Preparation and Characterization of Block and Graft Copolymers Using Macroazoinitiators Having Siloxane Units

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SYNOPSIS

α,ω-Amine terminated organofunctional polydimethylsiloxane (PDMS) was condensed with 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) to prepare macroazoinitiators containing siloxane units. Interfacial polycondensation reaction at room temperature was applied: ACPC was slightly dissolved in carbon tetrachloride and it was poured on aqueous NaOH solution of PDMS. Block copolymers containing PDMS as a block segment combined with polystyrene (PS) have been derived by the polymerization of styrene monomer initiated by these macroazoinitiators. PS-b-PDMS block copolymers were characterized by using nuclear magnetic resonance and infrared spectroscopy. Thermal and mechanical properties of the block copolymers were studied by using thermogravimetric analysis, differential scanning calorimetry, and a Tensilon stress–strain instrument. The morphology of block copolymers was investigated by scanning electron microscopy. PDMS-g-polybutadiene (PBd) graft copolymers were also prepared by reaction of PBd with the above macroazo-initiator. Increase in the amount of macroazoinitiator in the mixture of PBd (52% w/w) leads to the formation of crosslinked graft copolymers. Molecular weights of soluble graft copolymer samples were between 450 and 600 K with a polydispersity of 2.0–2.3. © 1996 John Wiley & Sons, Inc.
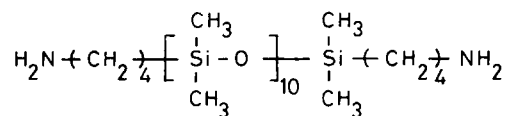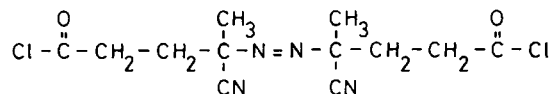
INTRODUCTION

A variety of macroazoinitiators have been reported for the synthesis of block and graft copolymers via radical process.[1–6]

Macroazoinitiators containing polysiloxane segments were proposed to be interesting intermediates useful for the synthesis of siloxane–vinyl block copolymers.[4] The macroazoinitiator derived from 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) and α,ω-bis(aminopropyldimethyl) polysiloxanes was used in the synthesis of polysiloxane–vinyl block copolymers, especially the polydimethylsiloxane (PDMS)-b-poly(methyl methacrylate) system.[2–4] A few results are reported for the block copolymers of PDMS-b-polystyrene (PS).[2]
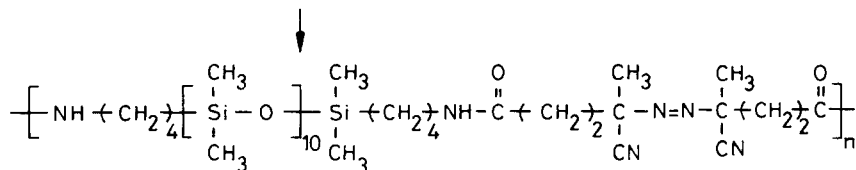
In the present study, macroazoinitiators containing siloxane segments were synthesized and used in the radical polymerization of styrene. PDMS-b-PS block copolymers were identified by using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. Copolymeric samples were characterized by thermal and mechanical analysis. The morphology of the block copolymers was studied by scanning electron microscopy.

Grafting is considered an important technique for modifying physical and chemical properties of polymers.[7] It was recently reported by Hazer[8] that graft copolymers of poly(ethylene oxide) on polybutadiene (PBd) chains can be obtained by reacting PBd with a macroazoinitiator. This article also describes the preparation of PDMS-g-PBd graft copolymers by using a similar technique. The siloxane-containing macroradicals (R) formed by thermal decomposition of the above-mentioned macroazoinitiators may react with the double bonds present in the PBd

$$H_2N+CH_2\underset{4}{\overset{}{\rightarrow}}\left[\begin{matrix}CH_3\\|\\Si-O\\|\\CH_3\end{matrix}\right]_{10}\begin{matrix}CH_3\\|\\Si+CH_2\underset{4}{\overset{}{\rightarrow}}NH_2\\|\\CH_3\end{matrix}$$

α, ω — amine terminated — PDMS

$$Cl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{CH_3}{\underset{CN}{\overset{|}{C}}}-N=N-\overset{CH_3}{\underset{CN}{\overset{|}{C}}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl$$

ACPC

↓

$$\left[NH+CH_2\underset{4}{\overset{}{\rightarrow}}\left[\begin{matrix}CH_3\\|\\Si-O\\|\\CH_3\end{matrix}\right]_{10}\begin{matrix}CH_3\\|\\Si+CH_2\underset{4}{\overset{}{\rightarrow}}NH-\overset{O}{\overset{\|}{C}}+CH_2\underset{2}{\overset{}{\rightarrow}}\overset{CH_3}{\underset{CN}{\overset{|}{C}}}-N=N-\overset{CH_3}{\underset{CN}{\overset{|}{C}}}+CH_2\underset{2}{\overset{}{\rightarrow}}\overset{O}{\overset{\|}{C}}\\|\\CH_3\end{matrix}\right]_n$$
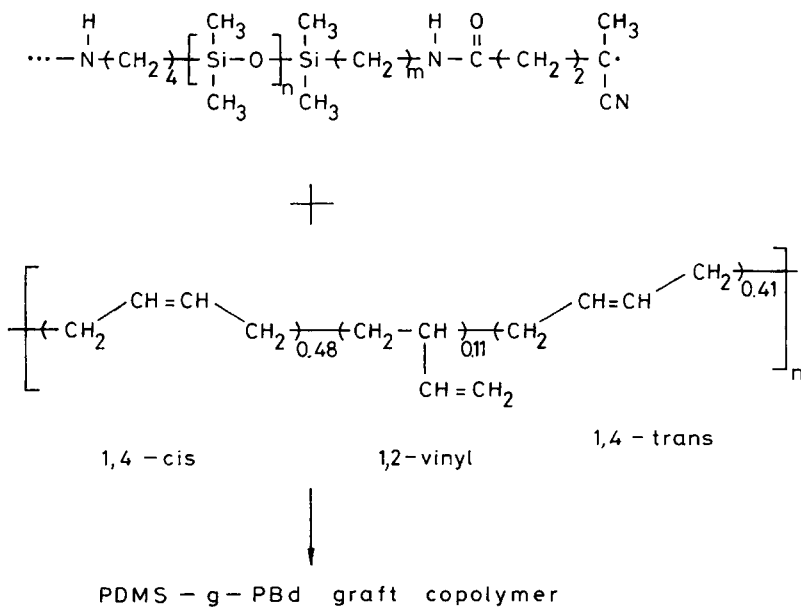
PDMS — macro — azo — initiator

Scheme 1

chains. The addition reaction takes place mostly on the pendant vinyl groups[8] on the polymer, as shown in reaction schemes 1 and 2. The first step shows the polycondensation reaction between ACPC and α-ω-amine terminated PDMS, and the resulting product is the macroazoinitiator used in the preparation copolymers (Scheme 1).

