Synthesis and Properties of New Multiblock Copolymers Based on Poly(dimethylsiloxane) and N-Phenylated Polyureas

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Received March 15, 1989; Revised Manuscript Received July 28, 1989

ABSTRACT: A new class of multiblock copolymers having well-defined structures was synthesized starting from poly(dimethylsiloxane) (PDMS) and N-phenylated polyureas by the solution polyaddition technique. Three synthetic methods, i.e., one-step, two-step, and chain-extension methods, were adopted for the synthesis of PDMS–polyurea multiblock copolymers with wide ranging compositions. In the two-step method, α,ω-diisocyanate-terminated polyurea oligomers, which were preformed from α,α'-dianilino-*p*-xylene (DAX) and 4,4'-methylenebis(phenyl isocyanate) (MBI) in anisole, were reacted with α,ω-bis(3-aminopropyl)–poly(dimethylsiloxanes) (PDMS–diamines) in the same flask leading to the formation of multiblock copolymers. In the one-step method, three reaction components, DAX, MBI, and a PDMS–diamine, were reacted all together in anisole. In the chain-extension method, PDMS–diamines were reacted first with MBI giving α,ω-diisocyanate-terminated PDMS oligomers, which were subjected to reaction with DAX in anisole forming multiblock copolymers. These polyadditions afforded multiblock copolymers having inherent viscosities of 0.2–0.7 $\mathrm{dL \cdot g^{-1}}$. They are readily soluble in a variety of solvents such as chloroform, tetrahydrofuran, *m*-cresol, and *N,N*-dimethylacetamide (DMAc). Transparent, ductile, and elastic films were obtained by casting from the chloroform solutions or directly from the reaction solutions just prepared. Calorimetric measurements showed that the films of the multiblock copolymers prepared by the two-step method has the best defined, microphase-separated morphology, and the films by the chain-extension method had the second best, compared with films by the one-step method. The multiblock copolymers obtained by the two-step method afforded films with the most balanced mechanical properties. The film mechanical properties were highly dependent on the PDMS content; at low PDMS levels the materials behave as rubber-toughened plastics, while at higher PDMS contents the materials are analogous to elastomers.

Introduction

Poly(dimethylsiloxane) (PDMS) has unique properties such as low glass transition temperatures (ca. −123 °C), good thermal and oxidative stability, low surface energy, high hydrophobicity, high oxygen permeability, and good biocompatibility. However, because of its poor mechanical properties, many of its initial potential applications have suffered in terms of performance. The weakness of PDMS can be effectively improved through block copolymerization. The block or segmented copolymers composed of a hard segment and PDMS as a soft segment have already been synthesized and characterized.[1,2] However, relatively few studies have been reported on the synthesis of block copolymers based on PDMS and hard segments having strong enough intermolecular forces such as polyamides and polyureas. The block copolymers recently synthesized have included ABA-type triblock copolymers comprising PDMS and an aromatic polyamide,[3,4] various types of PDMS–polyamide multiblock copolymers,[5-8] and PDMS–urea segmented copolymers.[9-12] Our interest is in the development of PDMS–polyurea multiblock copolymers with excellent solubility in organic solvents, since the PDMS–urea segmented copolymers have limited solubility; the intermolecular hydrogen bonding of a polyurea segment composed of 4,4'-methylenebis(phenyl isocyanate) (MBI) and 1,6-hexanediamine is too strong to be soluble in many organic solvents.

