Styrene Polymerization with a Macroinitiator Having Siloxane Units

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SYNOPSIS

Block copolymers containing segments of poly(dimethylsiloxane) (PDMS) and polystyrene were synthesized. Dihydroxy terminated PDMS M_n 2500 g/mol, was reacted with an aliphatic diisocyanate (isophorone diisocyanate) and an aliphatic hydroperoxide (*t*-butyl hydroperoxide). The resulting polymeric peroxycarbamate having siloxane units (a new macroinitiator) was used as free radical initiator for vinyl polymerization of styrene. Formation of block copolymers was illustrated by several characterization methods such as chemical and spectroscopic analysis, fractionation, and GPC. Mechanical and thermal characterization of the copolymers were made by stress–strain tests and DSC. The surface properties and the morphology of the block copolymers were investigated by contact angle measurements and SEM. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Siloxane containing copolymers are important types of multiphase copolymer systems. Due to their multiphase morphology, they display interesting properties of siloxanes in addition to the desirable mechanical properties of the organic polymers they are combined with.[1–5] Polysiloxanes, especially poly(dimethylsiloxane) (PDMS) have extremely low glass transition temperature (−127°C); very high chain flexibility; good oxidative, thermal, and UV stability; hydrophobicity; biocompatibility; high gas permeability; and low surface energy. Despite their many outstanding properties, many potential applications of these polymers are hindered by poor mechanical properties.

A very effective and important way to improve the mechanical strength of this material is by controlled synthesis of a block (AB or ABA) or segmented [(AB)n] copolymer where the soft, rubbery component is chemically linked to a glassy or a crystalline segment. The resulting copolymers can exhibit the properties of thermoplastics or thermoplastic elastomers depending on the nature of the blocks, block lengths, and the copolymer composition.[1,2,6,7] Siloxane containing multiphase copolymers have been studied for the last two decades by using the method of living anionic polymerization.[1] Synthesis of multiblock copolymers of PDMS and polystyrene (PS, and substituted PSs) was achieved by a hydrosilylation reaction between (Si—H) terminated PDMS and vinyl terminated PS. The block copolymers obtained by this technique are typical thermoplastic elastomers.[3,4] Siloxane containing block or graft copolymers can also be synthesized by the use of ring-opening polymerization or free radical copolymerization techniques.[5] Application of these techniques for the preparation of organosilicon copolymers is fairly new when compared with living anionic polymerization. Morphology and mechanical properties of anionically synthesized poly(dimethyl siloxane-*b*-styrene-*b*-dimethylsiloxane) block copolymers were investigated.[8] More detailed analysis of the surface activity of poly(styrene-*b*-dimethylsiloxane) copolymer was given recently.[9]

In this work, we describe the synthesis of a new macroinitiator having siloxane units and peroxide

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groups. Glassy segments of PS were incorporated by using this macroinitiator for polymerization of styrene at elevated temperatures. We studied poly(styrene–dimethylsiloxane–styrene), ABA type (polystyrene = A, PDMS = B) block copolymers obtained by this technique using various methods of characterization, such as fractionation, UV analysis, viscometry, GPC, DSC, and stress–strain measurements. Contact angle and SEM studies were performed to investigate surface characteristics of the block copolymers.

EXPERIMENTAL

Materials

α-ω-dihydroxy poly(dimethylsiloxane) (PDMS) a product of Goldschmidt Chemical Corporation (Tegomer H-Si 2311, $M_n = 2500 \pm 250$ g mol^{-1}) was dried at 30°C in a vacuum oven for 48 h before use. Isophorone diisocyanate (IPDI), a product of Fluka AG, was used without purification. The purity determined by isocyanate analysis was 95.1%. *t*-Butyl hydroperoxide (*t*-BHP) was a product of Fluka AG. It was distilled under reduced pressure. The peroxide content was 91.7%. It was used after drying over anhydrous magnesium sulfate. Dibutyltin dilaurate (T-12) was a product of Fluka AG. It was used as a catalyst without purification. Styrene was washed with 10% aqueous NaOH solution, dried over $CaCl_2$, and freshly distilled in a vacuum. Solvents used were products of Merck AG. They were carefully dried over molecular sieves (Linde Type 5A), followed by fractional distillation. PS (Union Carbide, SMD 3500) was used as reference material for characterization.

