

Synthesis and Properties of Multiblock Copolymers Based on Polydimethylsiloxane and Piperazine-Aromatic Polyamides

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Synopsis

Polydimethylsiloxane (PDMS)–polyamide multiblock copolymers were synthesized by three different methods, i.e., two-step low-temperature solution polycondensation, one-step solution polycondensation, and interfacial polycondensation. In the two-step method, α,ω -diacid chloride-terminated polyamide oligomers were prepared from *trans*-2,5-dimethylpiperazine (DMP) and terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC) in chloroform in the presence of triethylamine, which in turn were subjected to reaction with α,ω -bis(3-aminopropyl) polydimethylsiloxane (PDMS–diamine) in the same solvent to form multiblock copolymers. In the one-step method, the reaction components, DMP, TPC (or IPC), and PDMS–diamine, were reacted altogether in chloroform in the presence of triethylamine. In the interfacial method, the reaction components were also reacted altogether in an aqueous sodium hydroxide–chloroform two-phase system. These polycondensations afforded the multiblock copolymers having inherent viscosities of 0.1–1.3 dL g⁻¹ in *m*-cresol. The PDMS–polyamide multiblock copolymers dissolved in formic acid and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and transparent, ductile, and elastomeric films were obtained by casting from the HFIP solutions. The films of the multiblock copolymers prepared by three different methods exhibited similar properties by means of thermal analysis and tensile measurements. In the multiblock copolymers, the tensile strength and modulus of the films decreased with increasing the PDMS content, whereas the elongation at break increased.

INTRODUCTION

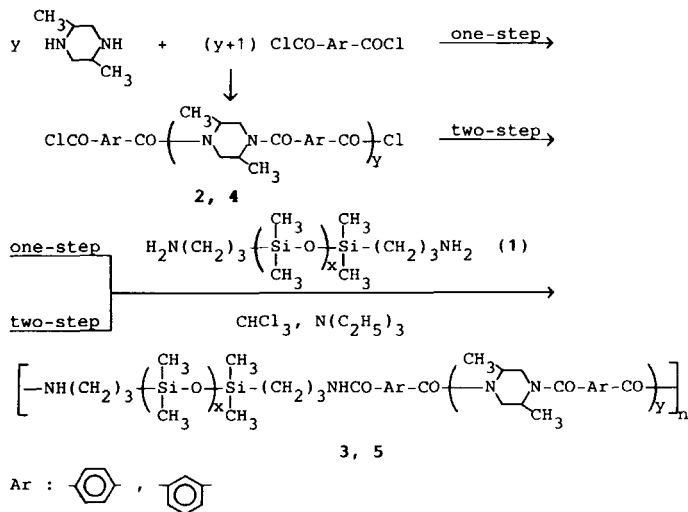
Polysiloxanes such as polydimethylsiloxane (PDMS) possess unique properties of extremely low glass transition temperatures (-123°C), high thermal and oxidative stability, low surface energy, high water repellency, good electrical properties, high permeability to many gases, and good biocompatibility, and have led to their widespread applications in many fields. Despite these unique properties, PDMS elastomers or resins have a shortcoming of rather weak mechanical properties. The weakness of PDMS can be effectively improved through block copolymerization. Several block copolymers composed of a hard segment and PDMS as the soft segment have already been synthesized and characterized.¹ However, little is known about the synthesis of the block copolymers based on PDMS and the hard segments having strong enough intermolecular forces such as polyamides and polyureas. Fellers and his co-workers^{2,3} reported the synthesis of ABA-type triblock copolymers of PDMS and poly(*m*-phenyleneisophthalamide) by the reaction of α,ω -diacid chloride-terminated PDMS oligomers with a large excess of α,ω -diamine-terminated polyamide oligomers in a mixture of dimethylacetamide and

dichloromethane in the presence of triethylamine. McGrath and his group⁴⁻⁷ demonstrated the preparation of segmented PDMS-urea copolymers by the solution polymerization of α,ω -bis(3-aminopropyl)polydimethylsiloxanes (PDMS-diamines) with various aromatic and cycloaliphatic diisocyanates such as methylenebis(4-phenyl isocyanate), 2,4-tolylene diisocyanate, and methylenebis(4-cyclohexyl isocyanate) in di(2-ethoxyethyl) ether or tetrahydrofuran.