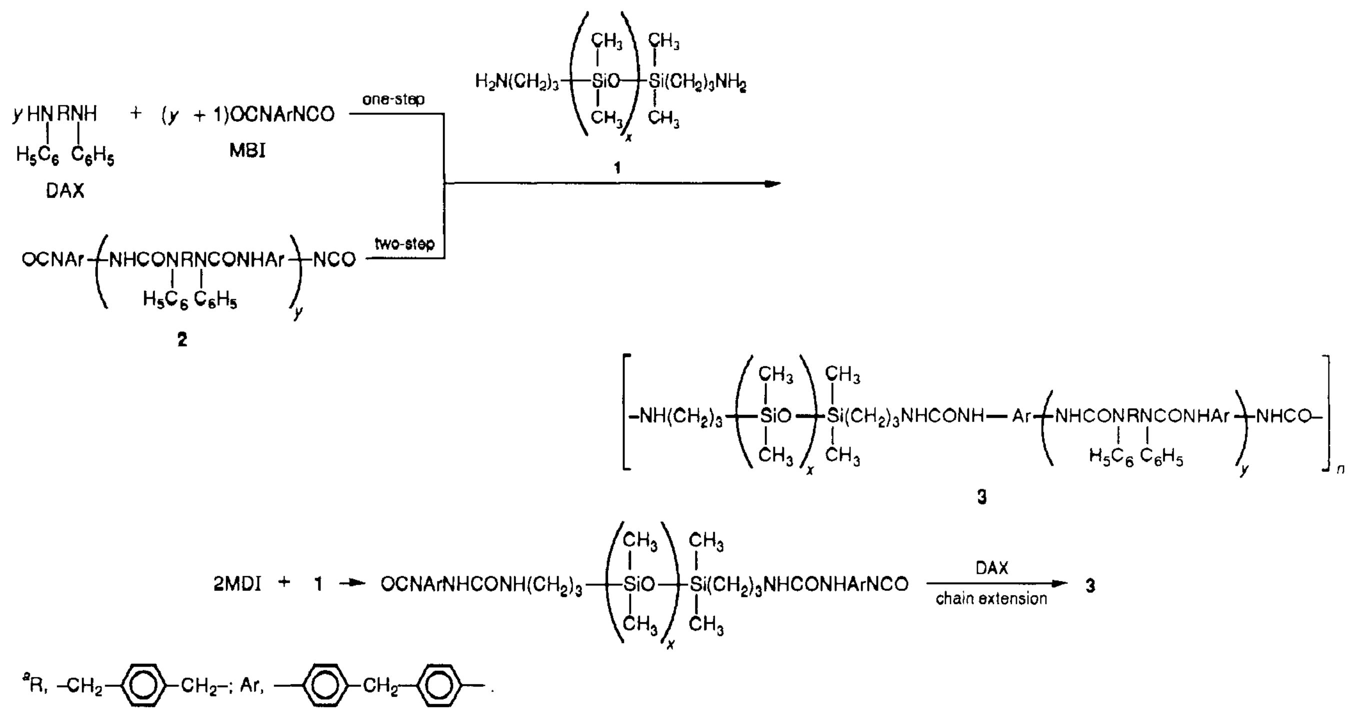
We have already reported that the N-phenylated polyurea of high molecular weight, prepared from α,α'-dianilino-*p*-xylene (DAX) and MBI, was soluble in a variety of solvents including chloroform and anisole, good solvents for PDMS.[13] This has led to the suggestion that DAX, coupled with MBI, would be a suitable hard component or chain extender for PDMS–polyurea multiblock copolymers with enhanced solubility. This article describes successful synthesis and properties of the multiblock copolymers comprised of PDMS soft blocks and the N-phenylated polyurea hard blocks of various molecular weights.

The PDMS–polyurea multiblock copolymers were prepared via the solution polyaddition technique. In the two-step method, a calculated excess of MBI was reacted with DAX in anisole giving α,ω-diisocyanate-terminated polyurea oligomers, which in turn were reacted with PDMS–diamines. This synthetic procedure is advantageous for the synthesis of multiblock copolymers having high structural regularity compared with the most convenient one-step method, where all the reactants were reacted together. Another synthetic procedure, a chain-extension method, where MBI-capped PDMS's were reacted with DAX, was also investigated for comparison.

Experimental Section

Materials. PDMS–diamines **1a** and **1b** were obtained from Shinetsu Chemical Co., Japan; their number-average molecular weights ($\bar{M}_n$) were 1720 and 2740 $\mathrm{g \cdot mol^{-1}}$, respectively. These oligomers were dried at 120 °C for 1 h under vacuum before use. DAX was synthesized according to the reported procedure[13] starting from *p*-xylene-α,α'-diol and aniline and purified by recrystallization from a mixture of ethanol and ben-

Scheme I[a]



zene. MBI, anisole, and dichloromethane were purified by distillation.