The types of macroradicals shown in Scheme 2 are produced by thermal decomposition of the initiator shown in Scheme 1.

$$\cdots-\overset{H}{\overset{|}{N}}+CH_2\underset{4}{\overset{}{\rightarrow}}\left[\begin{matrix}CH_3\\|\\Si-O\\|\\CH_3\end{matrix}\right]_n\begin{matrix}CH_3\\|\\Si+CH_2\underset{m}{\overset{}{\rightarrow}}\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}+CH_2\underset{2}{\overset{}{\rightarrow}}\overset{CH_3}{\underset{CN}{\overset{|}{C}}}\cdot\\|\\CH_3\end{matrix}$$

+

$$\left[+CH_2\diagup^{CH=CH}\diagdown_{CH_2}\underset{0.48}{\overset{}{\rightarrow}}+CH_2-\underset{\underset{CH=CH_2}{\overset{|}{CH}}}{\overset{}{CH}}\underset{0.11}{\overset{}{\rightarrow}}+CH_2\diagup^{CH=CH}\diagdown^{CH_2\underset{0.41}{\overset{}{\rightarrow}}}\right]_n$$

1,4 - cis   1,2-vinyl   1,4 - trans

↓

PDMS — g — PBd   graft copolymer

Scheme 2

EXPERIMENTAL

Materials

4,4'-Azobis (4-cyanopentanoic acid) (ACPA) was supplied by Fluka AG. ACPC was prepared by the reaction of ACPA with phosphorus pentachloride. The reaction was carried out in benzene. The solution was chilled in an ice bath and then allowed to warm at room temperature. The filtration and purification procedures were applied as described in the literature.[9]

PDMS was kindly supplied by Goldschmidt (ASI-2120) (Germany) with M_n = 1050 g/mol^{-1}.

Styrene was obtained from Fluka AG (Switzerland). It was freed from inhibitor by washing in 5% aqueous solution and distilled water. It was dried with Na_2SO_4 and freshly distilled under reduced pressure before use.

PBd was supplied by DuPont, (Wilmington, DE, USA) with M_n = 2.23 × 10^5 and M_w = 4.46 × 10^5 (measured by a Waters GPC instrument). Its molecular structure was (41% 1,4-*trans*), (48% 1,4-*cis*), (11% 1,2-vinyl). These isomeric contents were calculated by using Fourier transform infrared absorbance values at ν (cm^{-1}) = 740 (for 1,4-*cis* with relative absorbance coefficient ε = 0.175), at ν (cm^{-1}) = 967 (for 1,4-*trans* with ε = 0.647), and at ν (cm^{-1}) = 910 (for 1,2-vinyl with ε = 1.000).[10]

The other solvents and reagents used were extra-pure commercial products.

Synthesis of PDMS Macroazoinitiators

Two PDMS macroazoinitiators were synthesized having different molecular structures.

Synthesis of MI-PDMS(a). A solution of 20 mmol ACPC in 50 mL of carbon tetrachloride was added to the mixture of 40 mmol α, ω-amine terminated PDMS prepolymer and 30 mL of aqueous NaOH (10% w/w) and stirred for 24 h at room temperature. The molar ratio of ACPC to PDMS was 1 : 2. Then

the solution was washed with water 3 times to secure the removal of salts and ACPA from the product. The organic phase was dried with sodium sulfate overnight at 0°C. Solvent was evaporated. Viscous liquid was dried under vacuum and stored at 0°C until use.

Synthesis of MI-PDMS(b). MI-PDMS(b) was prepared by the same procedure with the molar ratio of ACPC to PDMS 1 : 1 to obtain a macroinitiator with chain extension.

Table I shows the preparation conditions and the characterization of these macroinitiators.

Synthesis of PDMS-b-PS Block Copolymer

A given amount of styrene and the macroinitiator MI-PDMS(a) or MI-PDMS(b) were charged into a pyrex tube. Nitrogen was introduced through a needle into the tube to expel the air. The tightly capped tube containing a small magnet was put in an oil bath at 60 or 70°C for 24 h. Subsequently the contents of the tube were dissolved in chloroform and then precipitated in methanol. The copolymeric sample obtained was dried in vacuum at room temperature for 48 h. Most of the copolymers were synthesized in bulk. Toluene was used as solvent in the polymerization of samples 10 and 11, given in Table II.

Tables II and III show the characteristic data of the resulting products.

Synthesis of PDMS-g-PBd Graft Copolymer

In a typical grafting procedure, a solution was prepared from a mixture of MI-PDMS(b), PBd, and chloroform (as solvent). The solution was stirred for 24 h, then spread onto an aluminum dish to obtain a polymeric film, and air-dried. The grafting reaction was carried out in an oven at 90°C, under nitrogen for 5 h. The grafted polymer mixture was fractionated by using the solvent ($CHCl_3$)–nonsol-

Table I   Preparation Conditions and Characterization of Macroazoinitiators

	Reactants							
Initiators	PDMS (g)	ACPC (g)	NaOH (10% Solution) (mL)	Solvent CCl_4 (mL)	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n	Appearance
MI-PDMS (a)	41.16	6.19	30	50	1750 (VP)	—	—	Pale yellow oil
MI-PDMS (b)	21.32	6.31	30	50	5200 (GPC)	6840 (GPC)	1.32	Viscous pale yellow oil

VP, Vapor pressure osmometry; GPC, gel permeation chromatography.

Table II Synthesis of PDMS-*b*-PS Block Copolymers

| Sample No. | Macroinitiator (g) | | Styrene (g) | MI-PDMS (w/w) | Polymer Temperature (°C) | Yield (w/w) |
	MI-PDMS (a)	MI-PDMS (b)				
1	0.50	—	4.171	10.6	70	28.5
2	0.83	—	4.303	16.2	70	33.4
3	1.06	—	2.028	34.4	70	32.0
4	1.99	—	2.435	43.8	70	25.5
5	—	—	2.770	—	70	15.0
6	—	0.046	1.331	3.35	60	41.0
7	—	0.110	1.258	8.04	60	51.0
8	—	0.178	1.237	12.6	60	64.0
9	—	0.247	1.314	15.8	60	55.0
10	—	1.434	2.650	35.1	60	40.0
11	—	3.368	1.929	63.6	60	45.0

Polymerization time: 24 h.

vent (CH_3OH) precipitation technique.[11] The results of grafting procedures are listed in Table IV.

Characterization

Number-average molecular weight (M_n) of MI-PDMS(a) was determined with a Knauer vapor pressure osmometer at 25°C in methylene chloride. The calibration of M_n was made by a benzil standard with an M_n of 210.12.

The fractional precipitation method[11] was carried out by measuring γ, the volume ratio of nonsolvent (methanol) to the solution of copolymers in chloroform to separate pure block and graft copolymers from the corresponding homopolymers.

