

Synthesis and Properties of New Poly(dimethylsiloxane)–Urea–Polyamide Multiblock Copolymers by Diisocyanate Method

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ABSTRACT: New poly(dimethylsiloxane)–urea–polyamide multiblock copolymers based on poly(dimethylsiloxane) and polyamides were synthesized *via* diisocyanate route by two-step method. Isocyanate-terminated telechelic polyamide oligomers, prepared from a mixture of isophthalic acid and azelaic acid with 4,4'-methylenedi(phenyl isocyanate), reacted with α,ω -bis(3-aminopropyl)poly(dimethylsiloxane)s at room temperature to give the multiblock copolymers with inherent viscosities of 0.25–0.89 dl g⁻¹. These multiblock copolymers were soluble in amide solvents, and transparent and ductile films could be cast from the solutions. The tensile strength and modulus of the films decreased with increasing the poly(dimethylsiloxane) content.

KEY WORDS Poly(dimethylsiloxane–Urea–Polyamide Multiblock Copolymers / Diisocyanate Method / Solubility / Thermal Behavior / Tensile Properties /

The synthesis of dimethylsiloxane-containing polymers has been of substantial interest, due to the desirable thermal, mechanical, chemical, electrical, and surface properties. Therefore, much efforts have been made on synthesizing the block copolymers composed of some hard segments and poly(dimethylsiloxane) (PDMS) as a soft segment.^{1–15} However, attempts to prepare the multiblock copolymers composed of PDMS and polyamides were of limited success with respect to inherent viscosity of the resulting polymers.^{7–9} Successful results were obtained by the use of chloroform-soluble polyamides.^{14,15}

Recently we reported the synthesis of polyether–polyamide^{16–18} and PDMS–polyamide¹⁹ multiblock copolymers by using aromatic diisocyanates. In the former case, the multiblock copolymers were prepared by the reaction of carboxy- or hydroxy-terminated telechelic polyether oligomer with α,ω -di-

isocyanate-terminated polyamide oligomers, derived from 4,4'-methylenedi(phenyl isocyanate) and dicarboxylic acids. In the latter case, the multiblock copolymers were prepared by the reaction of carboxy-terminated telechelic PDMS with α,ω -diisocyanate-terminated polyamide oligomers. In both cases, multiblock copolymers with high inherent viscosities could be obtained.

It is well known that isocyanate group can also react with amino group in addition to carboxy and hydroxy functionalities. Our next efforts were directed toward the synthesis of new PDMS–urea–polyamide multiblock copolymers *via* the diisocyanate route starting from commercially available amine-terminated telechelic poly(dimethylsiloxane)s. They have been used widely as a soft block component for the PDMS–polyurea,^{2–6} PDMS–polyamide,⁸ and PDMS–polyimide^{10–13} block copolymers.

In this article, we report a facile synthesis of

PDMS-urea-polyamide multiblock copolymers with high molecular weights in a mixture of 1,3-dimethyl-2-imidazolidone and triglyme (2,5,8,11-tetraoxadodecane) from α,ω -bis(3-aminopropyl)poly(dimethylsiloxane)s (PDMS-diamines) and α,ω -diisocyanate-terminated polyamide oligomers derived from 4,4'-methylenedi(phenyl isocyanate) and a mixture of isophthalic acid and azelaic acid. The properties of the resulting copolymers, such as solubility, thermal behavior, and mechanical properties, are also discussed in detail.

EXPERIMENTAL

Materials

PDMS-diamines, whose number-average molecular weights were ascertained to be 1700 and 3900 by titrimetry, were obtained from Shinetsu Chemical Co., Ltd., Tokyo, and dried at 80°C under vacuum before use. 4,4'-Methylenedi(phenyl isocyanate) (MDI) was purified by vacuum distillation before use. Azelaic acid (AZA) and isophthalic acid (IPA) were purified by recrystallization from water and aqueous ethanol, respectively. They were dried at 80°C for 24 h under vacuum before use. *N,N*-Dimethylacetamide (DMAc), 1,3-dimethyl-2-imidazolidone (DMI), and triglyme were purified by distillation over calcium hydride and stored over molecular sieves. Water content of the solvents, determined by use of a Karl Fischer automatic titrator, was found to be less than 30 ppm. Lithium chloride was used as received.

