Hexamethyl Cyclotrisiloxane–Styrene Block Copolymers and their Chemical Composition

S. K. VARSHNEY* and D. N. KHANNA, *Polymer and Fibre Science Laboratory, Indian Institute of Technology, New Delhi, 110029 India*

Synopsis

Triblock copolymers of hexamethyl cyclotrisiloxane (D_3) and styrene were synthesized by first preparing "living" species of polystyrene dianion followed by polymerization of D_3. The chain length of polymeric blocks could be controlled in a predictable fashion leading to a central hard block of polystyrene and the two end segments of amorphous polydimethylsiloxane having narrow molecular weight distribution, were characterized by gel permeation chromatography. The chemical composition of block copolymers was determined by silicon analysis and infrared and nuclear magnetic resonance spectra. Thermal aging of block copolymers at 150, 200, and 300°C was also discussed.

INTRODUCTION

The advent of block copolymerization has constituted a major milestone in polymer science. The exciting aspect of the block copolymers and other multiphase polymers is that they retain the basic properties of corresponding homopolymers. At the same time some unique properties emerge as a result of the morphological behavior of the block copolymer. One might anticipate that the segment block length and the degree of chemical compatibility, composition volume ratio, and the architecture of blocks are important factors for controlling the two-phase behavior.[1,2] The use of anionic living polymerization as a route to well-defined polymers is now well established and stems from the initial work by Szwarc.[3]

Block copolymer of polydimethylsiloxane–polystyrene presents an unusual situation where, within the same molecule two segments are present which can independently show the extremities in properties and characteristics of each homopolymer. Typical properties exhibited by poly(styrene-*b*-butadiene) arise from the basic differences in the nature of the constituting segments. An enhancement in properties such as retention of flexibility at low temperature, excellent electrical properties,[4] inertness toward chemicals, high degree of permeability toward gases, and an extremely low-solubility parameter[5] ($\delta 7.6$ cal/cm^3)$^{1/2}$ could be conceived because of the presence of polydimethylsiloxane blocks.

A number of approaches[6–10] have been employed to prepare block copolymers of polystyrene and polydimethylsiloxane. The most promising method takes advantage of the precise nature of "living" polystyrene species.

The present article discusses the molecular dispersity of poly(dimethylsiloxane-*b*-styrene-*b*-dimethylsiloxane) copolymers and their chemical composition by infrared and nuclear magnetic resonance spectra.

---

* Present address: Department of Materials Science and Engineering, College of Engineering, University of Florida, Gainesville, FL 32611.
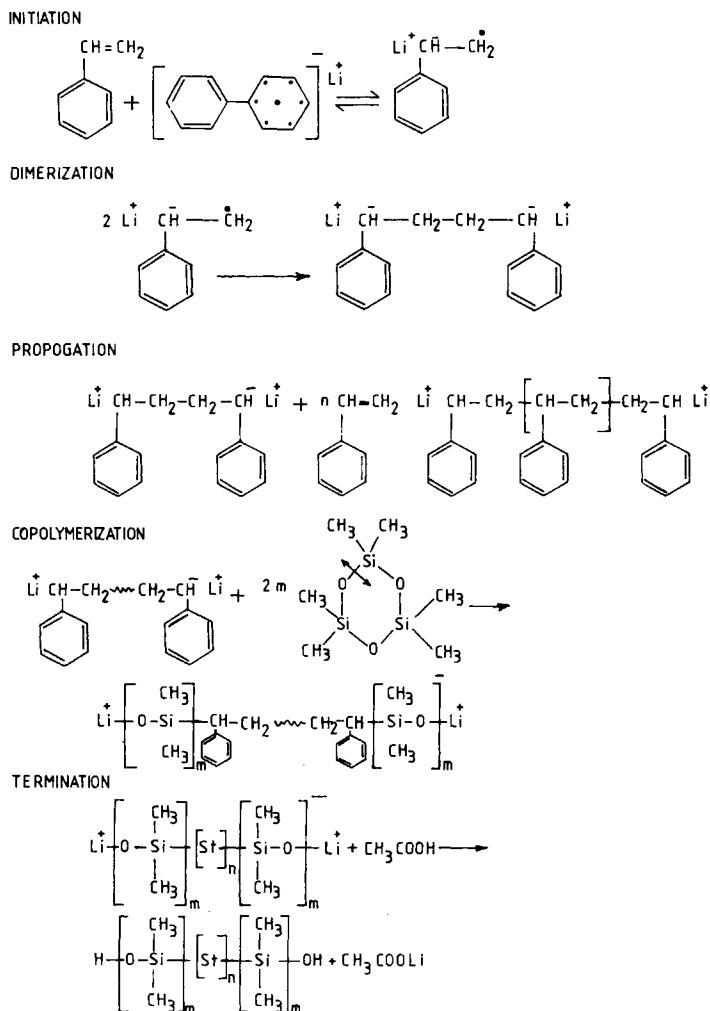
VARSHNEY AND KHANNA

