure 4*. *Table 3* summarizes the results of d.s.c. and d.m.a. measurements for all the multiblock copolymers. *Figure 5* shows the glass transition temperature (T_g) of the polyamide phase and that of the POTM phase plotted as a function of the polyamide block length (\bar{M}_n). These results clearly indicate that the POTM-polyamide multiblock copolymers had well microphase-separated morphology between the POTM and polyamide segments.

In general, the two-phase polymers that segregate into distinct domains exhibit two T_g values identical with those of the component polymers. In contrast, as shown in *Figure 5* (curve **3(II)**: d.s.c.), the T_g of the POTM domain in the multiblock copolymers of the **3a** series is substantially lower than that of POTM-diol **2a** ($T_g = -88^{\circ}\text{C}$). That is, depression of T_g takes place in the soft domain of the block copolymers. The T_g depression of the POTM domain was also confirmed by the d.m.a. measurements, in which the $\tan \delta$ peak temperature that corresponds to T_g was observed at -57 to -83°C . A

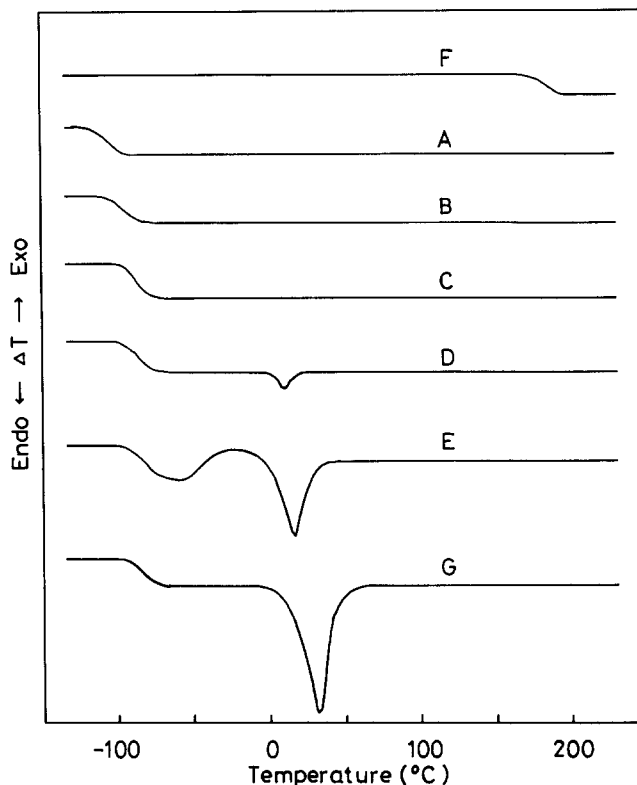


Figure 3 D.s.c. curves at a heating rate of $20^{\circ}\text{C min}^{-1}$ for multiblock copolymers **3aa(II)** (A), **3ab(II)** (B), **3ac(II)** (C), **3ad(II)** (D), **3ae(II)** (E), the parent polyamide (F) and POTM-diol **2a** (G)