Gel permeation chromatography (GPC) was used to determine molecular weights of the samples and their distributions with a Waters instrument (410 Differential Refractometer) in tetrahydrofuran. The elution rate was 1 mL/min^{-1}. Waters Styragel Col-

Table III Fractionation of PDMS-*b*-PS Block Copolymers

| Sample No. | Fractionation | | | Styrene Content | | GPC | | |
	$\gamma = 0.5$–0.6 Amount (w/w)	$\gamma = 1.0$ Amount (w/w)	$\gamma = 3.5$ Amount (w/w)	UV (w/w)	NMR (mol %)	$M_w \times 10^{-3}$ g mol^{-1}	$M_n \times 10^{-3}$ g mol^{-1}	M_w/M_n
1	100	—	—	95	—	446	249	1.79
2	100	—	—	99	—	397	222	1.78
3	100	—	—	93	—	294	159	1.84
4	100	—	—	100	—	253	137	1.85
5 Homo PS	100 ($\gamma = 0.4$)	—	—	100	—	109	778	1.40
6-1	—	73	—	93	—	383	106	3.55
6-2	—	—	27	—	—	222	38	4.19
7-1	—	65	—	—	99.5	373	106	3.52
7-2	—	—	35	91	—	148	38	3.89
8-2	—	—	100	100	—	222	48	4.60
9-2	—	—	100	96	95.5	170	42	4.05
10-1	—	17		—	81.1	108	49	2.20
10-2	—	—	83	—	62.8	112	20	5.60
11-2	—	—	100	—	34.3	23	19	1.18

Table IV Synthesis and Characterization of PDMS-*g*-PBd Graft Copolymers

Sample No.	MI-PDMS (b) (g)	PBd (g)	MI-PDMS (b) (w/w)	Crosslinked Polymer (w/w)	Oily Residue (w/w)	Pendant Vinyl Groups (%) IR	GPC		
							$M_n \times 10^{-3}$ (g mol^{-1})	$M_w \times 10^{-3}$ (g mol^{-1})	M_w/M_n
12	—	—	—	—	—	11.3	223	446	2.0
13	0.102	0.500	16.9	—	15.4	8.8	260	604	2.3
14	0.315	0.508	38.3	—	24.3	8.0	236	515	2.2
15	0.570	0.518	52.4	58	37.9	6.1	—	—	—

umns HR1 and HT6E were used for MI-PDMS(b) and the copolymer samples, respectively.

IR spectra of the macroinitiators and the copolymers were taken using a Perkin-Elmer 177 IR spectrometer.

^{1}H-NMR spectra of the products were recorded by a Bruker-AC 200L, 200 MHz NMR spectrometer.

Styrene content of the polymer fractions was determined by a Varian 635 D UV-VIS spectrometer. This method is based on measuring the absorbance of phenyl group of polystyrene at λ = 269 nm.[12]

Differential scanning calorimetry (DSC) thermograms were taken on a Schimadzu DSC-41 Model apparatus at a heating rate of 10°C/min. The glass
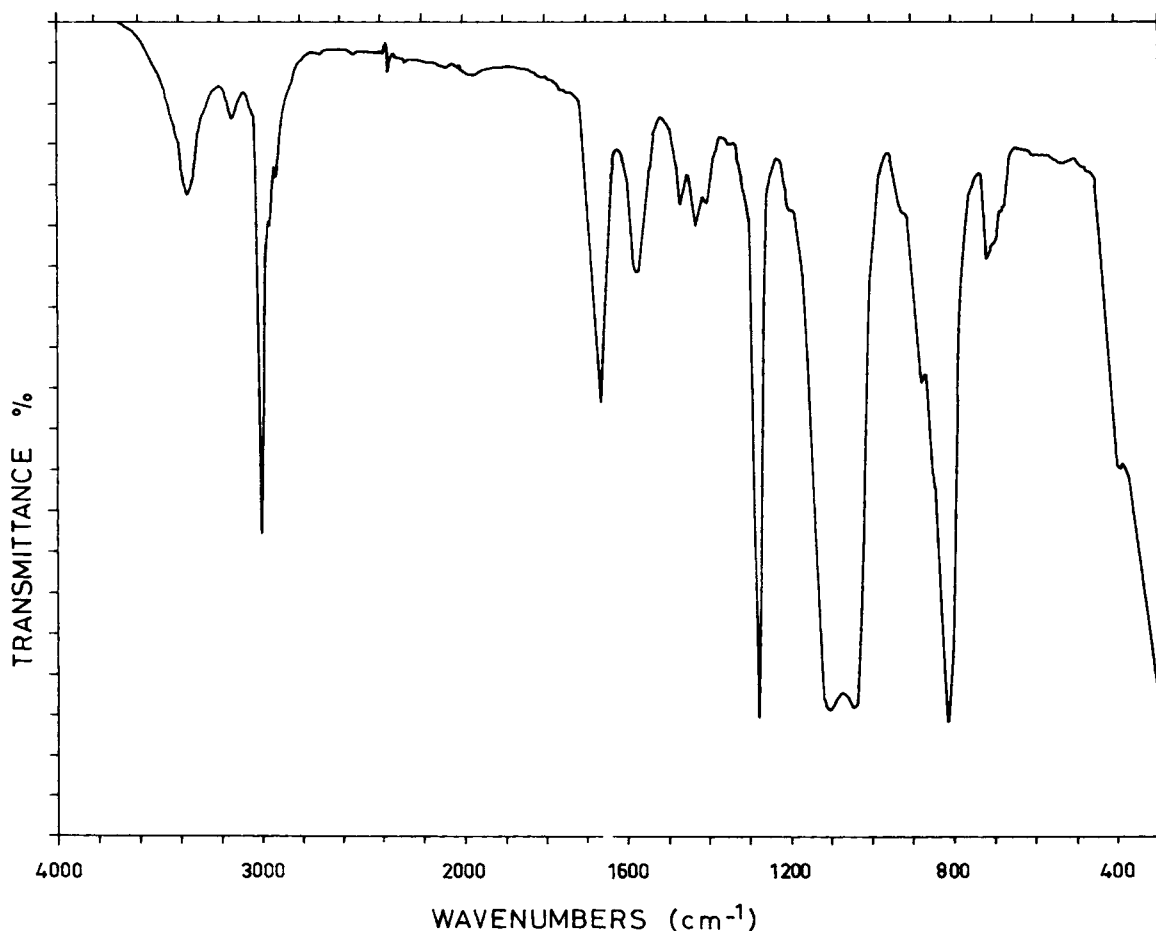
Figure 1 IR spectrum of macroazoinitiator MI-PDMS(b).

transition temperature (T_g) was taken at the onset of the corresponding heat capacity jump. Thermogravimetric analysis (TGA) measurements of macroinitiators were carried out by a DuPont TGA-951 under nitrogen atmosphere at a heating rate of 10°C/min.