Synthesis of Block Copolymers. Copolymer 3ab(II) by the Two-Step Method. A solution of 0.576 g (2.0 mmol) of DAX in 3 mL of anisole was added dropwise to a stirred solution of 0.750 g (3.0 mmol) of MBI in 1 mL of anisole at room temperature, and the mixture was stirred at 80 °C for 2 h under nitrogen. To the reaction solution, a solution of 1.72 g (1.0 mmol) of PDMS–diamine **1a** in 4 mL of anisole was then added, and the mixture was stirred at 80 °C for another 4 h under nitrogen. The viscous polymer solution obtained was poured into 700 mL of methanol. The precipitated polymer was collected by filtration, washed successively with methanol and hexane, and dried at room temperature under vacuum. The polymer weighed 2.74 g (90%) and had an inherent viscosity of 0.36 $dL{\cdot}g^{-1}$ in tetrahydrofuran (THF), measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ at 30 °C. The IR spectrum (film) exhibited absorptions at 3400 cm^{-1} (N–H), 1670 cm^{-1} (C═O), and 1090 and 1010 cm^{-1} (Si–O–Si). Anal. Calcd: C, 51.96; H, 6.99; N, 5.39. Found: C, 53.04; H, 6.98; N, 5.55.

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

Copolymer 3ab(I) by the One-Step Method. To a mixture of 1.72 g (1.0 mmol) of PDMS–diamine **1a** and 0.576 g (2.0 mmol) of DAX in 4 mL of anisole, a solution of 0.750 g (3.0 mmol) of MBI in 4 mL of anisole was added, and the mixture was stirred at 80 °C for 6 h under nitrogen. The polymer was isolated as described above. The yield was 2.52 g (83%), and the inherent viscosity of the polymer in THF was 0.20 $dL{\cdot}g^{-1}$. The IR spectrum (film) showed absorptions at 3400 cm^{-1} (N–H), 1670 cm^{-1} (C═O), and 1090 and 1010 cm^{-1} (Si–O–Si). Anal. Calcd: C, 51.96; H, 6.99; N, 5.39. Found: C, 52.22; H, 7.07; N, 5.81.

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

Copolymer 3ab(C) by the Chain-Extension Method. To a solution of 0.750 g (3.0 mmol) of MBI in 10 mL of dichloromethane, a solution of 1.72 g (1.0 mmol) of PDMS–diamine **1a** in 10 mL of dichloromethane was added, and the mixture was stirred at 0 °C for 1 h under nitrogen. After that, a solution of 0.576 g (2.0 mmol) of DAX in 8 mL of anisole was added to the reaction solution, and the mixture was heated to 80 °C to remove the dichloromethane by distillation. The solution was further stirred at 80 °C for 5 h under nitrogen. The polymer was isolated as described above. The polymer weighed 2.86 g (94%) and had an inherent viscosity of 0.34 $dL{\cdot}g^{-1}$ in THF. The IR spectrum (film) exhibited absorptions at 3400 cm^{-1} (N–H), 1670 cm^{-1} (C═O), and 1090 and 1010 cm^{-1} (Si–O–Si). Anal. Calcd: C, 51.96; H, 6.99; N, 5.39. Found: C, 50.56; H, 6.67; N, 5.00.

Other block copolymers of the **3**(C) series were obtained by the analogous chain-extension method.

Measurements. IR and NMR spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JEOL FX-100 Fourier transform spectrometer, respectively. Weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) were determined by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Waters ALC/GPC 201 apparatus with a microstyragel column using tetrahydrofuran as an eluent. DTA, TG, and DSC were performed with Shimadzu thermal analyzers DTA-30M, TGA-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%$\cdot min^{-1}$. 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. PDMS–polyurea multiblock copolymers were synthesized by the solution polyaddition technique according to Scheme I. PDMS–diamines **1a** and **1b** used in this study had $\bar{M}_n$'s of 1720 and 2740 and average degrees of polycondensation ($\bar{x}$) of 21 and 34, respectively. Table I summarizes the results of the polymerizations.

In the two-step method, α,ω-diisocyanate-terminated polyurea oligomers **2a–2f** having $\bar{M}_n$'s of 788–8800 and average degrees of polycondensation ($\bar{y}$) of 1–16 were prepared first by the reaction of a calculated excess of MBI with DAX in anisole. After that, the preformed polyurea oligomers were reacted with PDMS–diamines in anisole at 80 °C. The polyadditions proceeded readily in homogeneous solution affording the **3**(II) series PDMS–polyurea multiblock copolymers with inherent viscosities of 0.33–0.65 $dL{\cdot}g^{-1}$ in 80–99% yields.