INITIATION

DIMERIZATION

PROPOGATION

COPOLYMERIZATION

TERMINATION

Fig. 1. Polymerization scheme for synthesis of poly(dimethylsiloxane-b-styrene-b-dimethylsiloxane).

EXPERIMENTAL

The synthesis of poly(dimethylsiloxane-b-styrene-b-dimethylsiloxane) copolymers [P(DMS-b-st-b-DMS)] was carried out under high vacuum using a syringe technique in a specially designed reaction tube. Triblock copolymers were prepared by anionic polymerization using lithium biphenyl as anionic initiator in a tetrahydroforan–toluene mixture. Details of the polymerization have been described in a previous investigation.[11] The reaction mixture was neutralized with acetic acid followed by 1.0 g sodium bicarbonate solution to give a solution of the block copolymer with a silianol endgroup. This solution was washed with water and precipitated with methanol. Free homopolymers from the copolymer were estimated by the method described by Saam et al.[6]

TABLE I
Homo- and Copolymerization of Styrene and Hexamethylcyclotrisiloxane and their Molecular Dispersity[a]

Monomers	Lithium[b] biphenyl (mole 10^{-1} %)	Polymer yield (%)	Free homo polystyrene	Mole fraction of dimethyl siloxane	$\bar{M}_c$ (× 10^{-3})	$\bar{M}_n$ × 10^{-3} GPC	$\bar{M}_w$ × 10^{-3} GPC	$\bar{M}_w/\bar{M}_n$ GPC
Styrene	10.02	96	—	—	21.0	22.3	25.6	1.14
A Styrene + D$_3$[c]		80	8.3	0.514	40.3	44.2	54.2	1.22
Styrene	13.05	98	—	—	15.6	17.3	19.8	1.14
B Styrene + D$_3$		83	9.2	0.538	32.0	34.2	43.0	1.25
Styrene	16.07	98	—	—	12.7	15.0	16.8	1.12
C Styrene + D$_3$		85	8.8	0.594	26.65	28.3	34.0	1.20

[a] "Living" polystyrene dianion was prepared at −80°C, and the copolymerization was at room temperature.
[b] Initiator concentration on the basis of styrene monomer.
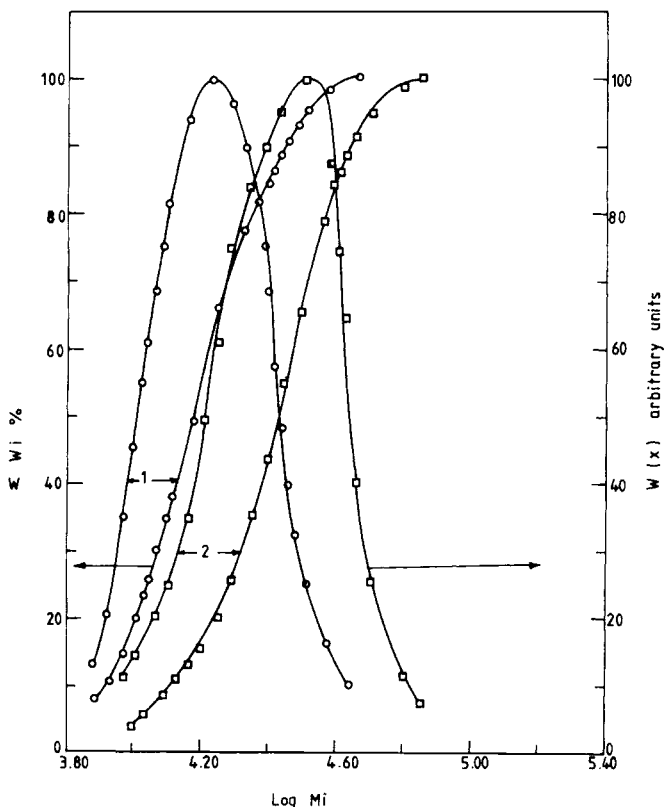[c] D$_3$: Hexamethylcyclotrisiloxane.

