Macromolecules

Volume 22, Number 11 November 1989

Synthesis and Characterization of New Multiblock Copolymers Based on Poly(dimethylsiloxane) and Aromatic Polyamides

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Received December 28, 1988; Revised Manuscript Received March 20, 1989

ABSTRACT: A new class of high-temperature-resistant block copolymer materials based on poly(dimethylsiloxane) (PDMS) and aromatic polyamides (aramids) was developed. PDMS–aramid multiblock copolymers of wide ranging compositions were successfully synthesized by low-temperature solution polycondensation through two different procedures. In the two-step method, α,ω-diacid chloride terminated aramid oligomers, which were preformed by the reaction of 3-(4-aminophenoxy)aniline (3,4′-ODA) with isophthaloyl chloride (IPC) in chloroform, were subjected to polycondensation with α,ω-bis(3-aminopropyl)poly(dimethylsiloxane) (PDMS-diamine) in the same flask, leading to the formation of the 3,4′-ODA series multiblock copolymers. In the one-step method, three reaction components, 3,4′-ODA, IPC, and PDMS-diamine, were reacted all together in chloroform. The other multiblock copolymers of the 4,4′-ODA series were synthesized in a similar manner starting from bis[4-[(trimethylsilyl)amino]phenyl] ether (N-silylated 4,4′-ODA), IPC, and PDMS-diamine through the one-step and two-step procedures. The multiblock copolymers of both series having inherent viscosities of 0.2–0.8 $dL \cdot g^{-1}$ were obtained by these polymerizations. They are soluble in *N,N*-dimethylacetamide (DMAc) and could be cast into transparent, ductile, and elastomeric films from the DMAc solutions. Calorimetric measurements showed that the multiblock copolymer films obtained by the two-step method had better defined, microphase-separated morphology than those obtained by the one-step method, and the 4,4′-ODA series multiblock copolymers had better defined structures than the 3,4′-ODA series copolymers. The mechanical properties of films of the PDMS–aramid multiblock copolymers depended markedly on the PDMS content; at low PDMS levels the materials behave as rubber-toughened aramid plastics, and at higher PDMS contents the materials are analogous to thermoplastic elastomers.

Introduction

Poly(dimethylsiloxane) (PDMS) and its block copolymers have many desirable features such as low-temperature flexibility based on a low glass transition temperature (ca. −123 °C), high thermal and oxidative stability, low surface energy, high gas permeability, good dielectric properties, and good biocompatibility, and consequently they have been used widely.[1] The ABA-type triblock copolymers based on PDMS and poly(*m*-phenyleneisophthalamide)[2,3] and the randomly coupled segmented PDMS–urea copolymers[4–7] were synthesized in sufficiently high molecular weights. However, our attempts to prepare multiblock copolymers composed of PDMS and aromatic polyamides (aramids) were of limited success with respect to inherent viscosity of the copolymers,[8,9] probably due to the high degree of imcompatibility of PDMS with aramids having strong intermolecular interactions and to inappropriate choice of the reaction systems. Quite recently, we have prepared multiblock copolymers of relatively high inherent viscosity, based on PDMS and polyamides with no intermolecular hydrogen-bonding forces, both of which are readily soluble in chloroform, by low-temperature solution polycondensation in chloroform.[10]

Morgan demonstrated earlier that poly(*m*-phenyleneisophthalamide) obtained by the low-temperature solution polycondensation remained in solution in chloroform in the presence of triethylamine hydrochloride.[11] This had led us to reinvestigate the synthesis of PDMS-aramid multiblock copolymers in homogeneous chloroform solution system.

We reported herein a successful synthesis of PDMS–aramid multiblock copolymers with high molecular weights from combinations of α,ω-bis(3-aminopropyl)poly(dimethylsiloxane) (PDMS-diamine) and α,ω-diacid chloride terminated aramid oligomers preformed from 3-(4-aminophenyl)aniline (3,4′-ODA) or bis[4-[(trimethylsilyl)amino]phenyl] ether (N-silylated 4,4′-ODA) and isophthaloyl chloride (IPC). This synthetic procedure, re-

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ferred to as two-step method, is advantageous for the preparation of multiblock copolymers having high structural regularity. Another synthetic procedure, the most convenient one-step method, where all the reactants are reacted together, was also investigated for comparison. A basic structure–property relationship are also presented.