Recently we reported the synthesis of the multiblock copolymers by the direct polycondensation of PDMS-diamines with α,ω -dicarboxylic acid-terminated aromatic polyamide oligomers, derived from 3,4'-oxydianiline and isophthalic acid, using triphenyl phosphite and pyridine as the condensing agents.⁸ The PDMS-polyamide multiblock copolymers obtained by this method were not of sufficiently high molecular weights, and this suggested the inadequate choice of reaction medium of pyridine, which is a good solvent for the polyamides but a poor solvent for PDMS. Thus we were encountered again by the problem of the restrictions with respect to the suitable solvents for both PDMS and polyamides.

Morgan and Kwolek⁹ demonstrated earlier that high-molecular-weight polyamide could be obtained in a clear solution by the polycondensation of *trans*-2,5-dimethylpiperazine (DMP) with terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC) in chloroform in the presence of triethylamine. This had led to the suggestion that the problem of solvents for the block copolymer synthesis might be overcome with the use of this polymerization system coupled with PDMS which are readily soluble in chloroform.

This article deals with a successful synthesis of PDMS-polyamide multiblock copolymers of high molecular weights from combinations of PDMS-diamine and α,ω -diacid chloride-terminated polyamide oligomers from DMP and TPC or IPC. This synthetic procedure, referred to as a two-step method, is advantageous for the synthesis of the multiblock copolymers having high structural regularity, compared with the most convenient one-step method, where all of the reaction components are reacted altogether (Scheme 1):



Scheme 1

Another synthetic procedure, interfacial method, where all the reagents are reacted altogether in an aqueous sodium hydroxide-chloroform system, was also investigated for comparison.

EXPERIMENTAL

Materials

Three PDMS-diamines (**1a-1c**), having number average molecular weights of 840, 1720, and 5600, were obtained from Shinetsu Chemicals Co., Tokyo and Chisso Co., Tokyo, and dried at 120°C *in vacuo* before use. DMP was purified by recrystallization from acetone. TPC, IPC, triethylamine (TEA), and chloroform were purified by distillation.

Synthesis of Multiblock Copolymers

Copolymer 3bb(II) by the Two-step Method

A solution of 0.342 g (3.00 mmol) of DMP and 0.9 mL (6.0 mmol) of TEA in 6 mL of chloroform was added dropwise to a stirred solution of 0.812 g (4.00 mmol) of TPC in 12 mL of chloroform at 0°C in an ice-water bath under dry nitrogen. After 1 h of stirring, to the reaction solution was added dropwise with stirring a solution of 1.72 g (1.00 mmol) of **1b** and 0.3 mL (2.0 mmol) of TEA in 12 mL of chloroform, and the mixture was stirred for 1 h under the same conditions. Then the ice-water bath was removed and the reaction was continued for another 1 h at room temperature. During this period, the polymerization proceeded in a homogeneous clear (but slightly turbid) solution. The polymer was isolated by pouring the reaction mixture into 700 mL of methanol. The product was purified by thorough washing with methanol and hexane, and dried *in vacuo*. The polymer weighed 1.91 g (74%) and had an inherent viscosity of 0.45 dL g⁻¹ in *m*-cresol at 30°C. The IR spectrum (film) exhibited an amide carbonyl absorption at 1620 cm⁻¹.

ANAL Calcd: C, 46.33; H, 7.64; N, 4.32%. Found: C, 46.83; H, 7.88; N, 5.02%.

Other multiblock copolymers of the **3(II)**-series were prepared by the analogous two-step procedure. Multiblock copolymers of the **5(II)**-series, where IPC was used in place of TPC, were also synthesized analogously except for the isolation of the copolymers through precipitation with boiling water.