Fig. 2. Integral and differential molecular weight distribution curves of polymers. (1) Polystyrene: $\overline{M}_n = 15,000$, $\overline{M}_w = 16,800$, $\overline{M}_w/\overline{M}_n = 1.12$. (2) Poly(DMS-$b$-St-$b$-DMS): $\overline{M}_n = 28,300$, $\overline{M}_w = 34,000$, $\overline{M}_w/\overline{M}_n = 1.20$.

The average molecular weights and molecular weight distribution (differential and integral) for the polymers were estimated using gel permeation chromatography GPC 244 (Waters Associates). Measurements were carried out at room temperature (25°C), utilizing four Styragel columns having nominal porosities of 10^5, 10^4, 10^3, and 500 Å, respectively. Toluene was employed as the solvent and the flow rate was 2 ml min^{-1}. Several standard polystyrene samples (Waters Associates) were used to calibrate the apparatus. No attempt was made to correct the apparent broadening of distribution in this analysis.

The composition of the block copolymer was determined by silicon analysis.

Infrared spectra of polymers were recorded in an infrared spectrometer, MK 11 (Grubb-Parson) by making pellets with dried KBr. For quantitative determination of weight percentage of dimethylsiloxane incorporated in block copolymers, a calibration curve was drawn by making blends of polystyrene with polydimethylsiloxane ranging from 80:20 to 20:80 wt % homopolymers. A quantitative analysis was performed using the band ratio technique. The base lines are drawn comparing the peak heights I_1/I_2 to obtain their ratio and finally plotting the ratio I_1/I_2 vs. wt % siloxane content in a blend of homopolymers. This method has been used for a quantitative analysis of block copolymers of styrene–acrylic copolymers[12] and aromatic–aliphatic copolyesters.[13]
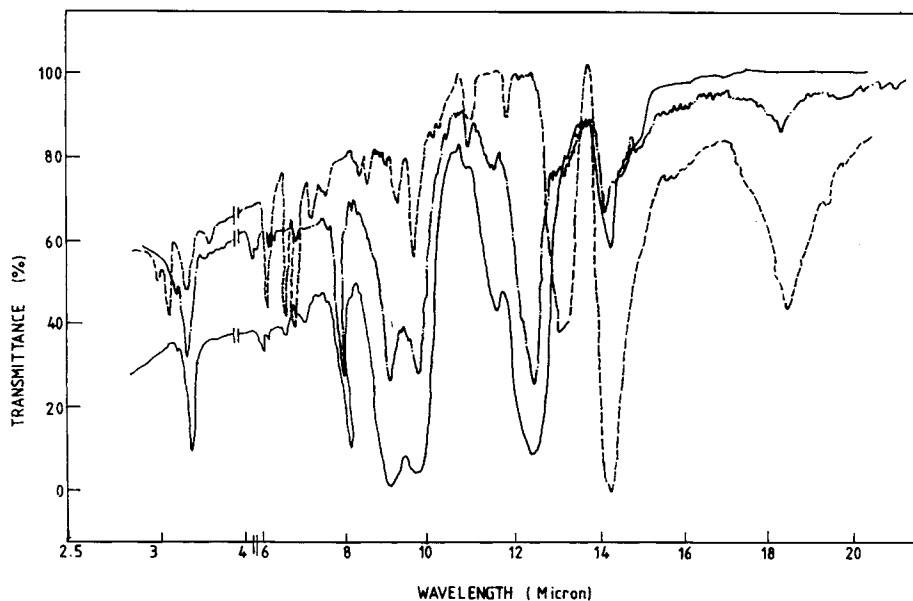
Fig. 3. Infrared curves of (- - -) polystyrene, (—) polydimethylsiloxane, (- · -) poly(DMS-*b*-St-*b*-DMS).