Experimental Section

Materials. PDMS-diamine was obtained from Shinetsu Chemical Co., Japan, with a number-average molecular weight of 1720 g·mol^{-1} determined by titration, and dried at 120 °C for 1 h in vacuo. 3,4′-ODA, bis(4-aminophenyl) ether (4,4′-ODA), and triethylamine hydrochloride (TEA·HCl) were purified by recrystallization from chloroform–hexane, tetrahydrofuran, and absolute ethanol, respectively. IPC, triethylamine (TEA), chloroform, and chlorotrimethylsilane were purified by distillation. N-Silylated 4,4′-ODA was prepared from 4,4′-ODA and chlorotrimethylsilane in the presence of TEA in toluene at 80 °C and purified by distillation.

Synthesis of Block Copolymers. Copolymer 3b(II) by the Two-Step Method. A mixture of 0.400 g (2.0 mmol) of 3,4′-ODA, 0.6 mL (4.0 mmol) of TEA, and 0.550 g (4.0 mmol) of TEA·HCl in 4 mL of chloroform was added dropwise with stirring to a solution of 0.609 g (3.0 mmol) of IPC in 4 mL of chloroform at 0 °C on an ice bath under dry nitrogen. After 2 h of stirring, a mixture of 1.72 g (1.0 mmol) of PDMS-diamine and 0.3 mL (2.0 mmol) of TEA in 10 mL of chloroform was added to the reaction solution and the mixture was stirred at 0 °C for 1 h. The ice bath was then removed and the reaction was continued at room temperature for another 3 h under nitrogen. The polymer was isolated by pouring the reaction mixture into 700 mL of methanol. The product was washed successively with methanol and hexane and dried at room temperature in vacuo. The polymer weighed 1.85 g (74% yield) and had an inherent viscosity of 0.36 dL·g^{-1} in DMAc, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. The film for mechanical testing was prepared by casting from a 20% DMAc solution onto a poly(tetrafluoroethylene) plate. The plate was heated at 80 °C for 6 h in air, and then the film was peeled off. The film was washed with hot methanol for 5 h and vacuum-dried at room temperature for 24 h. The IR spectrum (film) exhibited an amide carbonyl absorption at 1620 cm^{-1}. Anal. Calcd: C, 46.70; H, 7.07; N, 3.34. Found: C, 47.70; H, 6.54; N, 3.50.

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

Copolymer 3b(I) by the One-Step Method. To a mixture of 1.72 g (1.0 mmol) of PDMS-diamine, 0.400 g (2.0 mmol) of 3,4′-ODA, 0.550 g (4.0 mmol) of TEA·HCl, and 0.9 mL (6.0 mmol) of TEA in 10 mL of chloroform, 0.609 g (3.0 mmol) of IPC in 8 mL of chloroform was added, and the mixture was stirred at 0 °C for 1 h and at room temperature for another 5 h under nitrogen. The polymer was isolated as described the above. The yield was 2.05 g (82%) and the inherent viscosity in DMAc was 0.21 dL·g^{-1}. The IR spectrum (film) showed an amide carbonyl absorption at 1620 cm^{-1}. Anal. Calcd: C, 46.70; H, 7.07; N, 3.34. Found: C, 47.41; H, 7.00; N, 3.47.

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

Copolymer 5b(II) by the Two-Step Method. A mixture of 0.688 g (2.0 mmol) of N-silylated 4,4′-ODA in 4 mL of chloroform was added to a stirred solution of 0.609 g (3.0 mmol) of IPC and 1.650 g (12.0 mmol) of TEA·HCl in 5 mL of chloroform at 0 °C for 2 h under dry nitrogen. Then a mixture of 1.72 g (1.0 mmol) of PDMS-diamine and 0.3 mL (2.0 mmol) of TEA in 10 mL of chloroform was added to the reaction solution. The mixture was stirred at 0 °C for 1 h and at room temperature for another 3 h. The polymer was isolated by pouring the reaction mixture into 700 mL of methanol. The polymer weighed 2.24 g (89% yield) and had an inherent viscosity of 0.27 dL·g^{-1} in DMAc. The IR spectrum (film) exhibited an amide carbonyl absorption at 1620 cm^{-1}. Anal. Calcd: C, 46.70; H, 7.07; N, 3.34. Found: C, 48.17; H, 6.91; N, 3.62.