Copolymer 3bb(I) by the One-step Method

To a solution of 1.72 g (1.00 mmol) of **1b**, 0.342 g (3.00 mmol) of DMP, and 1.2 mL (8.0 mmol) of TEA in 18 mL of chloroform was added dropwise with stirring a solution of 0.812 g (4.00 mmol) of TPC in 12 mL of chloroform. The mixture was stirred at 0°C for 1 h and at room temperature for another 1 h under nitrogen. The reaction proceeded homogeneously and the polymer was isolated by the same procedure as that described above. The yield was 2.24 g (87%) and the inherent viscosity was 0.52 dL g⁻¹ in *m*-cresol. The IR spectrum (film) showed an amide carbonyl absorption at 1620 cm⁻¹.

ANAL Calcd: C, 46.33; H, 7.64; N, 4.32%. Found: C, 46.79; H, 7.58; N, 4.40%.

Other block copolymers of the 3(I)-series and the 5(I)-series were prepared by the analogous one-step procedure.

Copolymer 3bb(III) by Interfacial Polymerization

To a solution of 0.342 g (3.00 mmol) of DMP and 0.32 g (8.0 mmol) of sodium hydroxide in 20 mL of distilled water was added a solution of 1.72 g (1.00 mmol) of **1b** and 0.812 g (4.00 mmol) of TPC in 20 mL of chloroform in one portion, and the mixture was stirred vigorously at 25°C for 2 h. The polymer was isolated as described above. The product weighed 2.27 g (88%) – and had an inherent viscosity of 0.23 dL g⁻¹ in *m*-cresol. The IR spectrum (film) exhibited an amide carbonyl absorption at 1640 cm⁻¹.

Anal Calcd: C, 46.33; H, 7.64; N, 4.32%. Found: C, 50.00; H, 7.62; N, 5.51%.

Other block copolymers of the 3(III)-series and the 5(III)-series were synthesized by the analogous interfacial procedure.

Measurements

IR and ¹H-NMR spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JEOL FX-90Q Fourier transform spectrometer, respectively. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-30M and TGA-30M, respectively. Differential scanning calorimetry (DSC) was performed with a Daini Seikosha SSC-560 differential scanning calorimeter. Small-angle X-ray diffraction patterns were obtained on a Rigakudenki RU-200 X-ray diffraction apparatus with nickel-filtered CuK α radiation (50 kV, 200 mA). Tensile properties 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 (5 mm wide, 35 mm long, and 0.1 mm thick) and an average of at least five individual determinations was taken.

RESULTS AND DISCUSSION

Synthesis of PDMS–Polyamide Multiblock Copolymers

Synthetic scheme for PDMS–polyamide multiblock copolymers is shown in Scheme 1. PDMS–diamines **1a–1c** used in this study had M_n of 840, 1720, and 5600, and average degree of polycondensation (x) of 9, 21, and 73, respectively.

In the two-step procedure, the solutions of α,ω -dichloroformyl-terminated polyamides **2a–2d** having M_n of 376, 860, 1350, and 1840, and average degree of polycondensation (y) of 1,3,5, and 7, respectively, were prepared by the reaction of a calculated excess of TPC with DMP in the presence of TEA in chloroform. In a similar manner, the solutions of polyamide oligomers **4a**, **4b**, and **4d** were prepared from IPC and DMP. After that, PMDS-diamine **1** was added to the solution of **2** or **4** and the polycondensation was continued to form PDMS–polyamide multiblock copolymers **3** or **5**. As shown in Tables I