NMR measurements were made on 4% polymer solution in deutrochloroform on a Varian 100 MHz spectrometer at room temperature using tetramethylsilane (TMS) as the internal reference.

A thermogravimetric analysis of block copolymers was carried out using a Stanton model TG 750 thermobalance in static air. The samples were isothermally heated for 4 hr at 150, 200, and 300°C. Thermograms were obtained by plotting residual weight against time.
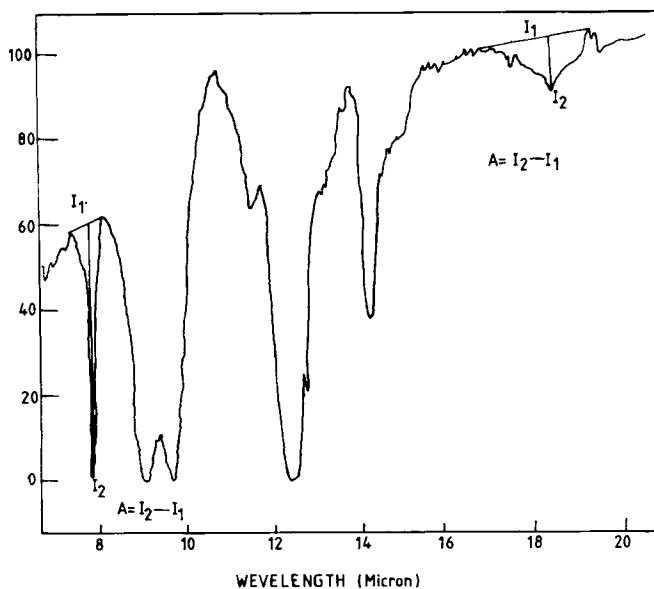

Fig. 4. Infrared curve showing region of analytical interest.

RESULTS AND DISCUSSION

In copolymerization a cyclic trimer D_3 is predominantly used as the monomer and may be attributed to the fact that it has greater reactivity than other cyclic monomers (Octamer, etc.), and can be polymerized more rapidly by much weaker bases such as lithium compounds[14] in an aprotic solvent or in an aprotic solvent mixture at room temperature. In this manner it is possible to prepare polydimethylsiloxane segments of narrow molecular weight distribution by the replacement of butyllithium with polystyryllithium.[15,16] The reactivity of the siloxanolate anion is much less than that of the styryl anion and so the silanolate anion Si—Ō M⁺ cannot be used to reinitiate styrene polymerization. Living polystyrene dianion prepared by the lithium biphenyl at −80°C reacts with D_3 at room temperature to give lithium dimethyl silanolate at both the ends of the polystyrene chain, as shown in Figure 1. The red color of the living polystyrene anion faded to a translucent pale pink with the increase in viscosity of the reaction mixture.

Molecular weight data for ABA triblock copolymers prepared by the above route are listed in Table I. $\overline{M}_c$ is the calculated molecular weight assuming that two initiator molecules initiate a single polymer chain. The discrepancies between $\overline{M}_c$ and the number-average molecular weight $\overline{M}_n$ is attributed to the loss of the catalyst by trace amounts of impurities present in the system and may be due to incomplete initiation of styrene monomer with lithium biphenyl. The results show a constant number of growing chain ends during the copolymerization. The molecular dispersity of homopolystyrene ranges from 1.12 to 1.14, while that of the block copolymer is slightly broader (Fig. 2). This may be due to the sluggish nature of the silanolate ion and from the use of higher concentration of tetrahydrofuran, which leads to the formation of the free ion.

In block copolymers the dimethylsiloxy content increases with increase in initiator concentration (Table I). This may be explained on the basis of availability of a greater number of living polystyryl ends for initiating the polymerization of cyclic siloxane.