Other block copolymers of **5(II)** series were prepared by the analogous two-step procedure.

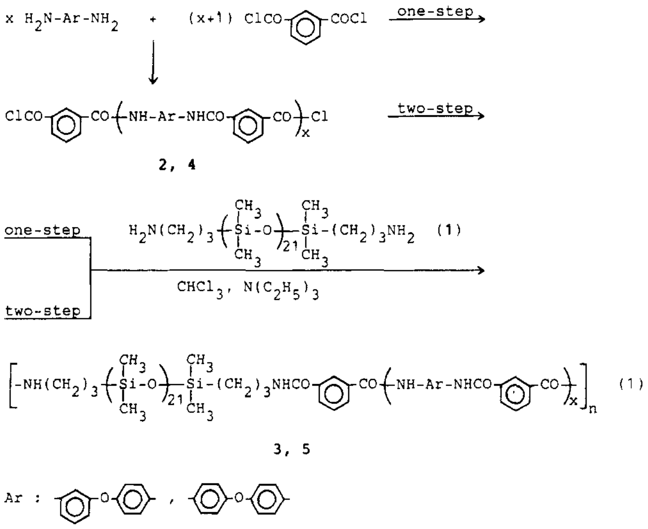
Copolymer 5b(I) by the One-Step Method. To a mixture of 1.72 g (1.0 mmol) of PDMS-diamine, 0.400 g (2.0 mmol) of 4,4′-ODA, 0.9 mL (6.0 mmol) of TEA, and 1.10 g (8 mmol) of TEA·HCl in 10 mL of chloroform, 0.8 mL (6.0 mmol) of chlorotrimethylsilane was added and the mixture of 0.609 g (3.0 mmol) of IPC in 8 mL of chloroform was added to the reaction solution at 0 °C, and the mixture was stirred for 1 h at that temperature and for another 5 h at room temperature under nitrogen. The polymer was isolated as described the above. The yield was 2.13 g (85%) and the inherent viscosity in DMAc was 0.37 dL·g^{-1}. The IR spectrum (film) showed an amide carbonyl absorption at 1620 cm^{-1}. Anal. Calcd: C, 46.70; H, 7.07; N, 3.34. Found: C, 47.47; H, 6.99; N, 3.48.

Other block copolymers of **5(I)** series were obtained by the analogous one-step procedure.

Measurements. IR and ^{1}H NMR spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JEOL FX-100 Fourier transform spectrometer, respectively. Differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) were performed with Shimadzu thermal analyzers DTA-30M, TG-30M, and DSC-41, respectively. 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 Multiblock Copolymers. The synthetic scheme for the PDMS-aramid multiblock copolymers is shown in eq 1. PDMS-diamine (**1**) used had a number-average molecular weight (M_n) of 1720 g·mol^{-1} and average degree of polycondensation of 21.



In the two-step procedure, α,ω-dichloroformyl-terminated aramid oligomers **2a–f** having M_n's ranging from 462 to 5100 g·mol^{-1} were prepared first by the reaction of a calculated excess of IPC with 3,4′-ODA in a chloroform–triethylamine hydrochloride (TEA·HCl) system in the presence of triethylamine (TEA) as a hydrogen chloride acceptor. The preformed aramid oligomers **2a–f** were then reacted with PDMS-diamine in the same solvent system, producing the 3,4′-ODA series multiblock copolymers **3a(II)–3f(II)**. In the one-step procedure, all the reaction components, PDMS-diamine, 3,4′-ODA, and IPC, were reacted all together in a chloroform–TEA·HCl system in the presence of TEA, yielding the 3,4′-ODA series multiblock copolymers **3a(I)–3f(I)**. In both cases, chloroform coupled with TEA·HCl was essential to facilitate the polycondensation in homogeneous solution. The 3,4′-ODA series multiblock copolymers **3a(I)–3f(I)** and **3a(II)–3f(II)** thus obtained had inherent viscosities ranging from 0.17 to 0.47 dL·g^{-1} (Table I).

