

ABA-Type Block Copolymers Containing Poly(dimethylsiloxane) and Ketonic Resins

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ABSTRACT: Block copolymer containing segments of poly(dimethylsiloxane) (PDMS) and ketonic resins were synthesized. Dihydroxy-terminated PDMS were reacted with the isophorone diisocyanate (IPDI) to obtain the diisocyanate-terminated PDMSs (urethane). These urethanes were reacted with reactive hydroxyl groups in the cyclohexanone–formaldehyde, acetophenone–formaldehyde, and *in situ* melamine-modified cyclohexanone–formaldehyde resins.

Formation of block copolymers was illustrated by several characterization methods, such as chemical and spectroscopic analysis and gel permeation chromatography. The solubilities of the block copolymers were determined, and their surface properties were investigated by contact angle measurements. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 643–648, 1998

Key words: copolymers; poly(dimethylsiloxane); ketonic resins

INTRODUCTION

Polysiloxane possesses a unique combination of many interesting properties, especially a high surface activity and an extremely low solubility parameter.^{1,2} These properties lead to the thermodynamic incompatibility of polysiloxanes with almost all other organic polymer systems. One method to overcome this difficulty is by blending the siloxane-containing copolymers with organic polymers since siloxane homopolymers can only provide a temporary surface modification to the blend. In siloxane-containing multiphase, block, segmented, or graft copolymers, siloxane segments migrate to the air–polymer surface; but the organic segments in the copolymers act as an “anchoring group” for the siloxane blocks, and then the permanent surface modification can be achieved.^{3,4} For this purpose, the synthesis of siloxane-containing copolymers have been studied

for about 30 years. In 1964, Jarvis, Fox, and Zisman reported first that the siloxane-containing copolymers were blended with the base resin to modify the surface.⁵ After that, the siloxane copolymers are used as surface-modifying agents in some important applications, such as paints, coatings, and textile fiber.

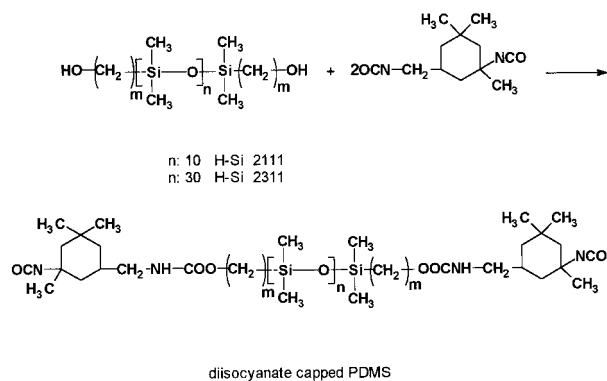
The synthesis and detailed characterization of a series of segmented siloxane–urethane copolymers were described earlier.⁶ Polymerization reaction was performed in a mixed tetrahydrofuran–dimethylacetamide solvent system in two steps. In the first step, siloxane oligomers were reacted with an excess of methylene diisocyanate at 60–70°C. The second step was the chain extension of the prepolymer with butanediol.

In the earlier studies, the reactive hydroxyl groups of the ketonic resins were used to synthesize linear block copolymers by way of a stepwise procedure.^{7–9} Also, it was shown that these hydroxyl groups in the resins were reacted easily with 2,4-toluene diisocyanate to obtain chain extended ketonic resins.¹⁰

The synthesis and characterization of ABA-type

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Scheme 1.

siloxane-containing block copolymers will be reported in this work. A reactive hydroxyl group containing cyclohexanone–formaldehyde, acetophenone–formaldehyde, and *in situ* melamine-modified cyclohexanone–formaldehyde resins were used as A blocks and poly(dimethylsiloxane) as B blocks in the copolymers. The method used to synthesize these ABA-type block copolymers was based on the chemical combination of hydroxyl groups in the ketonic resins with the diisocyanate-terminated poly(dimethylsiloxane)s.

EXPERIMENTAL

Materials

α - ω -Dihydroxy poly(dimethylsiloxane)s (PDMS), were the products of Goldschmidt Chemical Corporation (Essen, Germany). Tegomer H-Si 2111 and Tegomer H-Si 2311 with molecular weights of 950 ± 80 and 2500 ± 250 , respectively, were dried at 30°C in a vacuum oven for 48 h before use.

Isophorone diisocyanate (IPDI) was a product of Fluka A.G. (Buchs, Switzerland) and used without purification. The purity determined by isocyanate analysis was 95.1%.

Dibutyltin dilaurate (T-12) was a product of Fluka A.G. Solvents used were products of Merck A.G. (Darmstadt, Germany).