Polymerization

Multiblock Copolymer 3ab. A mixture of 0.3824 g (2.3 mmol) of IPA, 0.4329 g (2.3 mmol) of AZA and 1.0 mg (0.025 mmol) of lithium chloride in 4 ml of DMI was heated with stirring at 200°C under nitrogen. To this solution, 1.2513 g (5.0 mmol) of MDI in 4 ml of DMI was added dropwise with stirring. After 12 min, the reaction mixture was cooled rapidly to room temperature, and 0.6720 g (0.4 mmol)

of PDMS-diamine **2a** in 4 ml of triglyme was added dropwise. The mixture was stirred for another 2 h at room temperature. 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 80°C under vacuum. The yield of the polymer was 2.26 g (98%), and the inherent viscosity in DMAc was 0.89 dl g⁻¹, measured at a concentration of 0.50 g dl⁻¹ at 30°C. The infrared (IR) spectrum (film) exhibited absorptions at 3300 cm⁻¹ (N-H), 1655 cm⁻¹ (amide and urea C=O), 1260 cm⁻¹ (Si-CH₃), and 1090 and 1020 cm⁻¹ (Si-O-Si). *Anal.* Calcd for (C₁₂₄₁H₁₅₇₄N₁₀₈O₁₈₀Si₈₄)_n: C, 64.13%; H, 6.83%; N, 6.51%. Found: C, 64.36%; H, 7.07%; N, 6.72%.

Other multiblock copolymers were prepared by similar procedures.

Measurements

IR spectra were recorded on a Japan Spectroscopic IR-810 spectrophotometer. ¹H Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX-100 Fourier transform spectrometer at room temperature in dimethyl sulfoxide-*d*₆ or *N,N*-dimethylformamide-*d*₇ solution. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) of the polymers were determined with a Waters 150°C gel permeation chromatograph (GPC) apparatus at 140°C, being used *N,N*-dimethylformamide as an eluent and polystyrene as calibration standards. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed with a Daini Seikosha TG/DTA-20 thermal analyzer and a DSC-20 differential scanning calorimeter, respectively. Dynamic thermomechanical analysis (DMA) was performed with film specimens on a Toyo Baldwin Rheovibron DDV-II at 11 Hz in the temperature range from -150 to 250°C at a heating rate of 3°C min⁻¹. Tensile properties, such as

not be used as the catalyst, since undesirable crosslinking had occurred during the following second step reaction.

In the second step, PDMS-diamine **2** in triglyme was added to the DMI solution of α,ω -diisocyanate-terminated polyamide oligomer at room temperature, and the reaction was carried out at that temperature, giving PDMS-urea-polyamide multiblock copolymers **3**. The reaction temperature for the second-step reaction was found to be very important, since a crosslinked polymer was formed at a higher temperature like 200°C. By the same reason, the one-step procedure, in which the reaction components were reacted all together at 200°C, was not applicable to this reaction. This is probably because the urea group formed in the block copolymer can react further with the isocyanate group at that high temperature to form biuret linkage,²² giving rise to crosslinking.

In the synthesis of the multiblock copolymers, triglyme was used as the cosolvent in addition to DMI to improve the solubility of the multiblock copolymers. The ratio of these solvents used to synthesize the multiblock

copolymers varied according to the amount of PDMS component introduced. The results of the synthesis of the multiblock copolymers are summarized in Table I. The multiblock copolymers having inherent viscosities in the range of 0.25–0.89 dl g⁻¹ were obtained in excellent yields. The values of inherent viscosities generally decreased with increasing PDMS content in the multiblock copolymers. This can be explained by the fact that DMAc, the solvent for the viscosity measurement, is a good solvent for the polyamide but a poor solvent for PDMS. Therefore, in the present study, it should be noted that the inherent viscosity values do not directly correspond to the molecular weights of the multiblock copolymers with different PDMS content.