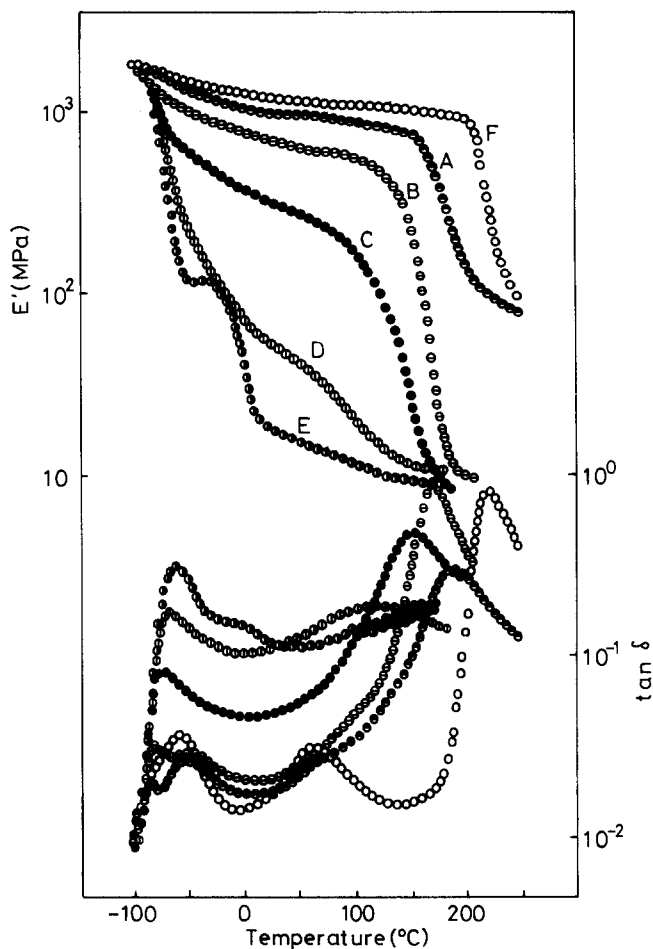
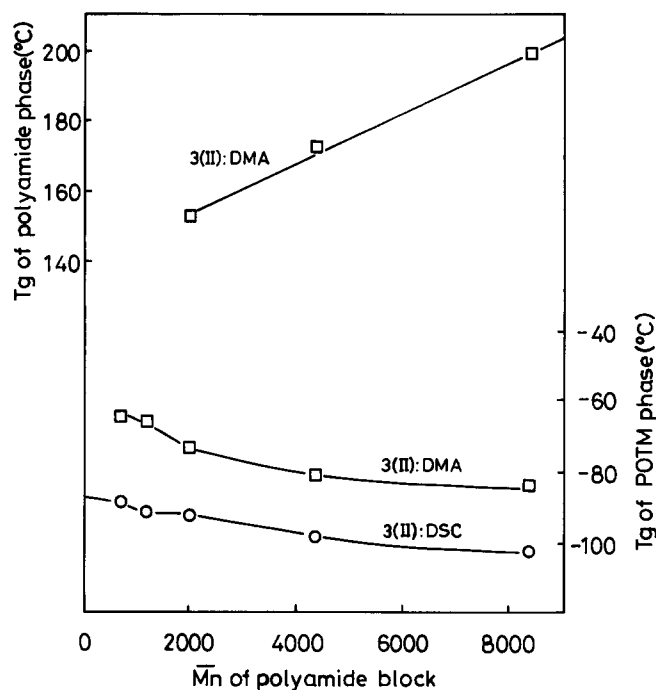


Figure 4 Temperature dependence of the dynamic mechanical storage modulus (E') and the dissipation factor ($\tan \delta$) at 11 Hz at a heating rate of $3^{\circ}\text{C min}^{-1}$ for multiblock copolymers **3aa(II)** (A), **3ab(II)** (B), **3ac(II)** (C), **3ad(II)** (D), **3ae(II)** (E) and the parent polyamide (F)

Table 3 Glass transition temperatures (T_g) and melting temperatures (T_m) of POTM-polyamide multiblock copolymers

Block copolymer	POTM content (wt%)	POTM phase			Polyamide phase
		T_m^a (°C)	T_g^a (°C)	T_g^b (°C)	T_g^b (°C)
3aa(I)	19	—	-100	-77	197
3aa(II)	19	—	-103	-83	199
3ab(I)	33	—	-97	-73	179
3ab(II)	33	—	-98	-81	173
3ac(I)	50	—	-93	-65	145
3ac(II)	50	—	-93	-73	153
3ad(I)	65	7	-90	-59	N.O. ^d
3ad(II)	65	9	-91	-65	N.O.
3ae(I)	76	11	-85	-57	N.O.
3ae(II)	76	18	-88	-63	N.O.
POTM-diol 2a	100	30	-88	—	—
3bc(II)	33	—	-85	-63	131
3bf(II)	65	—	-83	-53	N.O.
POTM-diol 2b	100	28	-87	—	—
3cg(II)	33	—	-99	-83	183
3ch(II)	65	20	-93	-65	N.O.
POTM-diol 2c	100	40	-91	—	—
Polyamide ^c	0	—	—	—	206 (184) ^a