Analyses

The PS content was measured by UV spectrometry on a Shimadzu Corp. UV-150-02 model double beam UV/VIS spectrometer. Gel permeation chromatographs were obtained on a Waters instrument. Tetrahydrofuran served as eluent at 25°C. The flow rate was 1 mL min^{-1}. FTIR spectra of the samples were collected on Perkin-Elmer 177 spectrometer. NMR spectra of the products were recorded by using a Bruker-AC 200L, 200-MHz NMR spectrometer. Stress–strain tests were performed on a Tensilon (Toyo Measuring Instruments Co., Ltd.) UTM II tester at room temperature with a crosshead speed of 5 mm min^{-1}. DSC thermograms were conducted in a Shimadzu DSC-41 apparatus at a heating rate of 10°C min^{-1}. Scanning electron micrographs were taken on a JEOL-JXA 840 A scanning electron microscope. The cast films from a toluene–methylene chloride mixture were prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å. Contact angle measurements of the copolymer films were done on a Kernco model GIII contact angle meter at room temperature using distilled, deionized water.

Procedure

Preparation of Peroxycarbamates

The dihydroxy terminated PDMS prepolymer (PDMS-2500) and the aliphatic diisocyanate (IPDI) were reacted at 40°C (72 h) and at 60°C (46 h) in bulk under a blanket of dry nitrogen. The molar ratio of diisocyanate to prepolymer was held at three to prevent undesired chain extension. The resulting product (compound I) was washed with dry acetonitrile 3 times in a separation funnel, isolated by decantation, and dried *in vacuo* at 25°C overnight. The isocyanate content of the end-capped products (compound I) was determined by end group titration of isocyanates.[10] The calculated molecular weights were consistent with the theoretical formula.

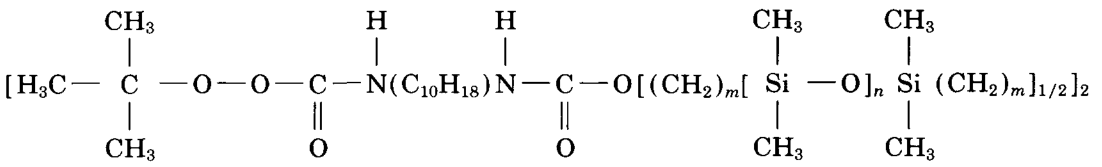
In the second step, the diisocyanate terminated siloxane was reacted with *t*-BHP in methylene chloride. A few drops of T-12 catalyst was added to the reaction mixture. The reaction was carried out under a nitrogen blanket at room temperature in the dark for 200 h.

Table I Preparation Conditions and Characterization of Macroinitiator

Sample	NCO/PDMS	Isocyanate Wt % of Capped PDMS	M_n (g mol^{-1})	[OOH]/[NCO]	Peroxide (Wt %)
Prepolymer PDMS-2500	—	—	2500 ∓ 250	—	—
Compound I	3.07	2.95	2850	—	—
		ca. 2.82	2980 *ca.*		
Compound II	—	—	3130	4.03	2.05
			3130 *ca.*		ca. 2.05

The molar ratio of *t*-BHP to isocyanate (—OOH/—NCO) was more than 3 to prevent chain extension.

The resulting product, peroxycarbamate (compound II), was extracted with acetonitrile at least twice, isolated by decantation, and dried in a vacuum at room temperature. The peroxide content determined by iodometric titration was identical to the theoretical value.[11] The preparation conditions and the results of isocyanate and peroxide analysis are given in Table I. The structural formula of the peroxycarbamate is



$$[\mathrm{H_3C}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\overset{\mathrm{H}}{\mathrm{N}}(\mathrm{C_{10}H_{18}})\overset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{O}[(\mathrm{CH_2})_m[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}]_n\,\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\,(\mathrm{CH_2})_m]_{1/2}]_2$$

$5 < m < 10, \quad n = 30$

Synthesis and Characterization of Copolymers

The peroxycarbamate (compound II) obtained was used as the macroinitiator in the synthesis of copolymers of poly(styrene–dimethylsiloxane–styrene).

The copolymers were synthesized in bulk or in toluene solutions. Weighed amounts of the peroxycarbamates were dissolved in predetermined amounts of styrene. Toluene was added to the mixture as the polymerization solvent. The mixture was then degassed on a vacuum line. The solutions were distributed in Pyrex tubes and immersed in thermostatically controlled oil baths at 80°C and polymerization was carried out for 120 h.

The solid products were dissolved in toluene and precipitated in large volumes of methanol. They were filtered and dried *in vacuo* at 30°C for 48 h.

The copolymers were also identified with the fractional precipitation method.[12] To separate block copolymers from their homopolymer blends, the samples were dissolved in chloroform and then copolymer was precipitated by gradually adding the nonsolvent, methanol.