The structure of the resulting copolymers was confirmed to be the proposed multiblock copolymers by means of IR and ¹H NMR spectroscopy, and elemental analysis. In the IR spectra, characteristic amide and urea absorptions at 3300 cm⁻¹ (N–H) and 1655 cm⁻¹ (C=O), and the absorptions due to siloxane group at 1260 cm⁻¹ (Si–CH₃), and 1090 and 1020 cm⁻¹ (Si–O–Si) appeared. In the ¹H

Table I. Synthesis of poly(dimethylsiloxane)-urea-polyamide multiblock copolymers

PDMS-Diamine		Polyamide oligomer		Multiblock copolymer				
Code	\bar{M}_n	Code	\bar{M}_n^a	Code	PDMS content/wt%		Yield	η_{inh}^d
					Calcd ^b	Found ^c	%	dl g ⁻¹
2a	1700	1a	8300	3aa	17	11	93	0.62
2a	1700	1b	4100	3ab	29	21	98	0.89
2a	1700	1c	1600	3ac	52	42	96	0.43
2a	1700	1d	990	3ad	63	56	95	0.36
2a	1700	1e	530	3ae	76	65	100	0.33
2b	3900	1f	16800	3bf	19	10	100	0.51
2b	3900	1a	8300	3ba	32	22	97	0.50
2b	3900	1b	4100	3bb	49	43	94	0.41
2b	3900	1g	2300	3bg	63	53	97	0.28
2b	3900	1h	1300	3bh	75	64	99	0.25

^a Calculated from feed ratio of the monomers.

^b Weight (PDMS)/[weight (PDMS)+weight (polyamide)] in the feed.

^c Calculated from Si–CH₃/aromatic ratio in the NMR spectrum.

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

Table II. Solubility of poly(dimethylsiloxane)-urea-polyamide multiblock copolymers^a

Solvent	PDMS	Polyamide ^b	Multiblock copolymer				
			3aa	3ab	3ac	3ad	3ae
<i>N</i> -Methyl-2-pyrrolidone	—	++	++	++	++	++	++
<i>N,N</i> -Dimethylacetamide	—	++	++	++	++	++	++
<i>N,N</i> -Dimethylformamide	—	++	++	++	+	++	++
Dimethyl sulfoxide	—	++	+	++	++	++	++
<i>m</i> -Cresol	++	++	++	++	++	++	++
Methanol	—	—	—	—	—	—	—
Diglyme	++	—	—	—	—	—	—

^a Solubility: ++, soluble at room temperature; +, soluble on heating; —, insoluble.

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

NMR spectra, three sets of remarkable peaks at 0 ppm (Si-CH₃), 1.4–3.1 ppm (aliphatic H) and 7.2–9.5 ppm (aromatic H) were observed. The PDMS content of the multiblock copolymers, calculated from the Si-CH₃/aromatics ratio in the ¹H NMR spectra, were also shown in Table I. These observed values agreed fairly well with the PDMS content calculated from the reactants in feed. The elemental analysis values were also in fairly good agreement with the calculated values.

The molecular weights of the multiblock copolymers were determined by means of GPC. The \bar{M}_n and \bar{M}_w values for the typical block copolymers of **3aa** and **3ad** were found to be 39000 and 109000, and 29000 and 61000, respectively, relative to standard polystyrene. Therefore, the copolymers obtained here were confirmed to be multiblock copolymers, and their average degree of polymerization (\bar{n}) was estimated to be 4–10.