The polymerizations by the simplest one-step method, where all the reactants, MBI, DAX, and PDMS–diamines, were reacted together in anisole, also progressed homogeneously and gave 80–95% yields of the **3**(I) series multiblock copolymers having inherent viscosities of 0.20–0.61 $dL{\cdot}g^{-1}$.

Table I
Synthesis of PDMS–Polyurea Multiblock Copolymers 3

synthetic method[a]	PDMS		polyurea		block copolymer				
						PDMS content, %			
	code	x	code	y[b]	code	calcd[b]	obsd[c]	yield, %	η_{inh},[d] dL·g^{-1}
I	**1a**	21	**2a**	1	**3aa**(I)	69	62	82	0.20
II	**1a**	21	**2a**	1	**3aa**(II)	69	67	83	0.33
C	**1a**	21	**2a**	1	**3aa**(C)	69	73	78	0.21
I	**1a**	21	**2b**	2	**3ab**(I)	56	55	83	0.20
II	**1a**	21	**2b**	2	**3ab**(II)	56	57	90	0.36
C	**1a**	21	**2b**	2	**3ab**(C)	56	58	94	0.34
I	**1a**	21	**2c**	3	**3ac**(I)	48	48	83	0.20
II	**1a**	21	**2c**	3	**3ac**(II)	48	49	87	0.37
C	**1a**	21	**2c**	3	**3ac**(C)	48	52	94	0.32
I	**1a**	21	**2d**	4	**3ad**(I)	42	39	90	0.25
II	**1a**	21	**2d**	4	**3ad**(II)	42	41	93	0.40
C	**1a**	21	**2d**	4	**3ad**(C)	42	42	97	0.31
I	**1a**	21	**2e**	9	**3ae**(I)	25	24	92	0.31
II	**1a**	21	**2e**	9	**3ae**(II)	25	25	100	0.41
C	**1a**	21	**2e**	9	**3ae**(C)	25	25	93	0.27
I	**1a**	21	**2f**	16	**3af**(I)	16	13	94	0.39
II	**1a**	21	**2f**	16	**3af**(II)	16	14	100	0.52
C	**1a**	21	**2f**	16	**3af**(C)	16	17	91	0.29
I	**1b**	34	**2a**	1	**3ba**(I)	78	81	80	0.41
II	**1b**	34	**2a**	1	**3ba**(II)	78	77	80	0.49
C	**1b**	34	**2a**	1	**3ba**(C)	78	74	81	0.51
I	**1b**	34	**2b**	2	**3bb**(I)	67	50	83	0.54
II	**1b**	34	**2b**	2	**3bb**(II)	67	67	84	0.65
C	**1b**	34	**2b**	2	**3bb**(C)	67	68	88	0.63
I	**1b**	34	**2c**	3	**3bc**(I)	60	48	93	0.60
II	**1b**	34	**2c**	3	**3bc**(II)	60	57	100	0.62
C	**1b**	34	**2c**	3	**3bc**(C)	60	59	97	0.44
I	**1b**	34	**2d**	4	**3bd**(I)	53	42	95	0.61
II	**1b**	34	**2d**	4	**3bd**(II)	53	53	96	0.62
C	**1b**	34	**2d**	4	**3bd**(C)	53	55	97	0.40
I		0		∞	**3c**[e]	0		94	0.52

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

The chain-extension method is well-known as a conventional synthetic method for the production of polyurethanes and their derivatives. This was applied further to the preparation of the PDMS–polyurea multiblock copolymers. The MBI-end-capped PDMS's were prepared from excess amounts of MBI and PDMS–diamines in the first step and then reacted with DAX affording the **3**(C) series multiblock copolymers. The polymerizations also proceeded homogeneously and the multiblock copolymers with inherent viscosities of 0.21–0.60 dL·g^{-1} were obtained in 78–97% yields. From these results (Table I), the two-step method was found to be the best among these three methods in terms of yield and inherent viscosity of the resulting block copolymers.