TABLE I
Synthesis of Polysiloxane-Polyamide Multiblock Copolymers 3

Method of synthesis ^a	PDMS-diamine		Polyamide oligomer		Block copolymer				
	Code	<i>x</i>	Code	<i>y</i>	Code	PDMS content (%)		Yield (%)	η_{inh}^d (dL g ⁻¹)
						Calcd ^b	Obs ^c		
I	1a	9	2a	1	3aa(I)	69	69	64	0.29
I	1b	21	2a	1	3ba(I)	82	80	63	0.19
I	1c	73	2a	1	3ca(I)	94	96	75	0.29
I	1b	21	2b	3	3bb(I)	67	68	87	0.52
I	1b	21	2c	5	3bc(I)	56	62	91	0.77
I	1b	21	2d	7	3bd(I)	48	49	97	0.81
II	1a	9	2a	1	3aa(II)	69	68	69	0.20
II	1b	21	2a	1	3ba(II)	82	76	67	0.22
II	1c	73	2a	1	3ca(II)	94	95	65	0.25
II	1b	21	2b	3	3bb(II)	67	65	74	0.45
II	1b	21	2c	5	3bc(II)	56	59	80	0.61
II	1b	21	2d	7	3bd(II)	48	47	93	0.72
III	1b	21	2a	1	3ba(III)	82	91	85	0.16
III	1b	21	2b	3	3bb(III)	67	61	88	0.23
III	1b	21	2d	7	3bd(III)	48	46	96	0.62
I	—	—	2e ^e	—	—	0	0	97	2.51

^aI, one-step method; II, two-step method; and III, interfacial method.

^bCalculated from the reactants in feed.

^cCalculated from Si-CH₃/aromatic ratio in the NMR spectrum.

^dMeasured at a concentration of 0.5 g dL⁻¹ in *m*-cresol at 30°C.

^ePolyamide homopolymer.

and II, the multiblock copolymers of the 3(II) and 5(II) series (3 and 5 by the two-step method) having inherent viscosities of 0.2–0.7 dL g⁻¹ were obtained readily.

The simplest one-step procedure, where the reaction components, 1, TPC (or IPC), and DMP, were reacted altogether with TEA in chloroform, gave the

TABLE II
Synthesis of Polysiloxane-Polyamide Multiblock Copolymers 5

Method of synthesis ^a	PDMS-diamine		Polyamide oligomer		Block copolymer				
	Code	<i>x</i>	Code	<i>y</i>	Code	PDMS content (%)		Yield (%)	η_{inh}^d (dL g ⁻¹)
						Calcd ^b	Obs ^c		
I	1b	21	4a	1	5ba(I)	82	84	98	0.12
I	1b	21	4b	3	5bb(I)	67	64	94	0.34
I	1b	21	4d	7	5bd(I)	48	50	94	0.59
II	1b	21	4a	1	5ba(II)	82	86	95	0.18
II	1b	21	4b	3	5bb(II)	67	69	96	0.28
II	1b	21	4d	7	5bd(II)	48	50	90	0.48
III	1b	21	4a	1	5ba(III)	82	89	96	0.09
III	1b	21	4b	3	5bb(III)	67	60	99	0.22
III	1b	21	4d	7	5bd(III)	48	47	87	1.27
I	—	—	4e ^e	—	—	0	0	99	1.70

^{a–e}See footnotes of Table I.

3(I) or **5(I)** series block copolymers (**3** or **5** by the one-step method), having almost the same inherent viscosity values as those obtained for the two-step method. In both two-step and one-step methods, the reactions proceeded in homogeneous solution.

Another synthetic method, interfacial polymerization, was further examined; an aqueous alkaline solution of DMP was reacted with a solution of **1** and TPC (or IPC) in chloroform with vigorous stirring at room temperature. The interfacial polycondensation afforded readily the block copolymers of the **3(III)** or **5(III)** series (**3** or **5** by the interfacial method) having inherent viscosities of 0.1–1.2 dL g⁻¹ (Tables I and II).

As can be seen from Tables I and II, regardless of the synthetic methods, the inherent viscosities of the block copolymers generally decreased with increasing PDMS contents, i.e., the block copolymers of high PDMS contents have low inherent viscosities and the copolymers of low PDMS contents have high viscosity values. This is because *m*-cresol as the solvent for viscosity measurement is a poor solvent for PDMS and a good solvent for the polyamides **2e** and **4e**. Therefore, in the present cases, it should be noted that the inherent viscosity values are not comparable to the molecular weights of the block copolymers. Taking into account the fact that all the block copolymers gave cast films having sufficient tensile properties as discussed later, these block copolymers should be of reasonably high molecular weights.