Properties of Multiblock Copolymers

Table II summarizes the qualitative solubility behavior of typical multiblock copolymers in organic solvents, as well as of the parent PDMS and the polyamide derived from MDI and a mixture of IPA and AZA (50/50 molar ratio). It was found that these multiblock copolymers were soluble in amide solvents, dimethyl sulfoxide, and *m*-cresol, which are good solvents for the polyamide but are poor

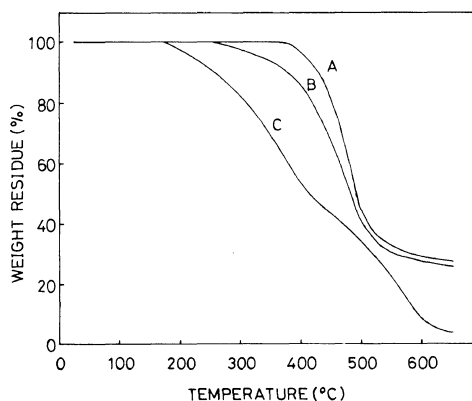


Figure 1. TG curves in nitrogen at a heating rate of 20°C min⁻¹ for the parent polyamide (A), multiblock copolymer **3ab** (B), and PDMS-diamine **2a** (C).

solvents for PDMS. Almost all of the multiblock copolymers gave transparent (or somewhat translucent), ductile and elastomeric films by casting from the solutions in a mixture of DMAc and bis(ethoxyethyl) ether. Multiblock copolymers **3bg** and **3bh** gave only brittle films by solution casting, probably due to rather low molecular weight of these multiblock copolymers.

The thermal behavior of the PDMS-urea-polyamide multiblock copolymers was evaluated by means of TG, DSC, and DMA. Figure 1 shows typical TG curves for the representative multiblock copolymer **3ab** in nitrogen, as well as the parent PDMS-diamine **2a** and the polyamide. In the TG curves, the

Table III. Glass transition temperatures of poly(dimethylsiloxane)-urea-polyamide multiblock copolymers

Multiblock copolymer	PDMS content wt%	Glass transition temperature/°C			
		PDMS segment		Polyamide segment	
		DSC ^a	DMA ^b	DSC ^a	DMA ^b
3aa	17		-125	177	204
3ab	29		-121	163	191
3ac	52	-119	-115		163
3ad	63	-118	-111		125
3ae	76	-118	-111		
PDMS-diamine 2a	100	-122			
3bf	19		-127	183	205
3ba	32		-123	180	203
3bb	49	-123	-125		198
3bg	63	-122			
3bh	75	-121			
PDMS-diamine 2b	100	-124			
Polyamide ^c	0			184	206

^a Determined by DSC in nitrogen at a heating rate of 20°C min⁻¹.

^b Determined by DMA at a heating rate of 3°C min⁻¹.

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

onset of decomposition of the multiblock copolymer was observed at around 300°C, indicating lower thermal stability than the PDMS-polyamide multiblock copolymers already reported.¹⁹ Lower thermal stability of the PDMS-urea-polyamide multiblock copolymers is probably due to the introduction of thermally unstable urea linkage.

The results of DSC and DMA measurements for all the multiblock copolymers are summarized in Table III. The dynamic mechanical storage modulus (E') and the dissipation factor ($\tan \delta$) of typical multiblock copolymers and the parent polyamide are plotted as a function of temperature (Figure 2). In the multiblock copolymers, the upper and lower two glass transition temperatures (T_g), corresponding to the hard polyamide and soft PDMS segments, respectively, were clearly observed. This observation suggested good microphase-separated morphology between the PDMS and polyamide phases in the multiblock copoly-

mers. The T_g of the PDMS segment was observed at -118 to -123°C by DSC, and at -111 to -127°C by DMA. It is evident that the T_g values of the PDMS segment lowered with decreasing PDMS content, or with an increase in the polyamide block length (M_n). The T_g of the polyamide segment was observed only for the multiblock copolymers having higher polyamide content in the range of 125 and 205°C by the DMA measurements and in the 163–183°C range by DSC, which markedly lowered with increasing the PDMS content. The T_g behavior of both PDMS and polyamide segments suggested that the multiblock copolymers having lower PDMS content exhibited a higher degree of microphase-separated morphology, compared with the multiblock copolymers with higher PDMS content, in which some interfacial phase mixing probably occurred (Figure 3). Similar structure-thermal behavior relationship was also observed in the polybutadiene-polyamide^{23,24} poly(oxytetra-