The styrene contents of the copolymers were determined by UV spectroscopy at 269 nm. This method is based on measuring the absorbance of pure polystyrene, peroxycarbamate, and the copolymer at 269 nm in chloroform.[13]

Specific viscosities of the copolymers were measured at 30°C in toluene. The following viscosity–molecular weight relationship was used[14]:

$$[\eta] = 1.1 \times 10^{-4} M_n^{0.725} \qquad (1)$$

The viscosity average molecular weights of these copolymers are obviously approximate values because the preceding relation was given for pure PS. M_n and M_w of the samples were determined from GPC measurements.

The intermediates and the products were characterized by FTIR spectroscopy.

Glass transition temperature of the samples were determined from the DSC thermograms. After obtaining a uniform thermal history, reproducible scans were recorded and glass transition temperature was taken at the onset of the corresponding heat-capacity jump.

Polymeric films were prepared from solutions of the toluene and methylene chloride (80/20, v/v) mixture. Dried films were used for mechanical testing.

Contact angle measurements were made at room temperature for water droplets on the block copolymers and reference PS films prepared by casting from 1% (w/v) chloroform solutions.

RESULTS AND DISCUSSION

In this study, we first prepared and characterized a new peroxycarbamate (PC) by reacting isocyanate capped PDMS and *t*-BHP. We used this macroinitiator as a starting material for the synthesis of PS-PDMS-PS block copolymers. Experimental data on preparation of copolymers are given in Table II.

This method of block copolymer preparation yields products that contain homopolymer of related monomer. The results are given in Table II. Homopolymer of styrene was separated from the block copolymeric samples by the fractional precipitation method[12] as described in the Experimental section. After fractional precipitation of PS, the styrene

Table II Preparation of PS–PDMS–PS Block Copolymers

Copolymer No.	Initial Composition (Wt %)		Yield (%)	Homopolymer of PS in Product (Wt %)	Styrene Content of Copolymers	
	PC[a]	Styrene			UV (Wt %)	NMR (Mol %)
1	9.1	90.9	90	51.7	88	96
2	16.7	83.3	73	50.4	85	96
3	23.1	76.9	61	21.5	83	99
4	28.6	71.4	63	6.6	82	92

[a] Macroinitiator (compound II). $T = 80°C$, polymerization period 120 h.

contents of the products were determined by UV analysis.[13]

Intermediates and the products were characterized by FTIR spectroscopy. In the FTIR spectra of dihydroxy-PDMS, the peaks at 3520 and 3590 cm^{-1} are due to the H-bonded OH groups. These OH absorption peaks disappeared at the end of the capping reaction with diisocyanate, as it can be seen from Figure 1(a). The peak at 2280 cm^{-1} is due to the stretching vibration of —NCO and it is the principal absorption peak for isocyanate groups (compound I). In the second reaction step, disappearance of this peak indicates the formation of PC (compound II), which is illustrated in Figure 1(b). In the IR spectra of the copolymers (given in Fig. 2 for copolymer 4), urethane peaks around 3440 cm^{-1} were observed in all copolymeric samples. This absorption is due to —NH stretching in the $-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-$ group of the macroinitiator. This absorption peak in the spectrum indicates the incorporation of the PC into the copolymers and it provides definite evidence for the formation of block copolymers. In Figures 1 and 2, the peaks at 1260 and 800 cm^{-1} from $Si-CH_3$ and the peak at 1024 cm^{-1} from $Si-O$ are the characteristic peaks of PDMS.[15]

^1H-NMR spectra of compounds I and II and copolymer 1 are represented in Figure 3(a–c). The ^1H-NMR spectra of compounds I and II confirm the structural formulas of these intermediates. In Figure 3(a,b), we observe the signals of the $-CH_2-$ groups (at 3.02 ppm) adjacent to —NH and the peaks of $-CH_3$ of aliphatic isocyanate (0.95–1.1 ppm). The signals appearing at 4.43 and 4.72 ppm may due to —NH groups in the structures. ^1H-NMR was also used to determine the siloxane contents in mole percent by calculating the peak areas of the phenyl protons in PS [6.48–7.0 ppm in Fig. 3(c)] and the dimethylsiloxy protons in siloxane segments [0.077 ppm in Fig. 3(c)].[16] The siloxane contents determined from NMR are roughly in agreement with the values found by UV analysis.[13,17]

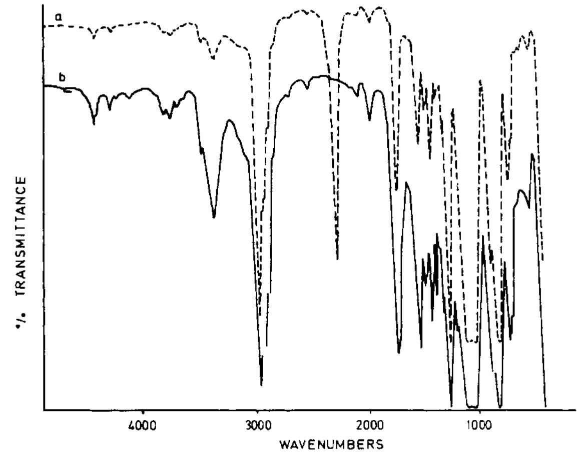


Figure 1 FTIR spectrum of (a) compound I and (b) compound II.