The molecular weights of some block copolymers were determined by means of GPC. The GPC curve of block copolymer **3ab**(I) having an inherent viscosity of 0.20 dL·g^{-1} indicated that the $\bar{M}_w$ and $\bar{M}_n$ values were 35 000 and 14 100, respectively, relative to standard polystyrene, and the ratio of $\bar{M}_w/\bar{M}_n$ was 2.5. An inherent viscosity of 0.36 dL·g^{-1} for block copolymer **3ab**(II) corresponded to the $\bar{M}_w$ and $\bar{M}_n$ values of 196 000 and 61 600, respectively, and the $\bar{M}_w/\bar{M}_n$ ratio was 3.2. In the case of block copolymer **3ab**(C), the $\bar{M}_w$ and $\bar{M}_n$ values were 277 000 and 37 400, respectively, and the $\bar{M}_w/\bar{M}_n$ ratio was 7.4.

The structure of the polymers thus obtained was confirmed to be the proposed block copolymers by means of IR and NMR spectroscopy and elemental analysis. The elemental analysis values were in good agreement with the calculated values. In the IR spectra, characteristic urea absorptions at 3400 cm^{-1} (N–H) and 1670 cm^{-1} (C=O) and two absorptions due to siloxane group at 1090 and 1010 cm^{-1} (Si–O–Si) appeared. In the ^1H NMR spectra, three characteristic peaks at 0 ppm ($Si{-}CH_3$), 3.7 and 4.6 ppm (benzylic H), and 7.0–7.8 ppm (aromatic H) were observed.

The observed PDMS contents of the block copolymers, which were calculated on the basis of the $Si{-}CH_3$/aromatic ratio on the NMR spectra, are also given in Table I. As can be seen from these results, the observed PDMS values of the **3**(II) series multiblock copolymers prepared by the two-step method agreed well with the PDMS contents calculated from the reactants in the feed. Also in the **3**(C) series block copolymers by the chain-extension method, the agreement between the observed and calculated PDMS contents was fairly good, although the observed values showed some scatter relative to the calculated values. On the other hand, the observed PDMS contents of the **3**(I) series block copolymers were somewhat lower than the calculated values. This is probably because the unreacted PDMS–diamines were mainly discarded during the purification of the block copolymers formed by the one-step method.

Properties of Multiblock Copolymers. The qualitative solubility behavior of the PDMS–polyurea multiblock copolymers of the **3**(II), **3**(I), and **3**(C) series in various organic solvents, as well as the parent homopolymers (PDMS–diamines **1** and N-phenylated polyurea **3c**), was examined. All the multiblock copolymers of the whole PDMS composition ranges, irrespective of the synthetic methods, dissolved quite readily in a variety of solvents such as *N,N*-dimethylacetamide, *m*-cresol, THF, and chloroform, which are good solvents for the parent N-phenylated polyurea.[13] The solubility of these multi-

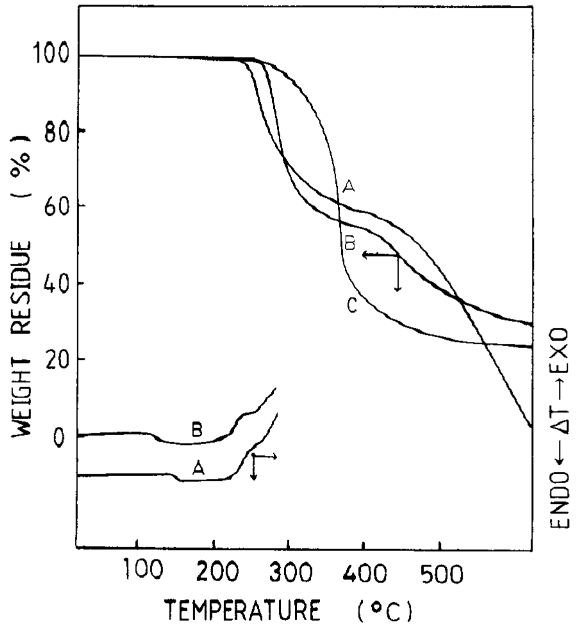


Figure 1. DTA and TG curves of (A) polyurea homopolymer **3c**, (B) PDMS–polyurea multiblock copolymer **3ae**(II), and (C) PDMS–diamine **1a**, at a heating rate of 10 °C·min^{-1} in air.

block copolymers differed appreciably from that of the parent PDMS–diamines, which are soluble in less polar solvents such as THF, chloroform, and hexane, indicating that the solubility was governed by the hard block polyurea species. The multiblock copolymers gave transparent, ductile, and elastic films by casting from the chloroform solutions or directly from the reaction solutions just prepared.