The other 4,4′-ODA series of multiblock copolymers **5a(I)–5f(I)** and **5a(II)–5f(II)** were prepared by similar

Table I
Synthesis of PDMS–Aramid Multiblock Copolymers of the 3 Series

	aramid oligomer		block copolymer				
synthesis[a]		x		PDMS content, % calcd[b]	PDMS content, % obsd[c]	yield, %	η_{inh},[d] dL·g^{-1}
I	**2a**	1	**3a(I)**	76	80	78	0.21
II	**2a**	1	**3a(II)**	76	77	76	0.17
I	**2b**	2	**3b(I)**	67	68	82	0.21
II	**2b**	2	**3b(II)**	67	62	74	0.36
I	**2c**	3	**3c(I)**	59	61	89	0.30
II	**2c**	3	**3c(II)**	59	57	96	0.36
I	**2d**	5	**3d(I)**	48	49	98	0.44
II	**2d**	5	**3d(II)**	48	45	81	0.39
I	**2e**	7	**3e(I)**	41	43	100	0.43
II	**2e**	7	**3e(II)**	41	40	100	0.47
I	**2f**	15	**3f(I)**	25	22	100	0.42
II	**2f**	15	**3f(II)**	25	20	100	0.41
I			**3g**[e]	0		100	0.47

[a] I, one-step method; and II, two-step method. [b] Calculated from the reactants in feed. [c] Calculated from the $SiCH_3$/aromatics ratio in the ^1H NMR spectrum. [d] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [e] Aramid homopolymer.

Table II
Synthesis of PDMS–Aramid Multiblock Copolymers of the 5 Series

	aramid oligomer		block copolymer				
synthesis[a]		x		PDMS content, % calcd[b]	PDMS content, % obsd[c]	yield, %	η_{inh},[d] dL·g^{-1}
I	**4a**	1	**5a(I)**	76	76	83	0.29
II	**4a**	1	**5a(II)**	76	75	89	0.19
I	**4b**	2	**5b(I)**	67	67	85	0.37
II	**4b**	2	**5b(II)**	67	68	89	0.27
I	**4c**	3	**5c(I)**	59	60	98	0.40
II	**4c**	3	**5c(II)**	59	57	94	0.41
I	**4d**	5	**5d(I)**	48	47	98	0.40
II	**4d**	5	**5d(II)**	48	46	95	0.60
I	**4e**	7	**5e(I)**	41	39	96	0.44
II	**4e**	7	**5e(II)**	41	37	99	0.87
I	**4f**	15	**5f(I)**	25	22	96	0.42
II	**4f**	15	**5f(II)**	25	23	100	0.77
I			**5g**[e]	0		100	1.03

[a–e] See footnotes to Table I.

Table III
Solubility of PDMS–Aramid Multiblock Copolymers[a]

	1	3a–f	3g	5a–f	5g
N,*N*-dimethylacetamide	–	+	+	+	+
pyridine	–	+	+	–	–
chroloform	+	–	–	–	–
tetrahydrofuran	+	–	–	–	–
n-hexane	+	–	–	–	–
methanol	–	–	–	–	–

[a] Solubility: +; soluble, –, insoluble.

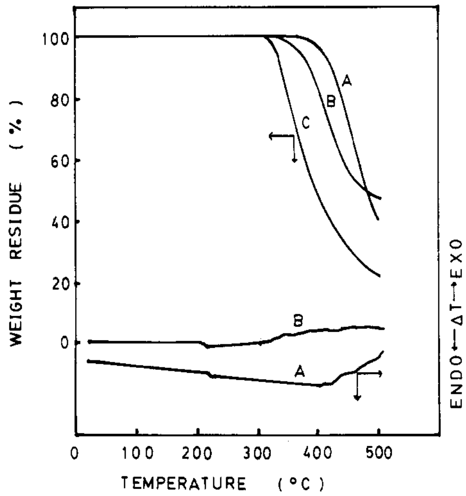


Figure 1. DTA and TG curves for (A) aramid homopolymer **3g**, (B) PDMS–aramid multiblock copolymer **3f(II)**, and (C) PDMS-diamine, at a heating rate of 10 K·min^{-1} in air.

one-step and two-step precedures, respectively, starting from PDMS-diamine, N-silylated 4,4′-ODA, and IPC in chloroform in the presence of TEA·HCl and TEA. As shown in Table II, the 4,4′-ODA series multiblock copolymers having inherent viscosities of 0.19–0.87 dL·g^{-1} were obtained readily.