Cyclohexanone–formaldehyde, acetophenone–formaldehyde, *in-situ* melamine-modified cyclohexanone–formaldehyde resins were prepared by the procedure described earlier^{7,11} and further dried by refluxing with Dean–Stark apparatus, using toluene as the solvent.

Analyses

Infrared (IR) spectra were recorded on A.T.I. UN-ICAM Mattson 1000 Series Fourier transform in-

frared spectrometer. $^1\text{H-NMR}$ was obtained for CDCl_3 solution on a Bruker AC (200 MHz).

M_n and M_w values of block copolymers were calculated from gel permeation chromatographic (GPC) methods according to standard polystyrene calibration using a Waters Instrument, and tetrahydrofuran (THF) served as eluent at 25°C . The flow rate was 1 mL/min.

The solubility properties of ketonic resins and the block copolymers were investigated as follows. 20 mg of solid sample in 2 mL of solvents were mixed in a test tube at room temperature and shaken. If the dissolution occurred in 5 min, it was considered to be soluble. If the dissolution was not completed, it was slightly soluble at room temperature. Then the solution was heated up to the boiling point of the solvent, and the same observation was repeated at that temperature. If the dissolution did not occur even in the hot solvent, it was considered insoluble.

Thin-layer chromatography (TLC) was done with silica gel 60 (0.20 mm) with a fluorescent indicator of 254 nm.

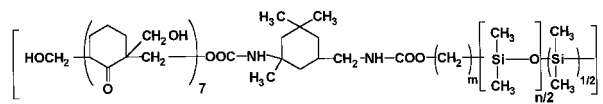
Contact angle measurements of the copolymer films were done on a Kernco model G III contact angle meter at room temperature using distilled water. The measurements were made in 20 s for water droplets on the copolymers and ketonic resin films prepared by casting from 1% (w/v) dichloromethane solutions.

Procedure

Preparation of Capped Siloxane Tegomers

The diisocyanate-terminated polysiloxane were prepared in two types. In the first type, the original PDMS was used. In the second type, the chain extension was made, and higher molecular weight diisocyanate-terminated siloxanes were obtained.

The dried hydroxyl-terminated prepolymers (Tegomer H-Si 2111 and Tegomer H-Si 2311) and the aliphatic diisocyanate (IPDI) were reacted at 60°C in a dichloro ethane solution under a blanket of dry nitrogen for 96 h to obtain the first type of samples. The molar ratio of diisocyanate to prepolymer was taken to be three in order to prevent chain extension.



Scheme 2.

Table I Preparation Conditions and Characterization of Diisocyanate-Capped PDMS

Sample	No.	NCO-PDMS at the Beginning	Isocyanate Wt % of Capped PDMS		\bar{M}_n (g mol ⁻¹)	
			Theoretical	Experimental	Theoretical	Experimental ^a
Prepolymer PDMS-2111	a	—	—	—	950 ± 80	—
Prepolymer PDMS-2311	b	—	—	—	2500 ± 250	—
Urethane (M_w kept constant)	1a	3.01	6.0	5.6	1400 ± 80	1500
Urethane (M_w kept constant)	1b	3.01	2.85	2.95	2950 ± 250	2850
Urethane (chain extended)	2a	1.00	—	1.88	—	4470

^a Calculated from the end-group analysis.

For the chain extension, the molar ratio of the diisocyanate to Tegomer H-Si 2111 were taken as equivalent (1 : 1) at the same reaction conditions, as described above for 30 h; then twofold of diisocyanate were added to the reaction mixture to cut the chain extension and to obtain diisocyanate-terminated polysiloxane.

The resulting products, either first type (Scheme 1) or chain-extended samples, were extracted with acetonitrile at least twice; isolated by decantation; and dried in vacuum at room temperature. The isocyanate content of the end-capped products was determined by end group titration of isocyanates, and the molecular weights were calculated.¹²

Preparation of Poly(dimethylsiloxane)-Ketonic Resin Block Copolymers

In a three-necked flask, 1 mol of ketonic resin and 1 mol of capped siloxane Tegomer were dissolved in 10 mL CH₂Cl₂ and heated to 40°C while stirring vigorously under the nitrogen atmosphere. After 1 h, one drop of T-12 catalyst was added, and the stirring continued for 4 h at 40°C. The mixture was poured into petroleum ether, and the precipitate was filtered and dried at 95°C under vacuum.

The structural formula of the block copolymer of poly(dimethylsiloxane)-cyclohexanone-formaldehyde resin copolymer was given as an example in Scheme 2.