The structure of the resulting copolymers was confirmed to be the proposed block copolymers by means of IR and NMR spectroscopy and elemental analysis. In the IR spectra, a characteristic amide carbonyl absorption at 1620 cm⁻¹ and two absorptions due to siloxane group at 1090 and 1010 cm⁻¹ appeared. In the ¹H-NMR spectra, three characteristic peaks at 0 ppm (Si-CH₃), 0.8–1.2 ppm (aliphatic H), and 7.0–7.4 ppm (aromatic H) were observed. The observed PDMS contents of the block copolymers, which were calculated from the Si-CH₃/aromatics ratio in the NMR spectra, agreed quite well with the PDMS contents calculated from the reactants in the feed. The elemental analysis values were in fairly good agreement with the calculated values of the block copolymers.

Properties of PDMS–Polyamide Multiblock Copolymers

Table III summarizes the qualitative solubility behavior of multiblock copolymers **3** and **5** in organic solvents, as well as of the parent homopolymers **1**, **2e**, and **4e**. A remarkable feature of the multiblock copolymers is that all the copolymers dissolve readily in *m*-cresol 1,1,1,3,3,3,-hexafluoro-2-propanol (HFIP), and formic acid, which are good solvents for homopolyamides **2e** and **4e** but are nonsolvents for PDMS **1**. Moreover, the multiblock copolymers having high PDMS contents are also soluble in chloroform, a good solvent for PDMS. It is quite reasonable that multiblock copolymers **5** having the unsymmetrical *m*-phenylene linkage in the polymer backbone have a wider range of solubility than multiblock copolymers **3** with a symmetrical structure. All the block copolymers gave transparent, ductile, and elastomeric films by casting from the HFIP or chloroform solutions.

The thermal behavior of the multiblock copolymers was evaluated by means of DTA and TG. Figure 1 shows typical DTA and TG curves of the

TABLE III
Solubility of Polysiloxane-Polyamide Multiblock Copolymers^a

	Polymer					
	1	2e	3aa, 3ba, 3ca, 3bb	3bc, 3bd	4e	5ba, 5bb, 5bd
<i>m</i> -Cresol	-	+	+	+	+	+
Formic acid	-	+	+	+	+	+
HFIP ^b	-	+	+	+	+	+
Chloroform	+	-	+	-	+	+
Tetrahydrofuran	+	-	-	-	-	±
Toluene	+	-	-	-	-	-
Hexane	+	-	-	-	-	-

^aSolubility: +, soluble; ±, swelling; and -, insoluble.

^b1,1,1,3,3,3-hexafluoro-2-propanol.

representative block copolymer **3bd**(II), as well as of the parent PDMS-diamine and homopolyamide **2e**. All the multiblock copolymers are stable up to temperature around 200°C in air, and the onset of decomposition was observed above 200°C in both DTA and TG curves. The limited thermal stability of the multiblock copolymers is mainly due to the presence of piperazine polyamide segments **2** and **4**.

Glass transition temperatures (T_g) of the multiblock copolymers were further evaluated by DSC. In the multiblock copolymers, a sharp T_g for PDMS component was observed at -103°--123°C (Table IV), whereas a T_g for polyamide component could not be detected below 200°C, the temperature of onset of decomposition for the piperazine-based polyamides. The fact that the T_g values are in good agreement with that of parent PDMS (-126°C) supports the microphase-separated structure of PDMS and polyamide segments in the multiblock copolymers. It is quite reasonable that the T_g values of the PDMS segment increased with decreasing PDMS content in the case of multiblock copolymers **3bb** and **3bd**. The T_g values of multiblock copolymer