The tensile strength and elongation measurements were performed at room temperature with a Tensilon (Toyo Measuring Instruments Co. Ltd.) UTM II tester with a crosshead speed of 10 mm/min.

Scanning electron micrographs were taken on a JEOL-JXA 840A scanning electron microscope

(SEM). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å on an Edwards S 150 B sputter coater.

RESULTS AND DISCUSSION

Synthesis of Macroinitiators

Two different types of macroinitiators containing siloxane units were synthesized by polycondensation
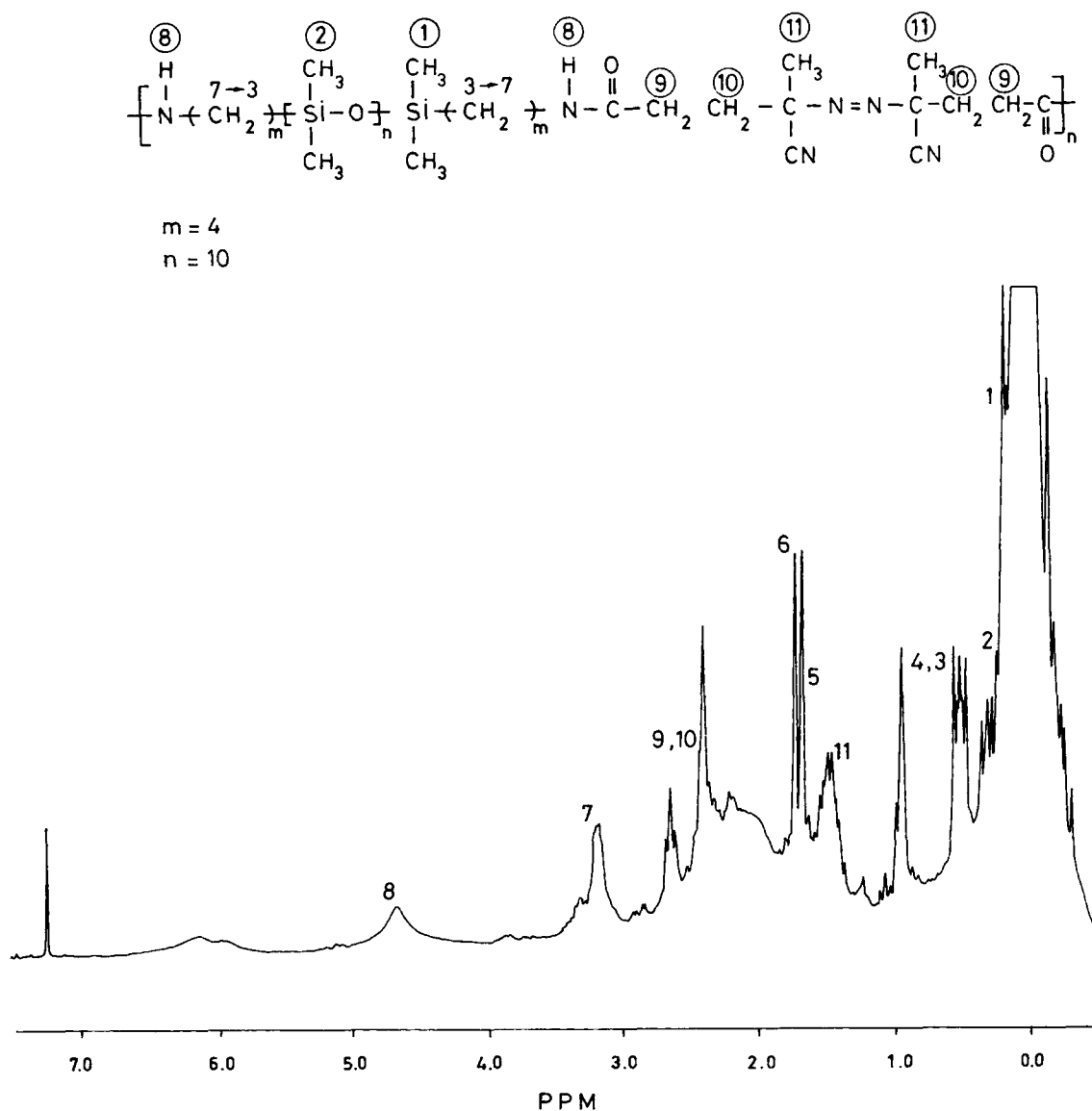
Figure 2 ^{1}H-NMR spectrum of macroazoinitiator MI-PDMS(b).

of ACPC and α-ω-amine terminated PDMS in molar ratios of (a) 1 : 2 and (b) 1 : 1, respectively. Table I shows the synthesis conditions and results of reaction between PDMS and ACPC. The M_n determined by vapor pressure osmometry and GPC indicate that the reactions proceed almost quantitatively. By keeping the molar ratio at 1 : 1, PDMS : ACPC, chain-extended macroinitiator (b) was obtained with higher M_n than that of (a), which is prepared in the ACPC : PDMS molar ratio of 1 : 2.

Figure 1 shows the IR transmittance spectrum of MI-PDMS(b) obtained. The characteristic peaks of MI-PDMS were observed at 3400 cm^{-1} for —NH stretching vibration band, at 1650 cm^{-1} and 1545 cm^{-1} for carbonyl absorption, at 1260 cm^{-1} and 800 cm^{-1} for Si—CH$_3$ deformation, and at 1024 cm^{-1} for Si—O—Si asymmetric stretching vibration.

The ^{1}H-NMR spectrum of macroazoinitiator MI-PDMS(b) confirms the structural formula. In Figure 2, we observed the signals of the —CH$_2$ groups (at 3.2 ppm) adjacent to —NH and the peaks —CH$_3$ (1.62–1.67 ppm) and —CH$_2$ (2.33–2.68 ppm) of ACPC. The signals that appeared at 4.68 ppm may be due to —NH groups in the macroazoinitiator.