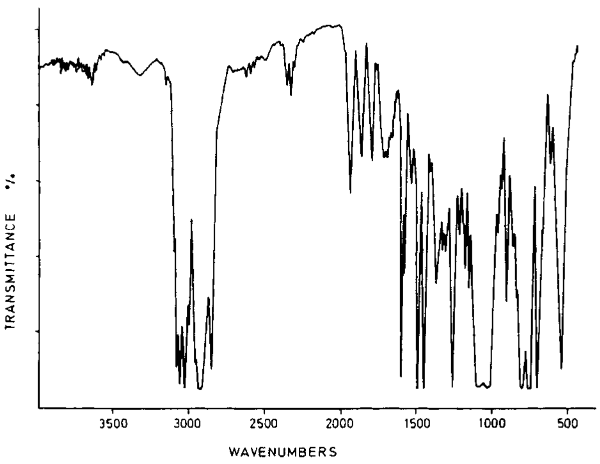
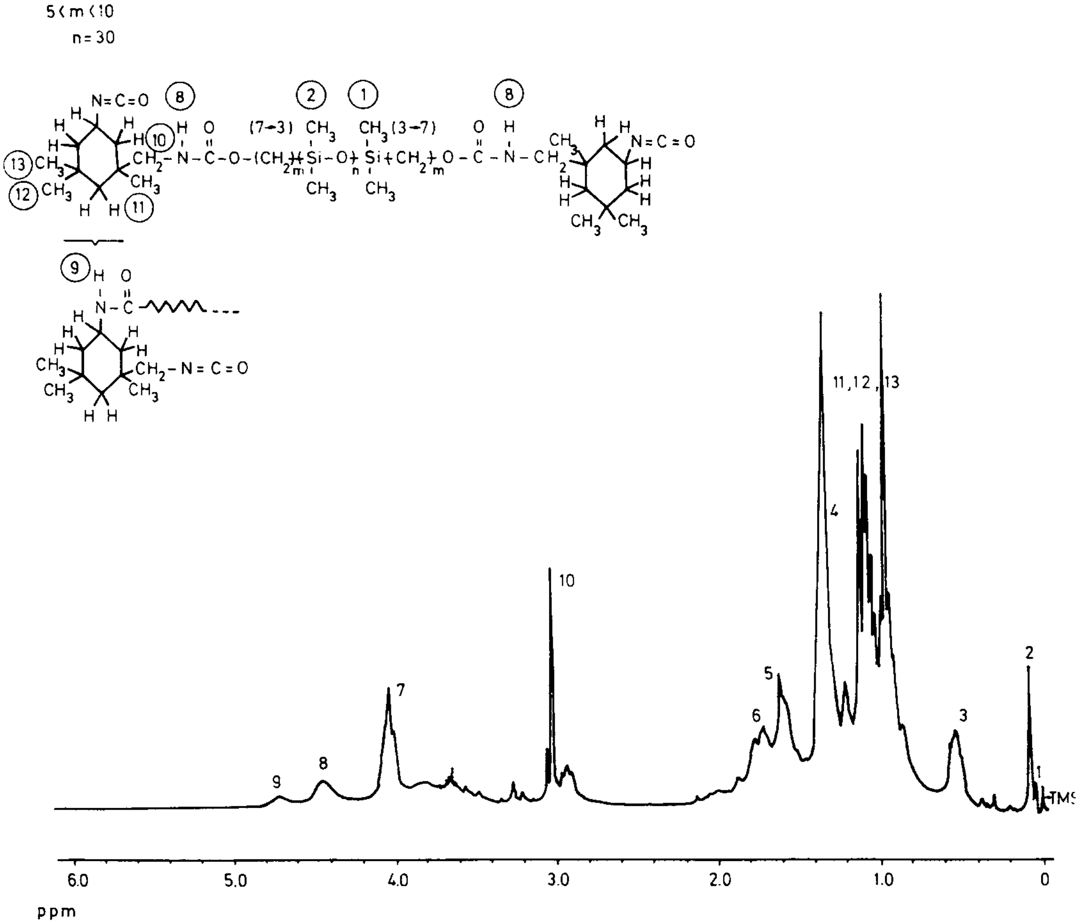


Figure 2 FTIR spectrum of copolymer 4.