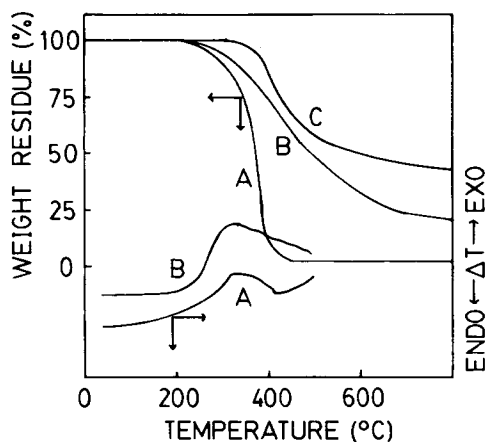


Fig. 1. DTA and TG curves for (A) homopolyamide **2e**, (B) polysiloxane-polyamide multiblock copolymer **3bd**(II), and (C) PDMS-diamine, at a heating rate of 10 K min⁻¹.

TABLE IV
Glass Transition Temperatures (T_g) of Polysiloxane Segment of
Polysiloxane-Polyamide Multiblock Copolymers

Copolymer	T_g^a ($^{\circ}\text{C}$)		
	(I) series	(II) series	(III) series
3bb	-123	-123	-110
3bd	-118	-118	-109
5bd	-114	-114	-103

^a Determined by DSC at a heating rate of 10 K min⁻¹ in air.

5bd having weaker intermolecular interaction due to less symmetrical structure of the polyamide segment **4** increased, compared with those of multiblock copolymer **3bd**.

Among the multiblock copolymers synthesized by three different methods, the **3(II)** and **5(II)** series copolymers, and the **3(I)** and **5(I)** series copolymers showed the same extent of T_g elevation, and this suggested that these copolymers are fairly defined multiblock copolymers with microphase separated structures. On the other hand, the more elevation in temperature of the T_g values of the **3(III)** and **5(III)** series copolymers suggested that these copolymers prepared by the interfacial method are randomly coupled block copolymers with less regular structures.

In order to determine the domain size of the multiblock copolymers, small-angle X-ray scattering studies were performed for the films of **3ba(I)**, (II), and (III), and **3bd(I)**, (II), and (III). A diffraction peak was observed at 0.4° and 0.2° for three **3ba** and three **3bd**, respectively, and the domain size was calculated to be 11 nm for **3ba** having a low content of PDMS component and 23 nm for **3bd** with high PDMS content. The results directly showed that

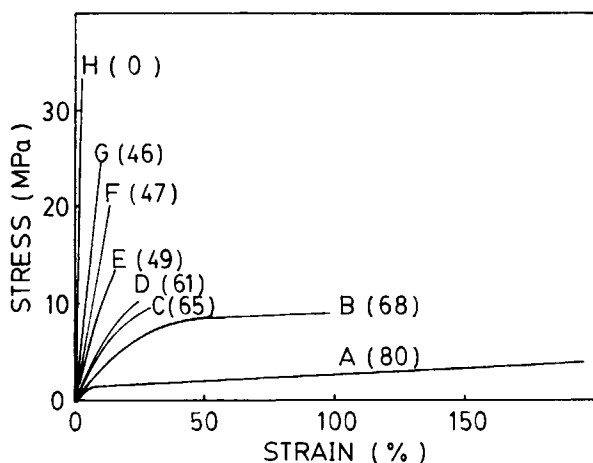


Fig. 2. Stress-strain curves of cast films from HFIP solutions for (A) polysiloxane-polyamide multiblock copolymer **3ba(I)**, (B) **3bb(I)**, (C) **3bb(II)**, (D) **3bb(III)**, (E) **3bd(I)**, (F) **3bd(II)**, (G) **3bd(III)**, and (H) homopolyamide **2e**. The value given in parentheses is the observed polysiloxane content.