The thermal behavior of the multiblock copolymers was evaluated by means of DTA and TG in air. Figure 1 shows typical DTA and TG curves of the representative block copolymer **3ae**(II) as well as of the parent PDMS–diamine **1a** and polyurea homopolymer **3c**. The TG curves of all the block copolymers lay between the curves of the PDMS–diamine and that of the polyurea homopolymer. The onset temperature of decomposition of these block copolymers was around 250 °C in air. The limited thermal stability is attributable to the thermal decomposition of the urea linkages existing in the block copolymer backbone. The DTA exothermic shift above 220 °C also supported the decomposition of the block copolymers. On the DTA curves, a small break was observed at around 120 °C for multiblock copolymer **3ae**(II), which corresponds to glass transition temperature (T_g) of the hard segment polyurea component. The T_g was almost identical with that of the N-phenylated polyurea (122 °C).[13]

The T_g's of the multiblock copolymers were further determined by means of DSC in detail. High and low T_g's, corresponding to hard polyurea segment and soft PDMS segment, respectively, were observed clearly on the DSC curves. The results are summarized in Table II. The high T_g's ranging from 80 to 127 °C in the whole PDMS composition ranges were depressed slightly relative to the T_g of polyurea homopolymer **3c**, and the low T_g's in the range of −129 to −93 °C increased from the T_g of PDMS–diamine **1a** (−126 °C). The existence of the two T_g's indicated indirectly good microphage separation. This is attributed to the great difference in solubility parameters between the polyurea homopolymer and PDMS.

Both high and low T_g values of the multiblock copolymers were greatly influenced by the microstructures of the block copolymers, which depend on the synthetic methods (Figure 2). The depression of the high T_g and the increase in the low T_g were observed most significantly for the **3**(I) series block copolymers. The high T_g depression and the low T_g increase were more gradual in the order of the **3**(I) series > **3**(C) series > **3**(II) series block copolymers. This suggests that the **3**(II) series copolymers are the best defined multiblock copolymers with the highest structural regularity among these three block copolymers, and the **3**(C) series copolymers are the sec-

Table II
Glass Transition Temperatures (T_g) of PDMS–Polyurea MultiBlock Copolymers 3[a]

block copolymer	PDMS content, %	T_g, °C	
		PDMS segment	polyurea segment
2a(PDMS)	100	−126	
3aa(I)	62	−124	
3aa(II)	67	−127	
3aa(C)	73	−128	
3ab(I)	55	−118	110
3ab(II)	57	−121	100
3ab(C)	58	−122	92
3ac(I)	48	−114	88
3ac(II)	49	−123	109
3ac(C)	52	−121	96
3ad(I)	39	−110	100
3ad(II)	41	−121	122
3ad(C)	42	−115	102
3ae(I)	24	−94	120
3ae(II)	25	−96	125
3ae(C)	25	−93	127
3ba(I)	81	−128	
3ba(II)	77	−127	
3ba(C)	74	−128	
3bb(I)	50	−123	80
3bb(II)	67	−127	95
3bb(C)	68	−128	85
3bc(I)	48	−117	81
3bc(II)	57	−127	90
3bc(C)	59	−121	93
3bd(I)	42	−114	74
3bd(II)	53	−124	98
3bd(C)	55	−123	90
3c	0		122

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

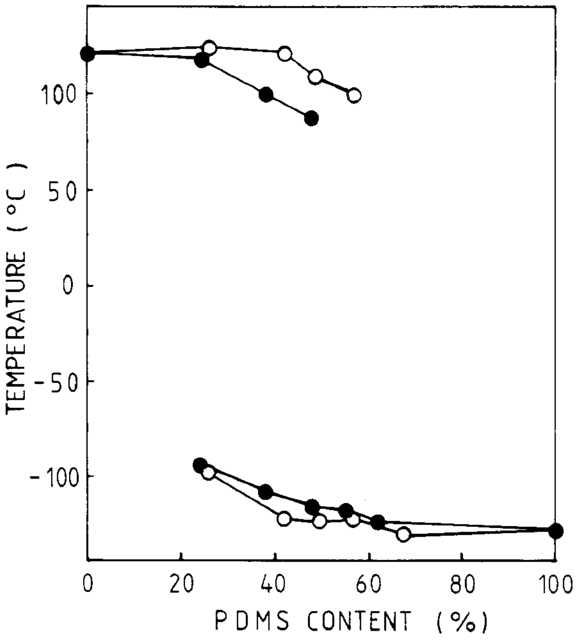


Figure 2. Glass transition temperatures of PDMS–polyurea multiblock copolymers: –○–, **3**(II) series block copolymers; –●–, **3**(I) series block copolymers.