RESULTS AND DISCUSSION

In this study, poly(dimethylsiloxane) containing ABA-type ketonic resin block copolymers were

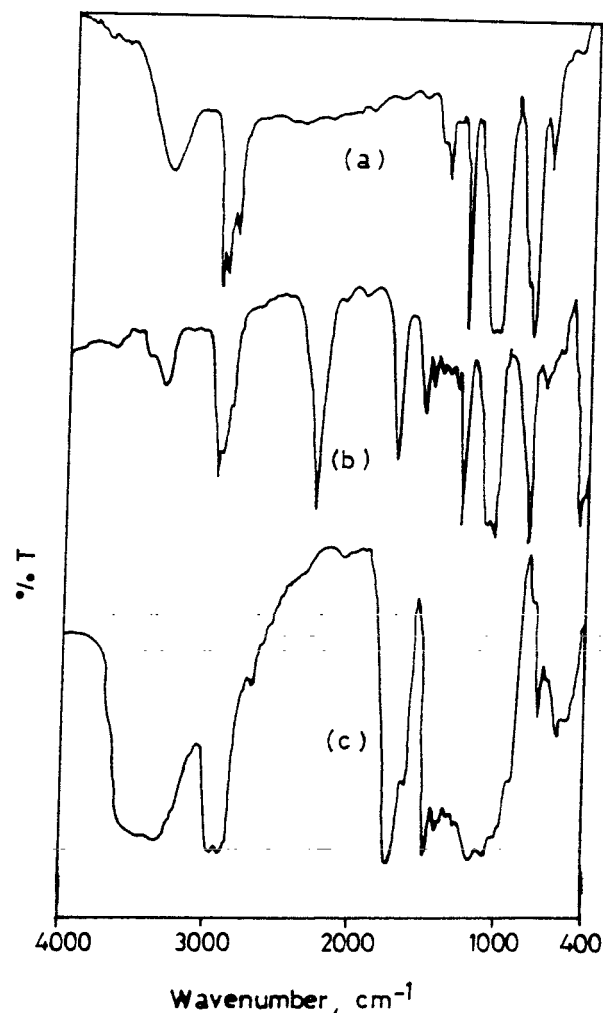


Figure 1 FTIR spectrum of (a) dihydroxy PDMS (Tegomer H-Si 2111), (b) diisocyanate-capped PDMS (urethane 1a), and (c) cyclohexanone-formaldehyde resin (CF).