(a)

Figure 3 (a) ^{1}H-NMR spectrum of compound I. (b) ^{1}H-NMR spectrum of compound II (numbers are the same for the same groups in the structures in (a) and (b). (c) ^{1}H-NMR spectrum of copolymer 1.

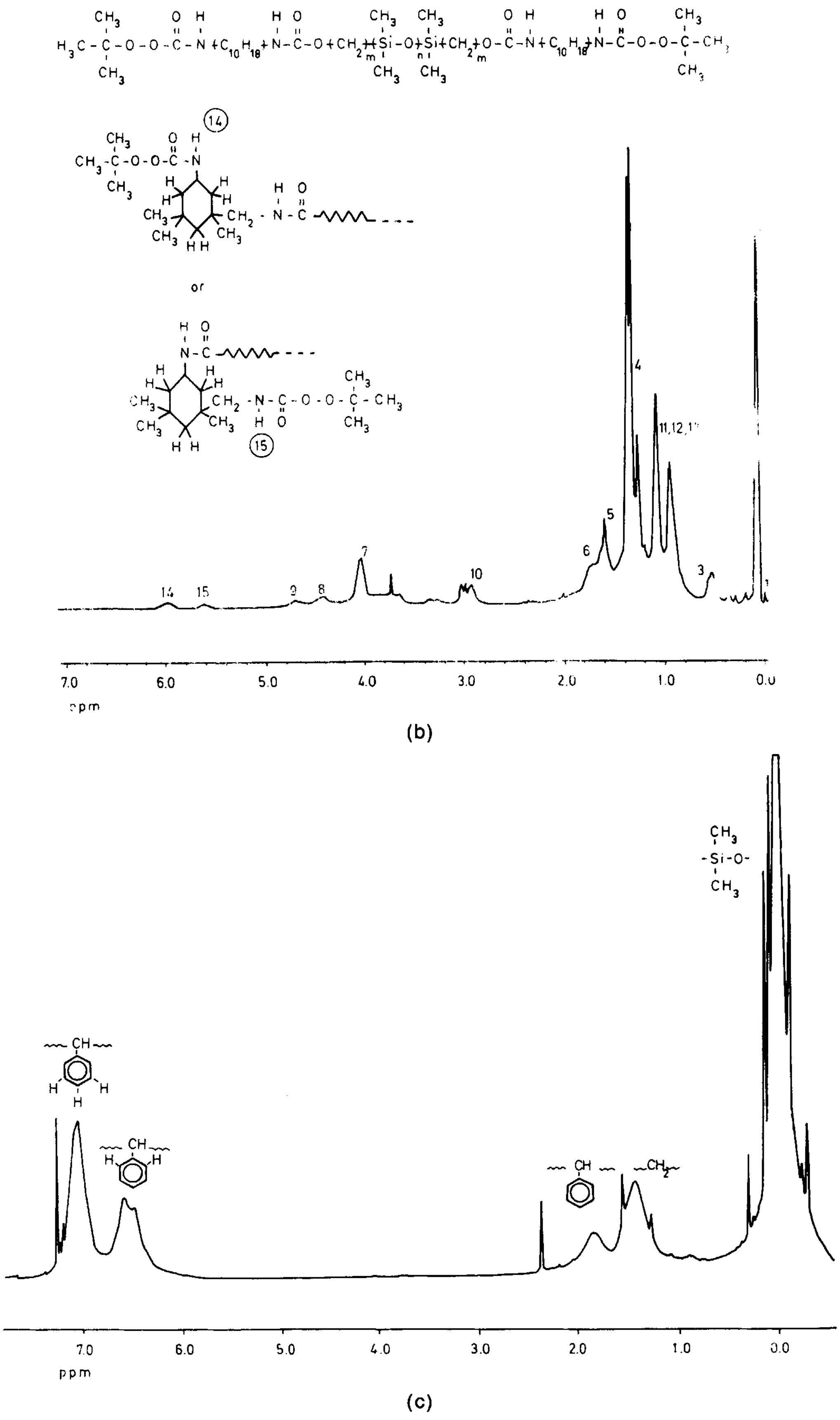
Intrinsic viscosities in toluene and average molecular weights of the block copolymers are given in Table III. Polydispersity of the copolymeric samples show a variation in the range of 2.47–3.73. Molecular weights of the samples decrease with increasing PDMS weight percent in the copolymer.