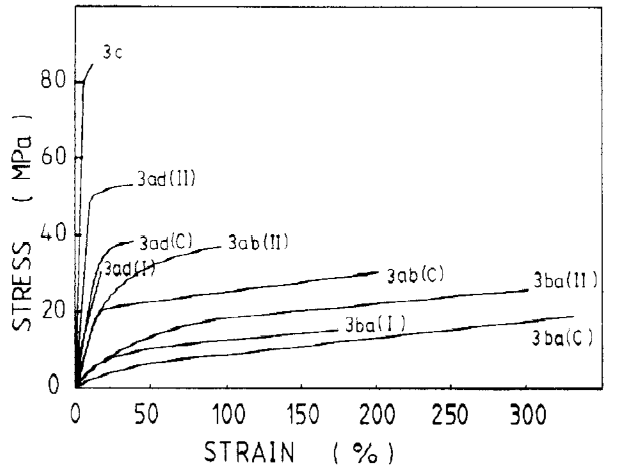


Figure 3. Stress–strain curves of films of PDMS–polyurea multiblock copolymers.

Table III
Tensile Properties of Films of PDMS–Polyurea Multiblock Copolymers 3

block copolymer	tensile strength, MPa	elongation at break, %	tensile modulus, MPa
3aa(I)	1.0	35	100
3aa(II)	1.3	40	138
3aa(C)	1.4	43	81
3ab(I)	8.0	29	300
3ab(II)	37	96	310
3ab(C)	30	200	290
3ac(I)	13	23	440
3ac(II)	46	52	510
3ac(C)	34	86	360
3ad(I)	30	17	750
3ad(II)	53	36	890
3ad(C)	38	37	520
3ae(I)	40	11	740
3ae(II)	56	20	800
3ae(C)	47	14	660
3af(I)	60	7	1400
3af(II)	80	10	1600
3af(C)	50	7	700
3ba(I)	15	175	150
3ba(II)	25	300	100
3ba(C)	20	330	78
3bb(I)	24	92	124
3bb(II)	59	132	191
3bb(C)	42	150	84
3bc(I)	23	90	90
3bc(II)	54	114	273
3bc(C)	30	165	60
3bd(I)	25	35	196
3bd(II)	63	42	640
3bd(C)	41	138	168
3c	84	7	2000

ond best, while the **3**(I) series copolymers are more randomly coupled block copolymers having more interfacial phase mixing.

The stress–strain curves of the block copolymer films are shown in Figure 3, and the tensile properties are summarized in Table III. The films have ductile and elastic properties depending markedly on the PDMS content in the multiblock copolymers. In general, tensile strength (*T*) and tensile modulus (*M*) decreased with increasing the PDMS content, whereas elongation at break (*E*) increased. Over the whole composition ranges, the films of the **3**(II) series multiblock copolymers were between a rubber-toughened ductile plastic film having a *T*/*E*/*M* of 80 MPa/10%/1.6 GPa and an elastomer film with a *T*/*E*/*M* of 25 MPa/300%/100 MPa.

The influence of the microstructures of the multiblock copolymers, mainly depending on the synthetic methods of the block copolymers, was further observed on the tensile properties. The **3**(II) series multiblock copolymers having higher structural regularity synthesized by the two-step method afforded the films with the most balanced mechanical properties. Although the films of the **3**(C) series block copolymers by the chain-extension method had somewhat lower *T* and higher *E* than those of the **3**(II) series multiblock copolymers, the difference in the tensile values was rather small between these two block copolymers. This is quite reasonable taking into consideration that the **3**(C) series block copolymers have some structural irregularity, compared with the **3**(II) series block copolymers. However, the films of the **3**(I) series block copolymers had apparently lower *T* and lower *E* than those of the **3**(II) series multiblock copolymers. This is probably because the **3**(I) series block copolymers prepared by the one-step method are more randomly coupled block copolymers. Similar structure–property relationships have been reported in several multiblock copolymers such as polyether–aramid,[14,15] polybutadiene–aramid,[16-18] and polysiloxane–polyamide multiblock copolymers.[7,8]

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