TABLE V
Tensile Properties of Films of Polysiloxane-Polyamide Multiblock Copolymers

Code	Block copolymer		Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
	PDMS content ^a (%)	Casting solvent ^b			
3ca(I)	96	HFIP	0.2	40	0.5
3ca(I)	96	Chloroform	1.5	395	1.1
3ca(II)	95	Chloroform	1.6	380	1.1
3ba(I)	80	HFIP	2.5	185	9.0
3ba(I)	80	Chloroform	2.3	345	9.5
3ba(II)	76	HFIP	3.2	140	7.3
3ba(II)	76	Chloroform	3.0	190	7.5
3ba(III)	91	HFIP	2.5	170	2.1
3ba(III)	91	Chloroform	4.0	475	17
3aa(I)	69	HFIP	11.1	60	35
3aa(I)	69	Chloroform	9.4	64	32
3aa(II)	68	Chloroform	10.0	68	35
3bb(I)	68	HFIP	8.7	86	36
3bb(I)	68	Chloroform	7.8	100	38
3bb(II)	65	HFIP	8.3	30	43
3bb(III)	61	HFIP	9.6	27	40
3bc(I)	62	HFIP	8.9	25	57
3bc(II)	59	HFIP	8.4	23	70
3bd(I)	49	HFIP	11.5	18	85
3bd(II)	47	HFIP	20	13	185
3bd(III)	46	HFIP	25	10	250
5ba(I)	84	Chloroform	1.7	150	7.5
5ba(II)	86	Chloroform	1.8	165	10.9
5ba(III)	89	Chloroform	2.8	280	10.4
5bb(I)	64	Chloroform	7.5	110	16
5bb(II)	69	Chloroform	8.3	125	17
5bb(III)	60	Chloroform	9.5	98	17
5bd(I)	50	Chloroform	20	44	63
5bd(II)	50	Chloroform	22	40	77
5bd(III)	47	Chloroform	20	5	400
2e	0	HFIP	35	6	960
4e	0	Chloroform	27	19	800

^a Observed value.

^b HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol.

these transparent films of the multiblock copolymers have microphase separated structures.

The stress-strain curves of the films of multiblock copolymers **3** are shown in Figure 2, and the tensile properties are summarized in Table V. All the films have ductile and elastomeric properties, depending markedly on the content of the polyamide segments which act as pseudocrosslinking sites. The values of both tensile strength and modulus generally increased with increasing the polyamide content, whereas those of elongation at break decreased. Similar structure-property relationships have been reported in polyether-aramid and polybutadiene-aramid multiblock copolymer systems.¹⁰⁻¹⁴

Figure 2 and Table V also revealed that the methods of synthesis of the multiblock copolymers influenced on the tensile properties of their films. The

tensile strength and modulus values tended to increase in the order: the 3(I) and 5(I) series copolymers < the 3(II) and 5(II) series copolymers < the 3(III) and 5(III) series copolymers, and the values of elongation at break tended to decrease in the same order. However, it is thought that these tensile values are governed not by the molecular structures of the multiblock copolymers based on the synthetic methods, but simply by the polyamide content of the multiblock copolymers, because the polyamide contents increase in the above-mentioned order.

The effect of casting solvents for the films was observed on the tensile properties. Since chloroform is a good solvent for PDMS, the films cast from the chloroform solution afforded higher quality films that had higher values of both tensile strength and elongation at break, compared with the films cast from the HFIP solution.

As can be expected, the values of tensile strength and modulus of 3 series multiblock copolymers were generally higher than those of 5 series copolymers. This is because the former 3 series copolymers contain more symmetrical and rigid polyamide backbones affording stronger pseudocrosslinking sites. The results correspond well to the behavior of T_g so that copolymer 3bd has lower T_g than 5bd.

In conclusion, a problem of the reaction solvent for the preparation of PDMS-polyamide multiblock copolymers was overcome with use of chloroform, which dissolves both PDMS and piperazine-based polyamides. These PDMS-polyamide multiblock copolymers having lower PDMS content behave as rubber-toughened polyamide plastics, whereas the block copolymers with higher PDMS levels are analogous to thermoplastic elastomers.

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