It was found that the inherent viscosities of the block copolymers formed by both synthetic methods generally decreased with increasing PDMS contents; i.e., the block copolymers of higher PDMS contents had lower inherent viscosity values. This relates to the fact that *N*,*N*-dimethylacetamide (DMAc) as the solvent for viscosity measurement is a poor solvent for PDMS and a good solvent for parent aramids **3g** and **5g**. Therefore, it should be noted that the inherent viscosity values are not comparable to the molecular weights of the block copolymers. The results that all the block copolymers gave ductile and elastomeric casting films as discussed later strongly suggest that these block copolymers have equally 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 the siloxane group at 1090 and 1010 cm^{-1} appeared. In the ^1H NMR spectra, three remarkable peaks at 0 ppm ($SiCH_3$), 0.8–1.2 ppm (aliphatic H), and 7.0–7.5 ppm (aromatic H) were observed. The observed PDMS contents of the block copolymers, which were calculated from the $SiCH_3$/aromatic ratio on 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 Multiblock Copolymers. The qualitative solubility behavior of multiblock copolymers **3** and **5** in organic solvents, as well as of the parent homopolymers (PDMS-diamine (**1**) and aramids **3g** and **5g**), was examined (Table III). All the block copolymers dissolve in DMAc, which is a good solvent for the aramid homopolymers, and are quite insoluble in chloroform, tetrahydrofuran, and hexane, which are good solvent for PDMS-diamine. This is a remarkable feature of the aramid-based multiblock copolymers.[12–16] These copolymers gave transparent, ductile, and elastomeric films by casting from the DMAc solutions.

The thermal behavior of the multiblock copolymers was evaluated by means of differential thermal analysis (DTA) and thermogravimetry (TG) in air. Figure 1 shows typical DTA and TG curves of the representative block copolymer **3f**(II), as well as of the parent PMDS-diamine (**1**) and aramid homopolymer **3g**. The TG curves of all the block copolymers fall between the curve of the PDMS-diamine and that of the aramid homopolymers. The onset temperature of these block copolymers was around 300 °C in air, similar to that of PDMS-diamine. Therefore, the PDMS–aramid multiblock copolymers are useful thermally stable materials that withstand up to 300 °C in air. On the DTA curves shown in Figure 1, a small break was observed at around 230 °C for multiblock copolymer **3f(II)**, which corresponds to glass transition temperature

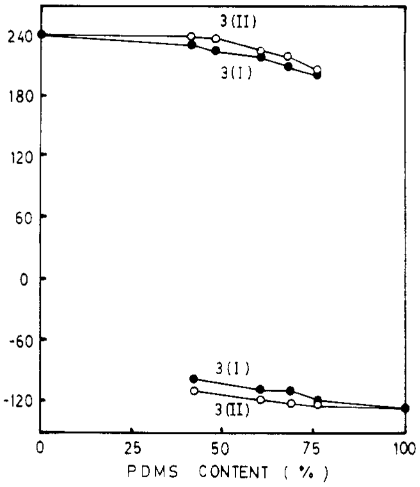


Figure 2. Glass transition temperatures of PDMS and aramid segments for PDMS–aramid multiblock copolymers.

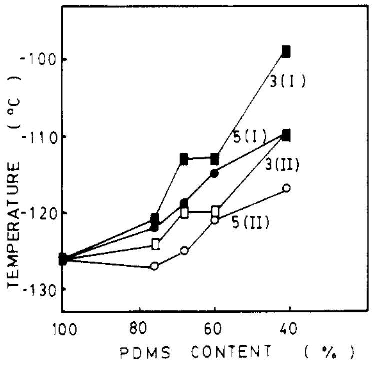


Figure 3. Glass transition temperatures of PDMS segment for PDMS–aramid multiblock copolymers.

(T_g) of the hard-segment aramid. The value was almost identical with the T_g of aramid homopolymer **3g** (240 °C). In some block copolymers of the **5** series, however, the T_g due to the aramid segment could not be detected clearly on the DTA curves.

The T_g's of the multiblock copolymers were further evaluated by means of DSC in detail. The upper and lower two T_g's, corresponding to hard aramid and soft PDMS segments, respectively, were observed clearly for the **3** series multiblock copolymers. The fact that the upper T_g's ranging from 200 to 237 °C in the whole PDMS composition ranges were depressed only slightly relative to the T_g of the aramid homopolymer (240 °C), and also that the lower T_g's ranging from −123 to −103 °C approached the T_g of PDMS-diamine (−126 °C), indirectly indicated good microphase separation. This is attributable to the great difference in solubility parameters between aramids and PDMS.