The glass transitions of the samples were determined by DSC thermograms. Figure 4(a–c) illustrates the thermograms of PDMS-2500 prepolymer, macroinitiator (compound II), and copolymer 1 as representative. Low T_g values of PDMS prepolymer and macroinitiator are illustrated in Figure 4(a) and (b), respectively.

The glass transition of PDMS component cannot be observed due to the lower molecular weight of siloxane with respect to PS blocks [Fig. 4(c)]. However, the T_g of PS is observed at around 70°C, which is lower than the T_g value of homo PS (100°C). This may show the plasticizer effect of PDMS blocks in the copolymers. The glass transition temperatures of the samples are also collected in Table III.

Stress and ultimate strain at break and Young's modulus were determined from the stress–strain curves of the block copolymer films. The average values of these mechanical properties are given in Table III. It is observed from this table that elongation at break for the PS reference is 2%; the elongations of the copolymers are in the range of 7–26%. Stress at break and Young's modulus are relatively lower than the PS reference. However, ultimate elongation of the copolymers were higher when compared with PS. PDMS contents of the copolymeric products are in the range of 12–18%. Copolymer 1, having the highest molecular weight, exhibited better elastomeric properties.

Electron micrographs of PS-PDMS-PS block copolymer films cast from toluene/methylene chloride



(b)

(c)

Figure 3 (*Continued from the previous page*)

Table III Characterization of PS–PDMS–PS Block Copolymers

			Molecular Weight (GPC Results)						
Copolymer	$[\eta]$ (dL/g)	$\bar{M}_v$ ($\times 10^{-3}$ g mol^{-1}) [eq. (1)]	$\times 10^{-3}$ M_n	$\times 10^{-3}$ M_w	PD	T_g (°C)	Strain at Break (%)	Stress at Break (MPa)	Young's Modulus, E (MPa)
1	1.49	500	185	691	3.73	70	26	17	510
2	0.77	201	90	312	3.46	73	7	15	420
3	0.73	187	100	288	2.87	70	7	16	310
4	0.55	127	71	177	2.47	67	7	15	370
PS	—	—	159	223	1.40	100	2	22	1600
PDMS-2500 (prepolymer)						−125.6	—	—	—
Macroinitiator (compound II)						−120.7	—	—	—

(80/20, v/v) mixture are shown in Figure 5(a–j).

Secondary electron images (SEI) and back scattered electron images (BEI) compositional contrast were applied in the SEM micrographs. Figure 6(a–e) shows the SEI micrographs. Figure 5(a) shows the homogeneous PS matrix. This micrograph can be interpreted as a rod–sphere structure of homo PS. The microstructure of the homopolymer was examined for comparison with the copolymers. The SEM micrograph of copolymer 1 with the lowest macroinitiator concentration (9.1%) is given in Figure 5(b) that shows the entrapment of the PDMS within PS matrix as a secondary cellular structure.