Block Copolymerization of Styrene with MI-PDMS

Styrene was polymerized with MI-PDMS(a) and MI-PDMS(b) at 70°C and 60°C, respectively. The polymerization reaction conditions and the yields are given in Table II. Block copolymer yields obtained with MI-PDMS(b) (chain-extended macroinitiator) were nearly 2 times higher than those obtained with MI-PDMS(a). In order to explain this situation, we can presume that relatively higher —NH$_2$ end groups and lower azo groups present at MI-PDMS(a) might cause lower yields. The reaction
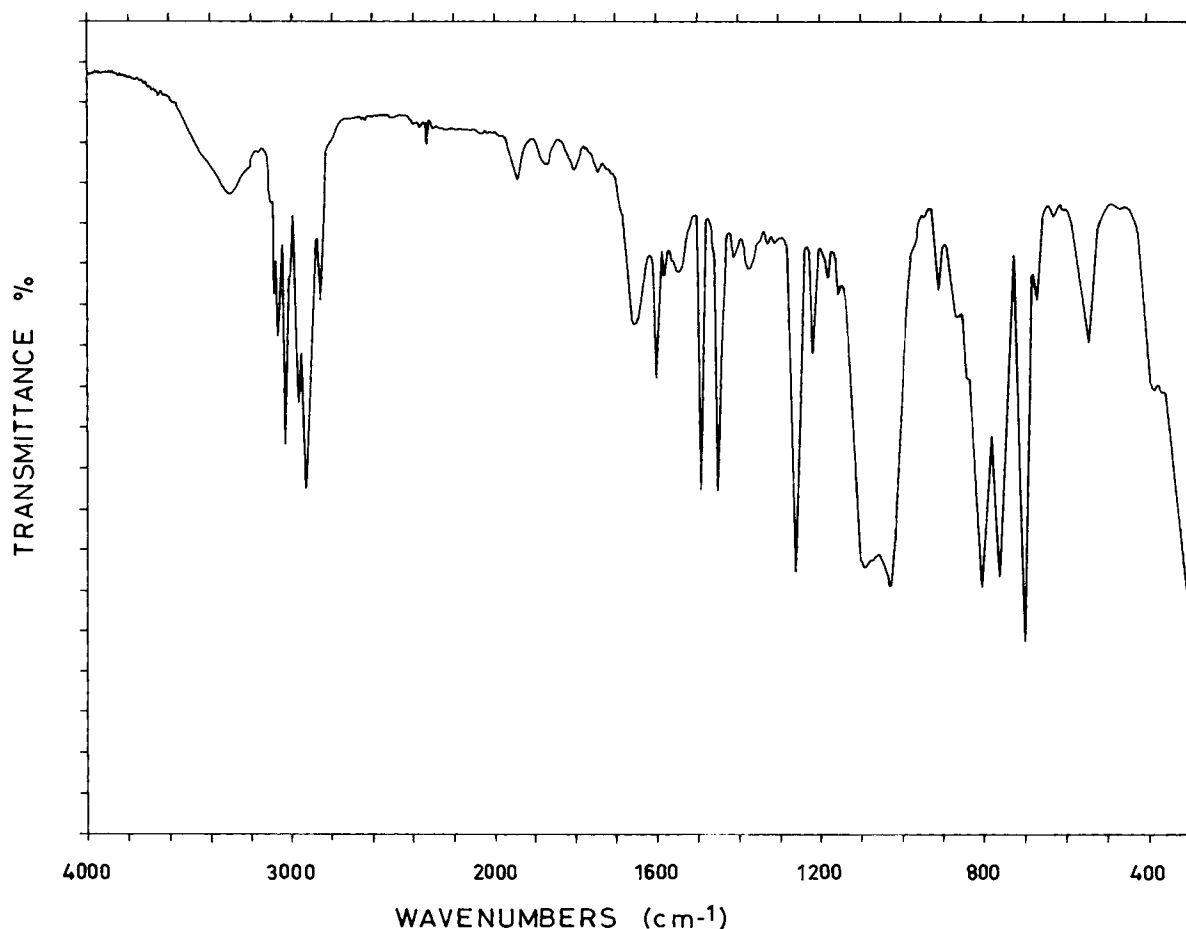

Figure 3   IR spectrum of PDMS-b-PS block copolymer, sample 10-2 in Table III.
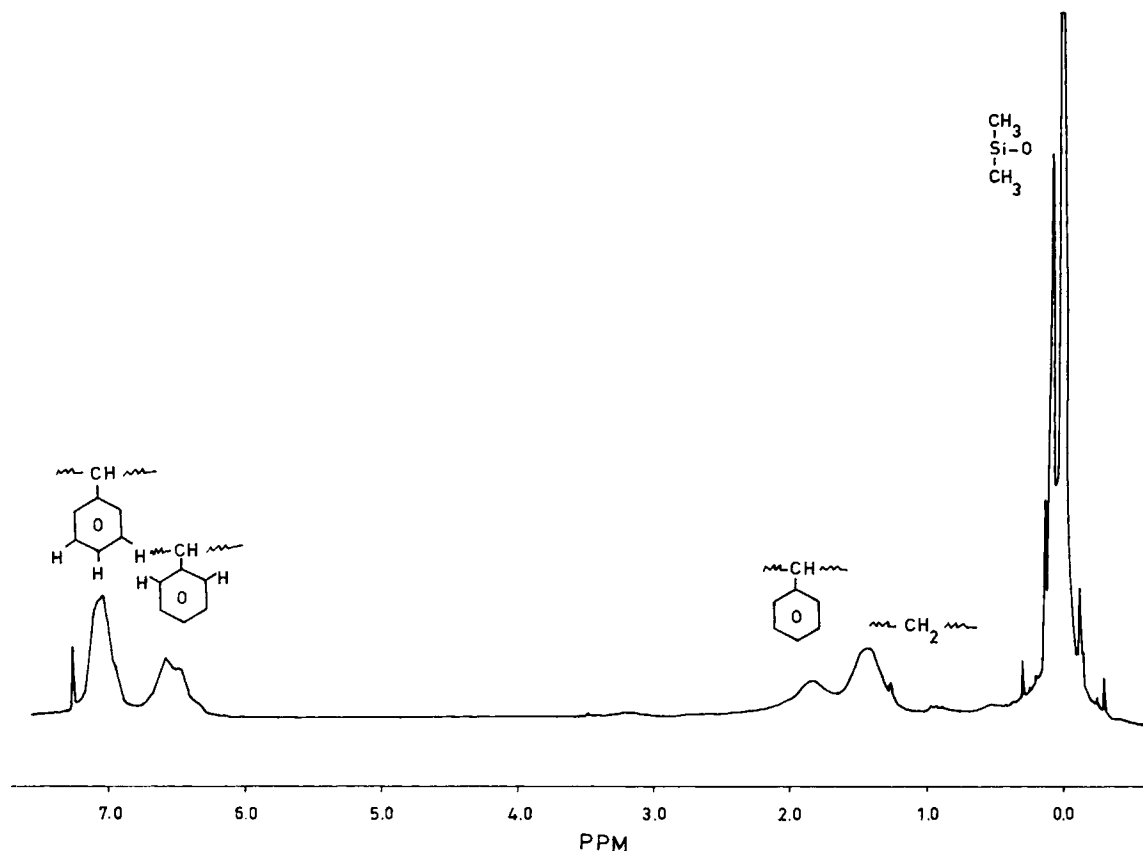
Figure 4 ¹H-NMR spectrum of PDMS-*b*-PS block copolymer, sample 10-2 in Table III.

products were analyzed by the fractional precipitation method. Volume ratio of nonsolvent (methanol) to the solution of the polymer, γ, for homopolystyrene is 0.5 while it is greater than 3.5 for most copolymers. In Figure 3 a typical IR spectrum of PDMS-*b*-PS block copolymer (sample 10-2 in Table III with 62.8 mol % PS) can be seen. This spectrum has a phenyl band of polystyrene at 1600 cm⁻¹ and characteristic bands of PDMS at 1260 cm⁻¹, 1024 cm⁻¹, and 800 cm⁻¹. A —NH peak in this spectrum (around 3400 cm⁻¹) indicates the incorporation of macroinitiator into the copolymers, and the IR spectrum provides definite evidence for the formation of copolymers.