Values of both upper and lower T_g's of the multiblock copolymers were found to be influenced by the kind of incorporated aramid structure and the synthetic method (Figures 2 and 3). Generally, the lower T_g's of the **3** series multiblock copolymers were higher than those of the **5** series block copolymers, because the **3** series copolymers had weaker intermolecular interaction than the **5** series copolymers due to the less symmetrical structure of aramid segment **2**, and thereby somewhat more interfacial phase mixing occurred. This may affect the tensile properties of the multiblock copolymer films (Table IV).

Among the multiblock copolymers synthesized by two different methods, the **3** and **5** series copolymers prepared by the two-step procedure showed much higher T_g's for the aramid hard segment and lower T_g's for the PDMS segment than the **3** and **5** series copolymers prepared by the one-step method. This suggests that the **3(II)** and **5(II)** series copolymers are better defined multiblock copolymers with higher structural regularity, and the **3(I)** and **5(I)** series copolymers are more randomly coupled block copolymers having less regulated structures.

Table IV
Glass Transition Temperatures (T_g) of PDMS–Aramid Multiblock Copolymers[a]

block copolymer	PDMS content, %	PDMS seg T_g, °C	aramid seg T_g, °C
1 (PDMS)	100	−126	
3a(I)	80	−121	200
3a(II)	77	−124	202
3b(I)	68	−113	209
3b(II)	62	−120	215
3c(I)	61	−113	216
3c(II)	57	−120	220
3e(I)	43	−99	230
3e(II)	40	−110	237
3g	0		240
5a(I)	76	−122	
5a(II)	75	−127	
5b(I)	67	−119	
5b(II)	68	−125	
5c(I)	60	−116	
5c(II)	57	−122	
5e(I)	39	−110	
5e(II)	37	−117	

[a] Determined by DSC at a heating rate of 20 K·min^{-1} in helium.

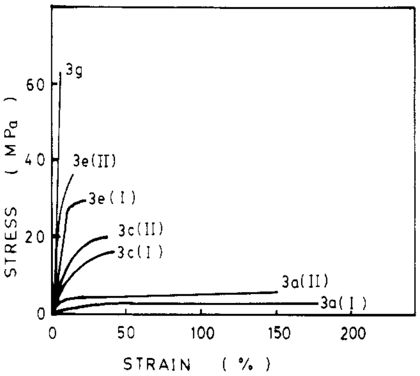


Figure 4. Stress–strain curves for PDMS–aramid multiblock copolymers of the **3(I)** and **3(II)** series.

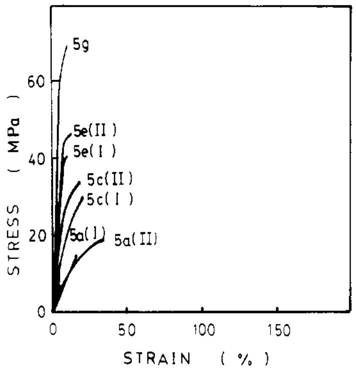


Figure 5. Stress–strain curves for PDMS–aramid multiblock copolymers of the **5(I)** and **5(II)** series.

The stress–strain curves of the multiblock copolymer films cast from the DMAc solutions are shown in Figures 4 and 5, and the tensile properties are summarized in Table V. The tensile properties of the films are highly dependent on the PDMS content in the multiblock copolymers. A comparison of the curves showed that significant decreases in both tensile strength (T) and tensile

Table V
Tensile Properties of Films of PDMS–Aramid Multiblock Copolymers

block copolymer	tensile strength, MPa	elongation at break, %	tensile modulus, MPa
3a(I)	3	175	4
3a(II)	6	140	68
3b(I)	4	80	6
3b(II)	15	52	80
3c(I)	17	34	200
3c(II)	19	33	250
3d(I)	18	28	250
3d(II)	27	22	350
3e(I)	30	20	210
3e(II)	34	13	500
3f(I)	52	12	1000
3f(II)	56	11	1200
3g	62	5	1400
5a(I)	16	18	15
5a(II)	18	30	120
5b(I)	25	25	100
5b(II)	30	22	130
5c(I)	30	18	500
5c(II)	33	17	1000
5d(I)	30	13	500
5d(II)	36	12	750
5e(I)	40	9	900
5e(II)	46	11	950
5f(I)	53	9	900
5f(II)	60	9	1100
5g	68	9	2000

modulus (M) by increasing the PDMS content and an increase in elongation at break (E) occurred. Over the whole composition ranges, the multiblock copolymer films were between a rubber-toughened ductile plastic film having $T/E/M$ of 60 MPa/9%/1.1 GPa and a thermoplastic elastomer film with $T/E/M$ of 6 MPa/140%/68 MPa.