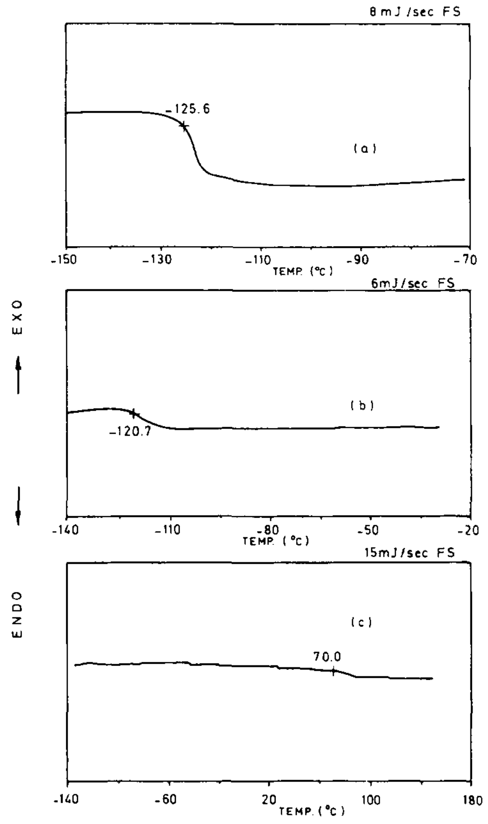


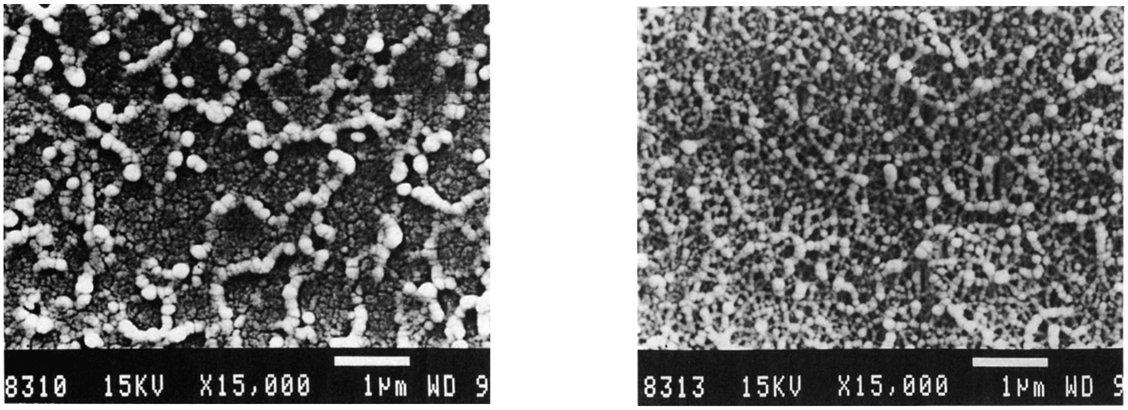
Figure 4 DSC thermogram of (a) PDMS-2500 prepolymer, (b) macroinitiator (compound II), and (c) copolymer 1.

The morphology of fractured surfaces of the copolymers is different from the PS reference. Figure 5(c–e) illustrates the microstructures of copolymers 2–4. They show heterogeneous and more complex morphology with respect to copolymer 1. The surface texture of copolymers 2–4 shows disordered holes remaining where the particles have pulled out of the matrix. Figure 6(a–e) shows the BEI micrographs of the same samples.

Contact angle measurements were made on block copolymeric films prepared by casting from 1% (w/

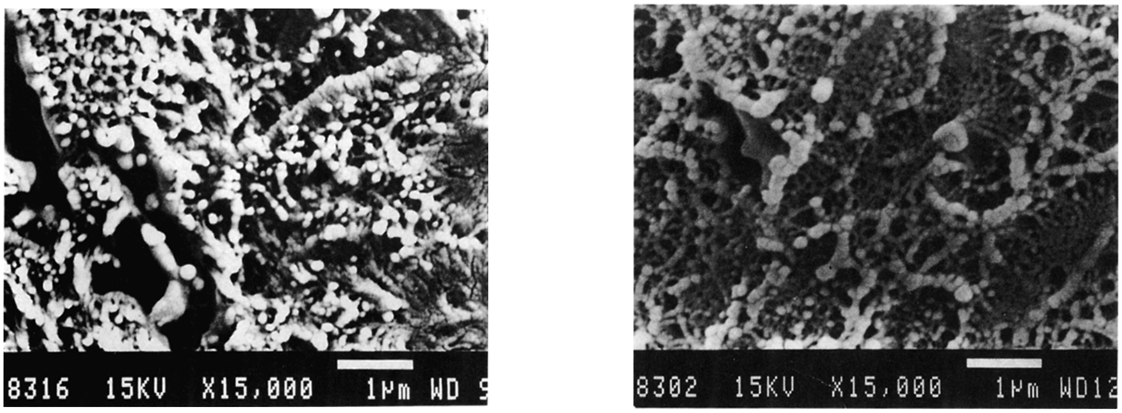
Table IV Contact Angle Measurements

	Contact Angle, θ (°)		
		Cast Films (from Chloroform)	
Copolymer	Films Cast on Glass Slides	Air Side	Glass Side
1	81	82	81
2	82	83	82
3	83	81	84
4	83	83	84
Pure PS	80	78	78