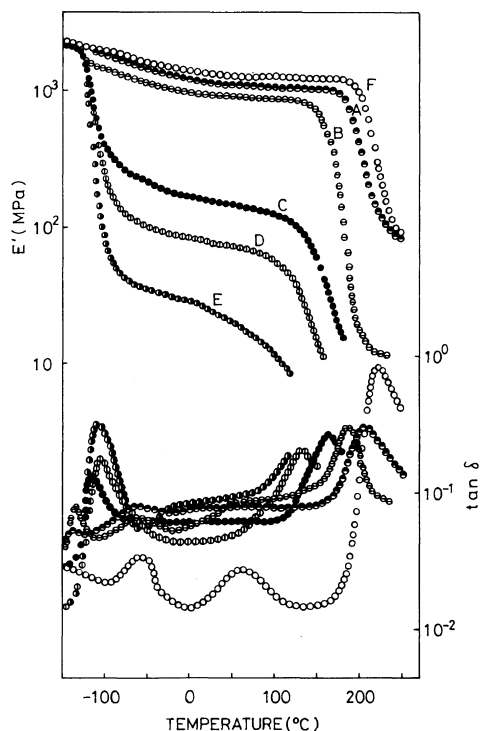


Figure 2. Temperature dependence of the dynamic storage modulus (E') and the dissipation factor ($\tan\delta$) measured at 11 Hz at a heating rate of 3°Cmin^{-1} of multiblock copolymer **3aa** (A), **3ab** (B), **3ac** (C), **3ad** (D), **3ae** (E), and the parent polyamide (F).

methylene)-polyamide,¹⁸ and PDMS-polyamide¹⁹ multiblock copolymers.

Furthermore, the effect of PDMS block length on the T_g of both segments was investigated (Figure 3). Multiblock copolymers **3bf-3bh** prepared from PDMS-diamine **2b** exhibited much lower T_g of PDMS phase than that of the corresponding block copolymers **3aa-3ae** derived from **2a**. It is noteworthy that the T_g of hard polyamide phase is influenced by the PDMS block length. The T_g of hard polyamide phase became lower with decreasing PDMS block length, as shown in **3aa** and **3ba** (also **3ab** and **3bb**), which have same hard block length. Such behavior suggested that the longer the PDMS block length the higher the degree of microphase separation.

Compared with the PDMS-polyamide mul-

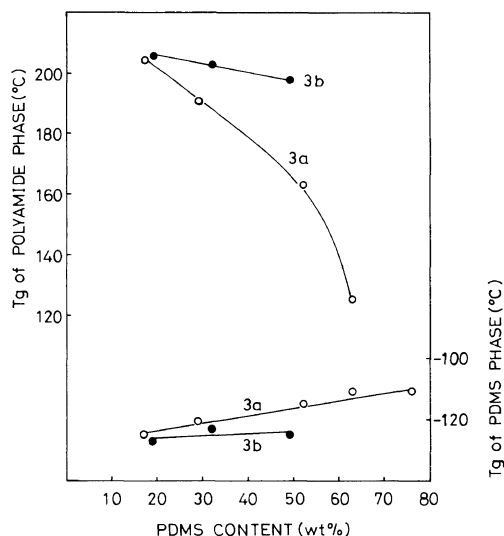


Figure 3. Glass transition temperatures of the multiblock copolymers of **3a** and **3b** series.

tiblock copolymers¹⁹ previously reported, the T_g values of both polyamide phase and PDMS phase in the PDMS-urea-polyamide multiblock copolymers exhibited almost identical values. This suggests that the PDMS-urea-polyamide multiblock copolymers still maintain high degree of microphase-separated morphology by the introduction of urea linkage.