Figure 4 exhibits typical ¹H-NMR spectrum of PDMS-*b*-PS block copolymer (sample 10-2 in Table III). ¹H-NMR was also used to determine the siloxane contents in mol % by calculating the peak areas of the phenyl protons in polystyrene (6.48–7.05 ppm) and the dimethylsiloxane protons in siloxane segments (0.072 ppm) given in Table III.

Grafting Reaction of PBd with MI-PDMS

Grafting reactions of PBd with MI-PDMS(b) produced PDMS-*g*-PBd graft copolymers, containing siloxane units (17–52% w/w) in high yields (62–85% w/w). These results are tabulated in Table IV. Figure 5 shows typical IR transmittance spectrum of PDMS-*g*-PBd graft copolymer [sample 14 in Table IV, 38.3% w/w MI PDMS(b)]. From the variation of 1,2-vinyl bands of PBd at 912 cm⁻¹ in the IR spectrum of PDMS-*g*-PBd copolymers, the structural unit concentrations of pendant vinyl groups can be calculated.[10] Table IV shows the decrease of pendant 1,2-vinyl bands of PBd copolymers with increasing macroazoinitiator concentration in the feed mixture.

Figure 6 shows a typical ¹H-NMR spectrum of PDMS-*g*-PBd copolymer, (sample 15 in Table IV). The peak at 4.9 ppm is due to the contribution of the hydrogens in the vinyl groups (=CH₂) and the peak at 5.4 ppm corresponds to the hydrogens of the
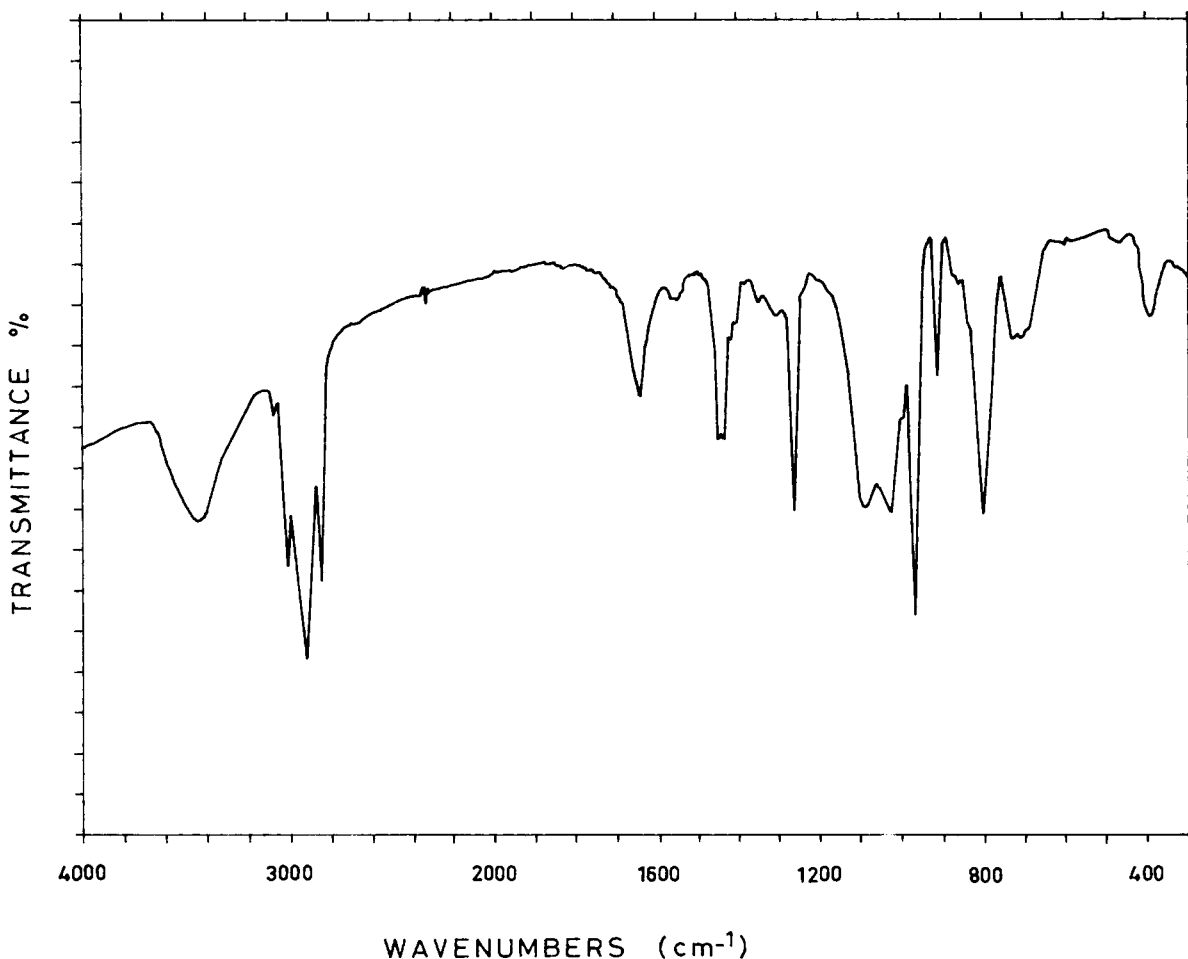
Figure 5 IR spectrum of PDMS-g-PBd graft copolymer, sample 14 in Table IV.

cis and trans units (CH═CH). The peak at 3.2 ppm is possibly due to the —CH₂ groups adjacent to —NH in the macroazoinitiator MI-PDMS(b).

Thermal, Mechanical, and Morphologic Studies of the Products

Thermal decomposition of MI-PDMS(b) was studied by using TGA. The elimination of N₂ from the macroazoinitiator stoichiometrically corresponds to 2.5%. The percentage weight loss at 100°C reached at the end of first derivate peak is 7.5% and it is roughly in agreement with the theoretical value given above. The TGA curve of MI-PDMS(b) can be seen in Figure 7.

Molecular weights of the copolymers determined by GPC technique are given in Tables III and IV. M_n and M_w values of block and graft copolymers

decrease with increasing PDMS content in the copolymers. Polydispersity of copolymeric samples show a variation in the range of 1.2–5.6.

The T_g for various typical block copolymers are shown in Table V. The T_g of the PDMS component cannot be observed due to lower PDMS block lengths with respect to the PS component in copolymers. However the T_g value of PS, because of the plasticizer effect of PDMS, is observed at around 90°C, which is lower than the T_g value of homo-PS (100°C).