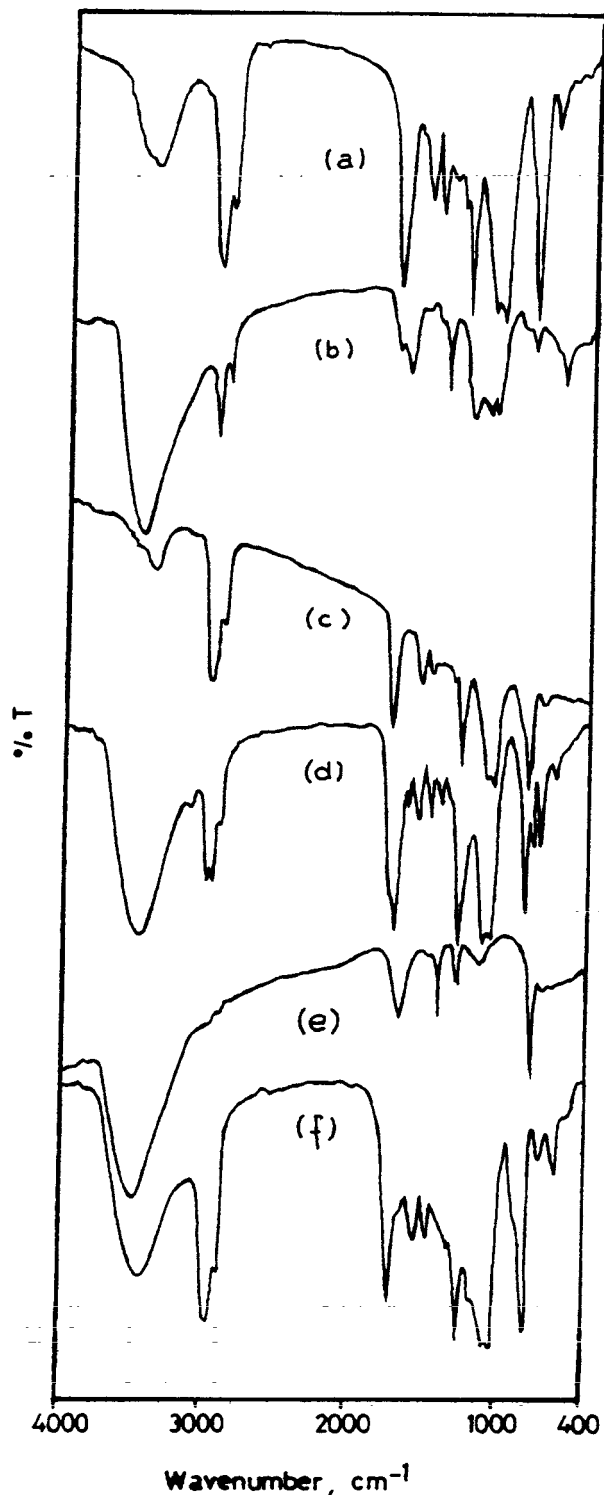


Figure 2 FTIR spectrum of (a) Block Copolymer No. 1a-CF (b) block copolymer No. 1b-CF, (c) Block Copolymer No. 2a-CF, (d) Block Copolymer No. 1a-AF, (e) Block Copolymer No. 1b-AF, and (f) Block Copolymer No. 1a-CMF.

Table II $^1\text{H-NMR}$ Spectral Data of the Samples: δ ppm (CDCl_3)

Sample	No.	$-\text{CH}_3$	$-\text{CH}_2-$	$-\text{CH}_2\text{OH}$	Aromatic CH	$-\text{Si}-\text{O}-$	$-\text{Si}-\text{CH}_2$	$\text{NH}-\text{CH}_2$	$-\text{CH}_2\text{OOCNH}-$
Ketonic resin ^a	CF	—	1.2-2.3	3.2-4.2	—	—	—	—	—
Ketonic resin ^a	AF	—	1.7-3.5	3.7-4.9	7.0-8.2	—	—	—	—
Ketonic resin ^a	CMF	—	1.3-2.8	3.3-3.9	—	—	—	3.5-3.9	—
Block copolymer	1a-CF	1.1	1.2-2.2	3.0-4.0	—	0.05-0.1	0.5	2.3	4.0
Block copolymer	2a-CF	1.05	1.4-2.6	3.2-3.8	—	0.06	0.5	2.2	4.0
Block copolymer	1a-AF	1.15	0.8-1.2	3.4-4.5	7.0-8.1	0.06	0.5	2.2	4.0
Block copolymer	1a-CMF	1.1	1.5-2.0	2.8-3.7	—	0.05-0.06	0.55	2.2-2.4	4.0

^a Kizilcan et al.⁷

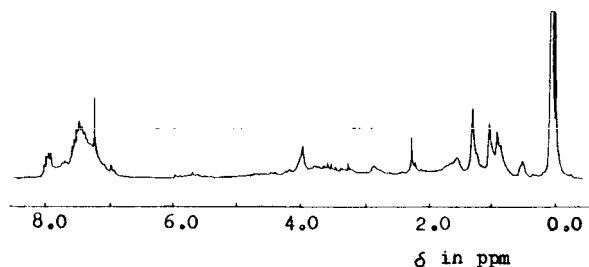


Figure 3 $^1\text{H-NMR}$ (partial) spectrum of block copolymer No. 1a-AF.

synthesized by reacting isocyanate-capped PDMS and hydroxyl-containing ketonic resin. Experimental data on the preparation condition of diisocyanate-capped PDMS are given in Table I. The chosen ketonic resins to synthesize the block copolymers were cyclohexanone-formaldehyde resin (CF), acetophenone-formaldehyde resin (AF), and *in situ* melamine-modified cyclohexanone-formaldehyde resin (CMF).

The block copolymers were examined with TLC. Diisocyanate-terminated PDMS (1a and 1b), ketonic resins (CF and AF), and block copolymers (1a-CF and 1b-AF) were applied to the TLC plate eluting with chloroform–benzene–ethyl alcohol, 1 : 5 : 1 mixed solvent; then each sample showed their own R_f values. TLC results that indicated those products were not a blends of ketonic resins and diisocyanate-terminated PDMS, but they were block copolymers.

Intermediates and the copolymeric products were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR)

analysis. In the FTIR spectra of dihydroxy PDMS, the peaks at 3520 and 3590 cm^{-1} are due to the —OH groups [Fig. 1(a)]. These OH absorption peaks disappear at the end of the capping reaction with isophorone diisocyanate (IPDI) [Fig. 1(b)]. The peak at 2280 cm^{-1} is due to the principal absorption peak for isocyanate groups. The disappearance of —NCO peak after the reaction of capped PDMS with ketonic resins [Fig. 1(c)] indicates the formation of copolymers (Fig. 2). Peaks around 3440 cm^{-1} in all copolymers were due to —NH stretching of urethane groups. In the CMF resin-containing block copolymer, the peaks between 1500–1750 cm^{-1} were due to both melamine groups and urethane groups [Fig. 2(f)].