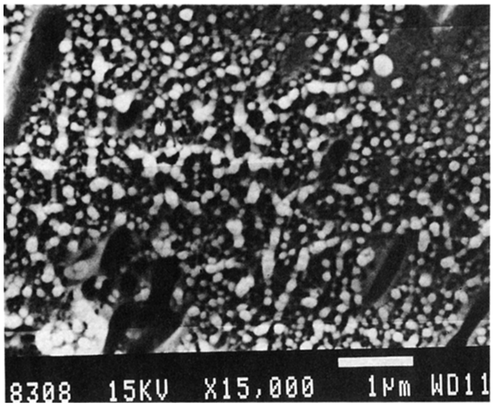
a) Homo Polystyrene

b) Copolymer No 1



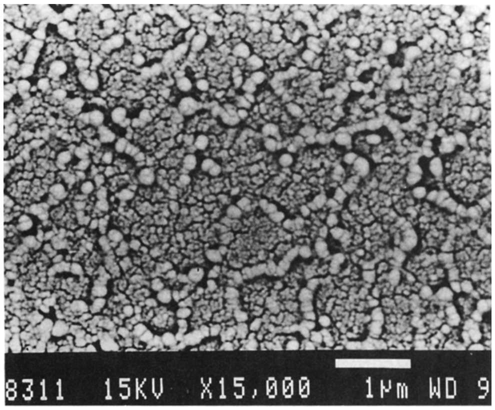
c) Copolymer No 2

d) Copolymer No 3

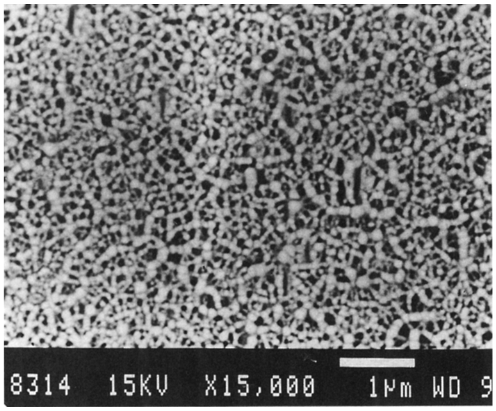


e) Copolymer No 4

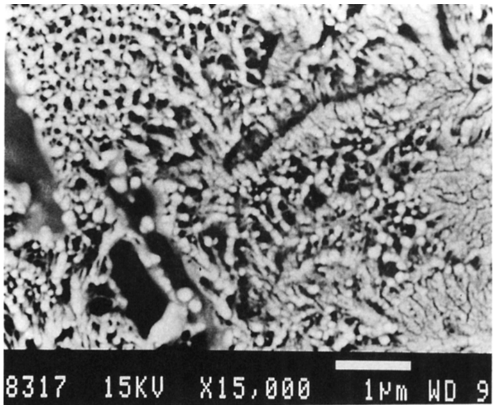
Figure 5 Scanning electron micrographs (SEI) of (a) homo polystyrene, (b) copolymer 1, (c) copolymer 2, (d) copolymer 3, and (e) copolymer 4.



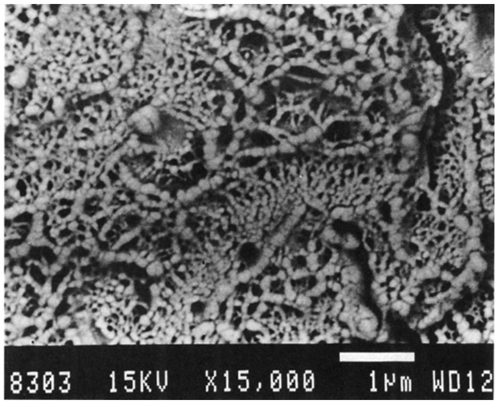
a) Homo Polystyrene



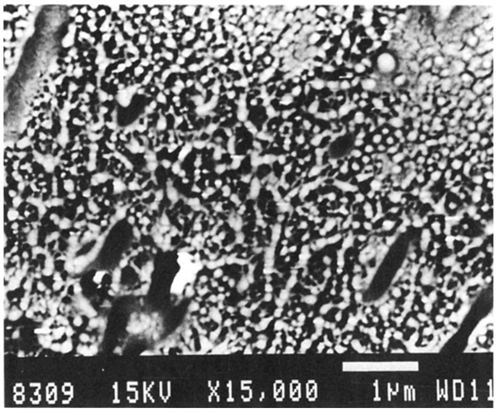
b) Copolymer No 1



c) Copolymer No 2



d) Copolymer No 3



e) Copolymer No 4

Figure 6 Scanning electron micrographs (BEI) of (a) homo polystyrene and (b–e) copolymer 1–4.

v) chloroform solutions on the glass slides. In a similar way, homo PS films were cast for comparison. Contact angles were measured at room temperature for the water droplet. The results were reproducible at ±1° in most cases and are given in Table IV.

To compare the glass and the air side of the films, the samples were also prepared by casting from chloroform on aluminum dishes and allowing the solvent to evaporate for 24 h. The films were detached from the dishes and dried under a vacuum for 2 days. The values of contact angles for both air and glass-side surfaces are given in Table IV. The contact angles of the copolymeric films exceeded 5–7% with respect to pure PS. Because PDMS chain lengths in block copolymers are rather small compared to the glassy segments, the surface accumulation of siloxane component is not negligible.[5,10]

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