The hard-segment aramid structures also had a large influence on the tensile properties of the block copolymer films. In a comparison of the tensile properties of block copolymers **3** and **5**, the films of the **5** series block copolymers had higher T and M and lower E, compared with the films of the **3** series block copolymers. This is because the **5** series block copolymers contain more symmetrical aramid backbones affording stronger intermolecular interaction than the **3** series block copolymers.

Furthermore, the synthetic methods of the block copolymers affected markedly on the film tensile properties, i.e., the films of the **3(II)** or **5(II)** series block copolymers having higher structural regularity generally exhibited higher T and M and lower E, compared with the films of block copolymers **3(I)** or **5(I)**. The results correspond well to the T_g behavior discussed the above. Similar structure–property relationships have been reported in several multiblock copolymers such as those of polyether–aramid, polybutadiene–polyamide, and poly(dimethylsiloxane)–polyamide series.[10,12-16]

In conclusion, these PDMS–aramid multiblock copolymers having lower PDMS content can be used as high-temperature rubber-toughened aramid plastics, whereas the multiblock copolymers with higher PDMS content can be considered as new candidates for high-temperature thermoplastic elastomers. For the preparation of the PDMS–aramid multiblock copolymers for most purposes, a convenient one–step procedure is sufficiently useful, instead of a tedious two-step method.

Registry No. (3,4'-ODA)(IPC)(PDMS-diamine) (block copolymer), 121617-30-9; (PDMS-diamine)(IPC)(N-silylated 4,4'-ODA) (block copolymer), 121599-00-6.

References and Notes

(1) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic Press: New York, 1977.
(2) Zdrahala, R. J.; Firer, E. M.; Fellers, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 689.
(3) Fellers, J. F.; Lee, Y.-D.; Zdrahala, R. J. *J. Polym. Sci., Polym. Symp.* **1977**, *60*, 59.
(4) Yilgor, I.; Riffle, J. S.; Wilkes, G. L.; McGrath, J. E. *Polym. Bull.* **1982**, *8*, 535.
(5) Tyagi, D.; Wilkes, G. L.; Yilgor, I.; McGrath, J. E. *Polym. Bull.* **1982**, *8*, 543.
(6) Yilgor, I.; Shaaban, A. K.; Steckle, W. P., Jr.; Tyagi, D.; Wilkes, G. L.; McGrath, J. E. *Polymer* **1984**, *25*, 1800.
(7) Tyagi, D.; Yilgor, I.; McGrath, J. E.; Wilkes, G. L. *Polymer* **1984**, *25*, 1807.
(8) Kajiyama, M.; Nishikata, Y.; Kakimoto, M.; Imai, Y. *Polym. J.* **1986**, *18*, 735.
(9) Kakimoto, M.; Kajiyama, M.; Imai, Y. *Polym. J.* **1986**, *18*, 935.
(10) Kajiyama, M.; Kakimoto, M.; Imai, Y., submitted for publication in *J. Appl. Polym. Sci.*
(11) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.
(12) Imai, Y.; Kajiyama, M.; Ogata, S.; Kakimoto, M. *Polym. J.* **1984**, *16*, 267.
(13) Imai, Y.; Kajiyama, M.; Ogata, S.; Kakimoto, M. *Polym. J.* **1984**, *17*, 1173.
(14) Ogata, S.; Kakimoto, M.; Iami, Y. *Macromolecules* **1985**, *18*, 851.
(15) Ogata, S.; Maeda, H.; Kakimoto, M.; Imai, Y. *Polym. J.* **1985**, *17*, 935.
(16) Ogata, S.; Maeda, H.; Kakimoto, M.; Imai, Y. *J. Appl. Polym. Sci.* **1987**, *33*, 775.