$^1\text{H-NMR}$ spectra of the samples confirm also the purposed structural formulas. The peaks appearing at 0.05–0.1 ppm are due to —Si—CH₂— and —Si—CH₃ in the block copolymers, which indicates the incorporation of poly(dimethylsiloxane) into the copolymers (Table II). The ABA structure of the copolymers were determined by using $^1\text{H-NMR}$ spectrum of Copolymer No. 1a-AF (Fig. 3). The ratio of aromatic C—H peaks integral at 7.0–8.1 ppm due to AF resin to —Si—CH₃ peak integral at 0.006 ppm, plus —Si—CH₂— peak integral at 0.5 ppm due to PDMS, gives the combining of two moles of ketonic resin with one mole of PDMS.

The molecular weight of the block copolymers were measured by GPC. The results are given in the Table III. Although the molecular weights of the ketonic resins were between 1000–3000 g mol^{-1} , the molecular weights (M_n) of the block copolymers were obtained between 7000–13,000

Table III The Physical Properties of the Copolymers

Sample	No.	\bar{M}_n (g mol^{-1})	\bar{M}_w (g mol^{-1})	Solubilities ^a					
				THF	CHCl_3	$(\text{CH}_3)_2\text{CO}$	CCl_4	MeOH	$\text{C}_6\text{H}_5\text{CH}_3$
Ketonic resin	CF	1500 ^b	1600 ^b	s	s	sl	hsl	sl	sl
Ketonic resin	AF	1000 ^b	1000 ^b	s	s	sl	hs	hs	hsl
Ketonic resin	CMF	9900 ^b	20,000 ^b	s	s	s	hs	sl	hs
PDMS		1200	—	s	s	s	s	sl	s
Block copolymer	1a-CF	7000	16,500	s	s	s	s	hs	s
Block copolymer	1b-CF	8300	18,500	s	s	s	sl	hsl	sl
Block copolymer	2a-CF	13,000	33,800	s	s	s	sl	hs	s
Block copolymer	1a-AF	—	—	sl	s	s	hsl	hsl	s
Block copolymer	1b-AF	—	—	sl	s	s	sl	i	s
Block copolymer	1a-CMF	10,000	24,200	s	s	s	i	i	sl

^a Abbreviations are as follows: s, soluble; sl, slightly soluble; hs, hot soluble; hsl, hot slightly soluble; i, insoluble.

^b Kizilcan et al.⁷

Table IV Contact Angle Measurements

Sample	No.	Cast Film (from Dichloromethane) Air Side
CF		75
AF		80
CMF		78
Block copolymer	1a-CF	88
Block copolymer	1b-CF	92
Block copolymer	2a-CF	95
Block copolymer	1a-AF	98
Block copolymer	1b-AF	99
Block copolymer	1a-CMF	103

g mol⁻¹; and the molecular weight dispersity of the copolymers were around 2.3.

The solubilities of the copolymers were investigated by using different solvents. As seen in the Table III, the solubilities of copolymers were appreciably different than the corresponding ketonic resins and PDMS.

Melting points of the used ketonic resins were found as 110, 65, and 102°C for CF, AF, and CMF resins, respectively.⁷ The Melting point of the Copolymer No. 1a-CF was determined as 105°C. The melting points of the other copolymers could not be measured by this method because they were already soft and elastic products at room temperature. The elasticities of the products depend on the chain length of PDMS segments incorporated into the copolymers, while Copolymer No. 1b-CF is elastic.

Contact angle measurements were made on block copolymeric films prepared by casting from dichloromethane solution on the glass slides. The results are given in Table IV. Copolymers have considerably higher contact angles than ketonic resins.

CONCLUSION

PDMS-containing ketonic resins showed the unique properties by combining high surface ac-

tivity of siloxane segments and good compatibility of ketonic resins.

Pure poly(dimethylsiloxane)s are mechanically too weak to be used directly and they show cold flow, even at very high molecular weights (M_n equal to 500,000 g mol).² Solid copolymers produced in this work may be useful for many applications as additives. The poly(dimethylsiloxane)s are also extremely nonpolar and have very low experimental solubility parameters when compared with other organic polymers.² This leads to the thermodynamic incompatibility of PDMS with almost all other organic polymers. This type of copolymer may be used as a compatibilizer since the ketonic resin segments are compatible with many organic polymers. Therefore, these copolymers may be used as compatibilizer resins and additives in many applications.

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