The stress-strain curves for typical multiblock copolymer films cast from the solutions in a DMAc and bis(ethoxyethyl) ether mixture are shown in Figure 4, and the tensile properties of the cast films are summarized in Table IV. The films of multiblock copolymers **3aa-3ae** and **3ba-3bb** have ductile and elastomeric properties depending markedly on the content of the PDMS segments. The films of multiblock copolymers **3bg** and **3bh** were too brittle for measurement of tensile properties. By increasing the soft PDMS content, the values of both tensile strength (T) and tensile modulus (M) generally decreased and the elongation at break (E) increased. In the films of multiblock copolymers **3ab** and **3bf** with rather low PDMS content, yield points were observed at an

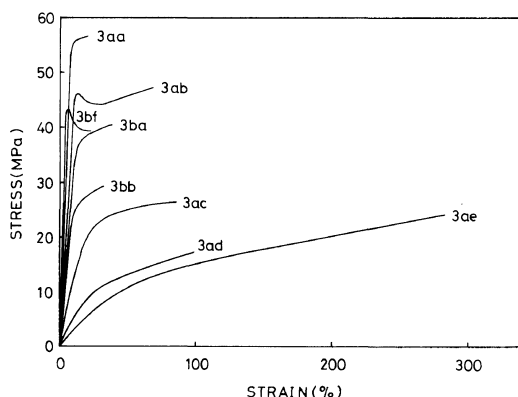


Figure 4. Stress-strain curves of the films of PDMS-urea-polyamide multiblock copolymers, **3aa-3ae** and **3ba-3bb**.

Table IV. Tensile properties of cast films of poly(dimethylsiloxane)-urea-polyamide multiblock copolymers

Multiblock copolymer	PDMS content	Tensile strength	Elongation at break	Tensile modulus
	wt%	MPa	%	MPa
3aa	11	56	21	910
3ab	21	47	69	730
3ac	42	26	86	171
3ad	56	17	98	61
3ae	65	24	284	32
3bf	10	43	22	1170
3ba	22	40	38	584
3bb	43	29	33	526
Polyamide ^a	0	73	15	2200

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

elongation between 6 to 10%, which strongly suggested a continuous nature of the polyamide phase. At higher PDMS content in the multiblock copolymers, on the other hand, a marked elastic property was observed, due to more continuous nature of the PDMS phase. Over the whole composition ranges, the multiblock copolymer films were between a rubber-toughened ductile plastic film having T/E/M of 47 MPa/69%/730 MPa and a thermoplastic elastomer film with 24 MPa/284%/32 MPa. Relatively low elongation at break of

the PDMS-urea-polyamide multiblock copolymers may be due to an inaptitude of the casting solvent for the PDMS segment. It was observed that the PDMS-urea-polyamide multiblock copolymer films had a lower tensile modulus and higher elongation (E) compared with PDMS-polyamide multiblock copolymers^{14,19} and had a similar tensile modulus to PDMS-piperazine aromatic polyamide multiblock copolymers.¹⁵

The tensile properties of the PDMS-urea-polyamide multiblock copolymer films obtained in this work are almost comparable to those of commercial thermoplastic elastomers. For example, the T/E/M values of a film of multiblock copolymer **3ae** are 24 MPa/284%/32 MPa, while Du Pont's "Hytrel" polyether-polyester and ATO Chem's "Pebax" polyether-ester-polyamide thermoplastic elastomers have the tensile values of 21 MPa/550%/66 MPa and 33 MPa/620%, respectively.

In conclusion, the diisocyanate method could be applied to the synthesis of multiblock copolymers starting from amine-terminated oligomers in addition to carboxy- or hydroxy-terminated oligomers. Furthermore, the PDMS-urea-polyamide multiblock copolymers obtained could be considered as new candidates for tough polyamide plastics or thermoplastic elastomers with excellent mechanical properties.

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