^a Determined by d.s.c. at a heating rate of 20°C min⁻¹ in nitrogen^b Determined by d.m.a. at a heating rate of 3°C min⁻¹^c Polyamide prepared by the reaction of MDI with IPA/AZA (50/50)^d Not observed**Figure 5** Glass transition temperatures of POTM phase and polyamide phase as a function of polyamide block length

similar unusual phenomenon of T_g depression of soft polybutadiene domain was observed in the polybutadiene-polyamide multiblock copolymers⁹⁻¹¹. To our knowledge, this is the first example of T_g depression of soft polyether domain in polyether-based multiblock copolymers. The T_g depression of the POTM domain may be explained plausibly on the basis of the negative pressure resulting from differential contraction due to thermal expansion mismatch upon cooling from the liquid state⁹.

In more detail, the T_g of the soft POTM phase lowered with decreasing POTM content or with increasing polyamide block length (\bar{M}_n). The T_g of the hard

polyamide phase was also observed in the range of 145–199°C for 3aa–3ac block copolymers by the d.m.a. measurements, which markedly rose with increasing polyamide block length. The T_g behaviour of both POTM and polyamide phases suggested that the POTM-polyamide multiblock copolymers having lower POTM content or composed of longer polyamide block length exhibited a higher degree of microphase-separated morphology, compared with block copolymers with higher POTM content, in which some interfacial phase mixing occurred.

Furthermore, the effect of POTM block length on the T_g behaviour of both segments was investigated. Multiblock copolymers 3cg(II) and 3ch(II), based on POTM-diol 2c with longer POTM block length, exhibited much lower T_g of soft POTM phase at -99 and -93°C, compared with corresponding block copolymers 3ab(II) and 3ad(II), derived from 2a. On the other hand, block copolymers 3bc(II) and 3bf(II), derived from POTM-diol 2b with shorter POTM chain length, exhibited much higher T_g of POTM phase, and T_g depression of the soft phase was no longer observed. It is also noteworthy that the T_g of hard phases is influenced by the soft-block length. The T_g of hard polyamide phase became lower with decreasing POTM block length, as shown in 3ac(II) and 3bc(II), which have the same hard-block length. These behaviours suggested that the longer the POTM block length, the higher the degree of microphase separation.

The T_g values of both soft and hard phases were also greatly influenced by the synthetic method for the block copolymers. The extent of the low- T_g depression was more gradual and that of the high- T_g depression was more steep for the 3(I) series of block copolymers than for the 3(II) series. This fact may suggest that the 3(I) series block copolymers are more randomly coupled block copolymers with some irregular structures, while the 3(II) series block copolymers have better-defined microphase-separated structures. The d.s.c. endothermic peak due to the melting temperature (T_m) of the POTM crystallites was observed in the range from 7 to 18°C for block copolymers 3ad and 3ae with higher POTM content. A much higher T_m of the block copolymers 3ad(II) and 3ae(II) than that of the corresponding 3(I) series block copolymers may also reflect higher structural regularity of the former block copolymers.

Tensile properties. Figure 6 shows the stress-strain curves of the films of the multiblock copolymers prepared by solution casting with DMAc, and the tensile properties are summarized in Table 4. All the films have ductile and elastic properties depending markedly on the POTM content, i.e. the content of the polyamide segments, which act as pseudo-crosslinking sites. The values of both tensile strength (T) and tensile modulus (M) generally decreased with increasing POTM content, whereas those of elongation at break (E) increased. In the case of the films of block copolymers 3aa and 3ab with lower POTM content, yield points were observed at an elongation between 5 to 10%, which strongly suggested a continuous nature of the polyamide phase. Thus, the tensile properties of the parent polyamide film could be greatly improved by the incorporation of POTM units into the block copolymer backbone, giving 3aa and 3ab with tough and ductile properties. At higher POTM content, on the other hand, a more pronounced elastic property was observed