Stress and ultimate strain at break, Young's modulus, were determined from the stress–strain curves of block copolymer films. Table V gives the results of the determination of the mechanical properties on solvent-cast films (from chloroform) of PDMS-b-PS block copolymers. In general, they have higher elongations (6–8%) when compared to
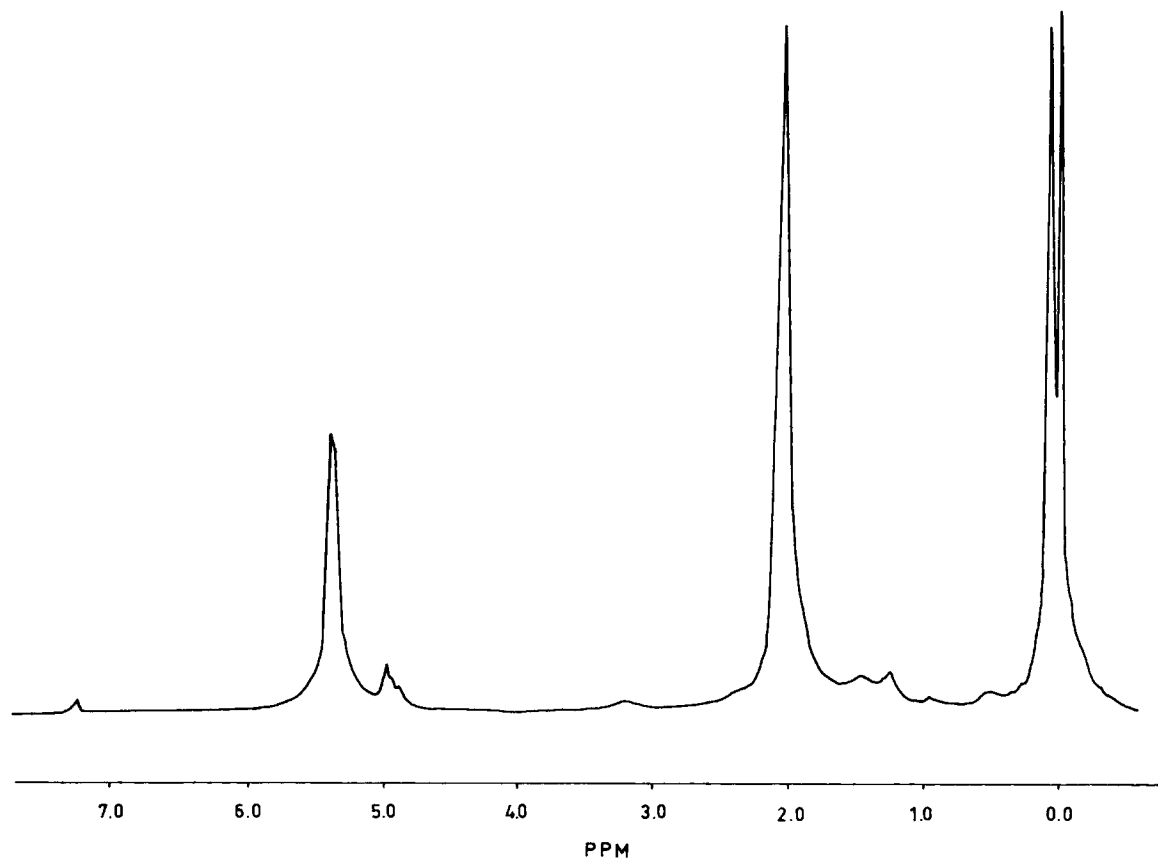
Figure 6   ¹H-NMR spectrum of PDMS-*g*-PBd graft copolymer, sample 15 in Table IV.

the reference homo-PS (2%).[13] However, tensile strengths of the copolymers reported here are very close to those reported in the literature for polystyrene (22–50 MPa) and Young's modulus values calculated for the PDMS-*b*-PS block copolymers are lower than homo-PS (1600–3400 MPa).[13,14]

Secondary electron images were applied in the SEM micrographs. Figure 8(a) shows the fractured surface of the homo-PS (sample 5 in Table III). The microstructure of the homopolymer was examined for comparison with the PDMS-*b*-PS copolymers. Figure 8(b–d) shows the electron micrographs obtained for copolymer films of samples 9-2 and 10-2 given in Table III (cast from chloroform) with different PDMS content and molecular weight. Sample 9-2 [Fig. 8(b)] with M_n = 42 × 10³ and PDMS content of 5 w/w has a cellular structure showing the entrapment of PDMS within copolymer. Sample 10-2, with lower M_n (20 × 10³) and PDMS content of 37 w/w exhibited rod–sphere structure in Figure 8(c). The morphology of this sample can be better seen at different magnification in Figure 8(d). The changes in the morphologies of the samples 9-2 and

10-2 are due to composition and molecular weight. Other electron micrograph studies for similar systems also indicate that structure of PS surrounded by darker regions of siloxane changes as a function of block copolymer molecular weight and composition.[15]

CONCLUSION

Two different kinds of MI-PDMS, (a) and (b), were prepared by reactions between ACPC and PDMS with mol ratios: (a) 1 : 2, and (b) 1 : 1. Because of equimolar feeds of ACPC and PDMS, MI-PDMS(b) was obtained as a chain-extended macroazoinitiator. When compared the polymer yields obtained from styrene polymerization initiated by PDMS macroazoinitiators, it was observed that MI-PDMS(a) gave lower block copolymer yields than those obtained from MI-PDMS(b). In this manner molecular weight values of the block copolymer samples obtained by using MI-PDMS(a) were higher than those obtained by MI-PDMS(b), since MI-
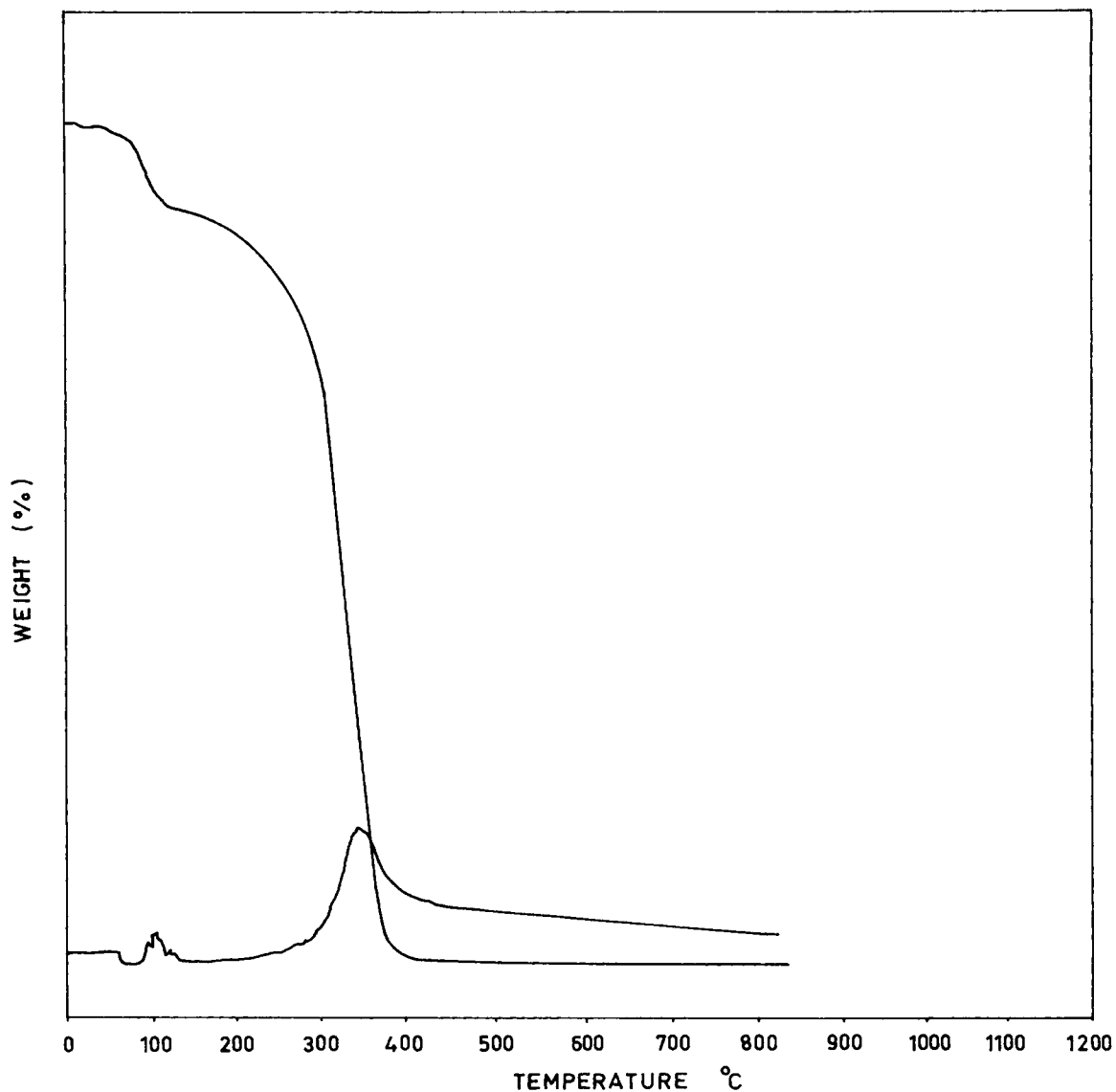
**Figure 7** TGA curve of macroazoinitiator MI-PDMS(b).

PDMS(a), with lower molecular weight, has higher —NH$_2$ end groups and lower azo groups. The structure of block copolymers obtained by using MI-

PDMS(a) can be considered as BAB type of three-block copolymers. However, MI-PDMS(b) might lead to (AB)$_n$-type block copolymers. Grafting re-
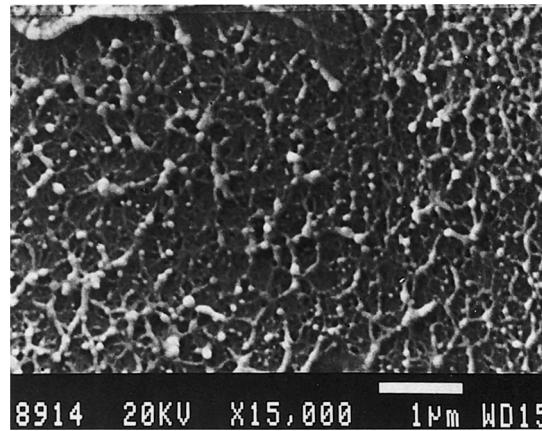
Table V   Mechanical and Thermal Properties of PDMS-*b*-PS Block Copolymers

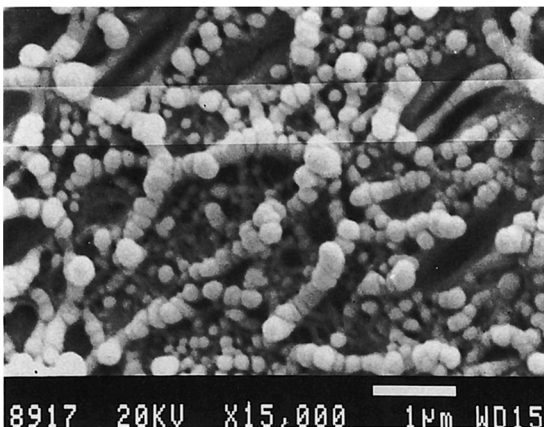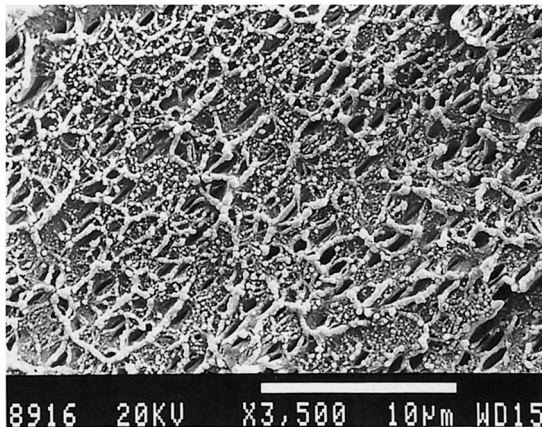| Sample No.	T_g (°C)	Stress at Break (MPa)	Strain at Break (MPa)	E Young's Modulus (MPa)
PS[a]	100	31	2.0	1670
6-1	87.9	29	6.5	1020
7-1	88.3	26	4.3	1450
8-2	—	20	5.7	750
9-2	—	19	7.2	860
10-2	91.3	18.5	7.7	468

[a] See Uyanik and Baysal.[13]
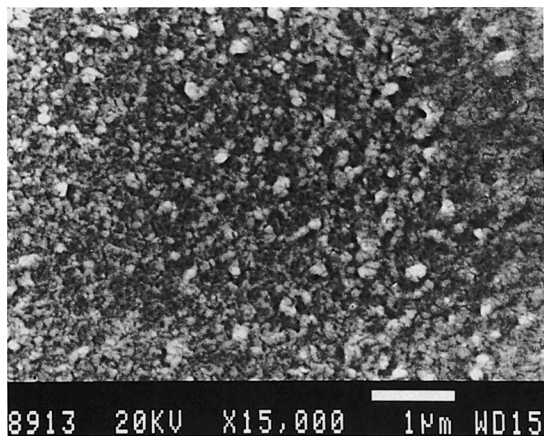
(a)

(b)

(c)

(d)

Figure 8   SEM micrographs of (a) homo-PS and PDMS-*b*-PS block copolymers, (b) sample 9-2, (c) sample 10-2 at magnification (×15,000), (d) sample 10-2 at magnification (×3,500) given in Table III.

actions of macroazoinitiators containing siloxane segments on PBd proceed by attaching macroradicals to pendant vinyl groups of PBd.

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