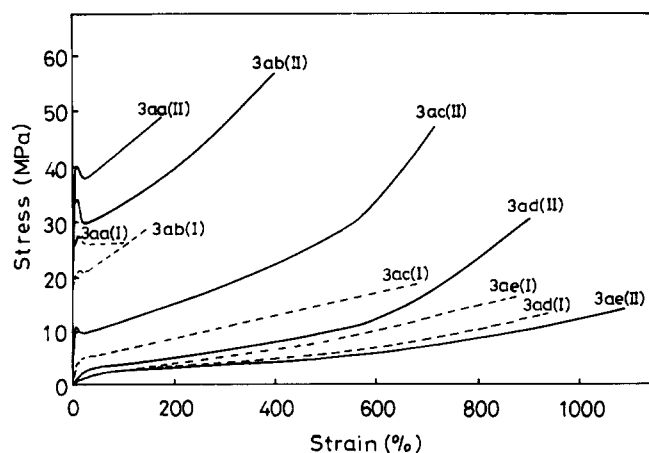


Figure 6 Stress-strain curves for multiblock copolymers 3aa-ae(I) and 3aa-ae(II)

Table 4 Tensile properties of films of POTM-polyamide multiblock copolymers^a

Block copolymer		Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
Code	POTM content ^b (%)			
3aa(I)	18	26	90	480
3aa(II)	20	49	180	900
3ab(I)	31	28	140	420
3ab(II)	35	57	400	720
3ac(I)	47	18	670	61
3ac(II)	52	48	720	220
3ad(I)	63	13	930	5.8
		(16)	(810)	(7.6)
3ad(II)	63	31	900	15
		(33)	(840)	(13)
3ae(I)	71	16	870	4.3
		(12)	(740)	(3.9)
3ae(II)	75	14	1100	5.4
		(18)	(890)	(8.1)
3bc(II)	31	49	300	530
3bf(II)	66	25	1000	12
3cg(II)	32	60	460	540
3ch(II)	68	28	620	25
Polyamide ^c	-	73	15	2200

^a Tensile data given in parentheses are those of hot-pressed film

^b Observed value

^c Polyamide prepared by the reaction of MDI with IPA/AZA (50/50)

for the multiblock copolymers, no doubt due to the more continuous nature of the POTM phase. Over the whole composition ranges, the multiblock copolymer films were between a tough and ductile film having $T/E/M$ values of 49 MPa/180%/900 MPa and an elastic film with values 14 MPa/1100%/5.4 MPa.

The effect of soft POTM block length at constant POTM content on the tensile properties of the films was not clearly observed. A decrease of the POTM block length generally led to the films having slightly lower T and lower M .

The multiblock copolymer films could also be obtained by hot-pressing, and the tensile data of some hot-pressed films are given in Table 4. The films of block copolymers 3ad and 3ae prepared by hot-pressing were found to be very similar in tensile properties to those prepared by solution casting.

The method of preparation of the multiblock copolymers also had a strong influence on tensile properties of the films, and the films of the 3(II) series block copolymers prepared by the two-step method generally exhibited higher T , higher E and higher M , compared with the films of the 3(I) series obtained by the one-step method. This suggested that the 3(II) series block copolymers had higher structural regularity, while the 3(I) series had irregularly coupled structures. Similar results were reported for the polyoxyethylene-polyamide multiblock copolymers^{7,12}.

The films of POTM-polyamide multiblock copolymers thus obtained had balanced, excellent tensile properties and compared favourably with commercial thermoplastic elastomers. For example, the tensile properties of block copolymer 3ac(II) film with $T/E/M$ values of 48 MPa/720%/220 MPa were almost comparable to Du Pont's 'Hytrell' poly(ether-ester) thermoplastic elastomer with values 21 MPa/550%/66 MPa, and to ATO Chem.'s 'Pebax' poly(ether-amide) thermoplastic elastomer with T/E values of 33 MPa/620%.

In conclusion, the POTM-polyamide multiblock copolymers with lower POTM content can be used as transparent and toughened polyamide plastics, whereas the multiblock copolymers having moderate to high POTM content may be considered as new candidates for transparent thermoplastic elastomers.

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