INFRARED ANALYSIS

The characteristic absorption band resulting from the phenyl ring and siloxane linkage confirm the presence of both the segments. Typical absorption bands at 2920 and 2850 cm⁻¹ for aliphatic C—H stretching are observed. Absorption bands at 1602 and 1455 cm⁻¹ are due to in-plane bending vibration of the phenyl ring, and bands at 760 cm⁻¹ for out-of-plane hydrogen deformation of the phenyl ring are also present in the copolymers.

The presence of a characteristic absorption band at 1265 cm⁻¹ owing to δ Si—CH₃ groups and a doublet between 1020 and 1100 cm⁻¹ for γ as Si—O—Si band, and at 688 cm⁻¹ owing to γ as Si—CH3, Figure 3 confirms the presence of dimethyl siloxy units. It is interesting to note that some small bands at 905, 1194, 1155, and 1040 cm⁻¹ due to helical conformation are also observed. The intensities of these helical bands are closely related to the conformation. The difference in sensitivity of the helix bands suggests that a certain sequence lengths of regular structure is necessary to give rise to each helix band.

However, a characteristic band at 1070 cm⁻¹ for atactic polystyrene,[17] which splits into two bands at 1082 and 1050 cm⁻¹ in isotactic polystyrene cannot be

TABLE II
Data Obtained from Infrared Absorption Analysis of Block Polymers

Polymer	A, $\delta(CH_3)$—Si 1265 cm^{-1}	A, (Styrene) 560 cm^{-1}	$\dfrac{A\ \delta(CH_3)Si}{A\ \delta(styrene)}$	% (Me_2SiO) calculated	Mole fraction of Me_2SiO
A	40	8	5.0	41.0	0.494
B	51	10	5.1	44.0	0.524
C	63	12	5.25	53.0	0.613

identified in block copolymer since γ as Si—O—Si band also shows a sharp doublet between 1000 and 1100 cm^{-1}.

For quantitative determination of incorporation of dimethylsiloxy units, we chose the absorption band at 1265 cm^{-1}, γ as Si—CH$_3$ and the 560 cm^{-1} of the bending vibration of styrene. Quantitative analysis was performed using the band ratio technique, with the base line drawn as illustrated in Figure 4 (Table II).

The calibration curve was drawn from the infrared spectra of blended samples (Fig. 5). This technique permits the rapid estimation of the weight percentage of blocks in copolymer.

NUCLEAR MAGNETIC RESONANCE SPECTRA

H NMR spectra of block copolymer show the characteristic peaks of both the segments, e.g., orthoprotons of phenyl ring at 3.35 τ and meta- and paraprotons at 2.85 τ owing to polystyrene segment and a sharp signal at 9.8 τ resulting from Me$_2$ Si protons of polydimethylsiloxane. The position and the resolution of chain protons, i.e., methine and methylene protons (CH—CH$_2$) is influenced by the

$$\overset{|}{C_6H_5}$$

stereospecificity of the polymer. Well-resolved signals for methylene and methine protons appear at 8.5 and 8.1 τ, respectively (Fig. 6), which indicates the isotactic nature of the polystyrene segments. Bovey[18] also observed the partial resolution of methylene and methine proton peaks in isotactic polystyrene. Furthermore, Uryu et al.[19] reported that polystyrene prepared by sodium napthalene gave a syndiotactic rich configuration as revealed from its ^{13}C NMR spectra.
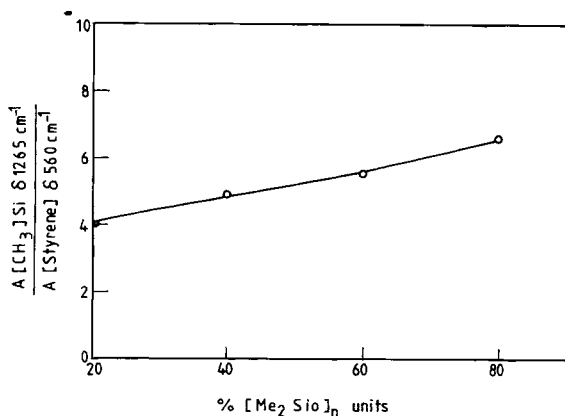
Fig. 5. Calibration curve of A(Si—CH$_3$)/A styrene vs. % dimethylsiloxy unit.
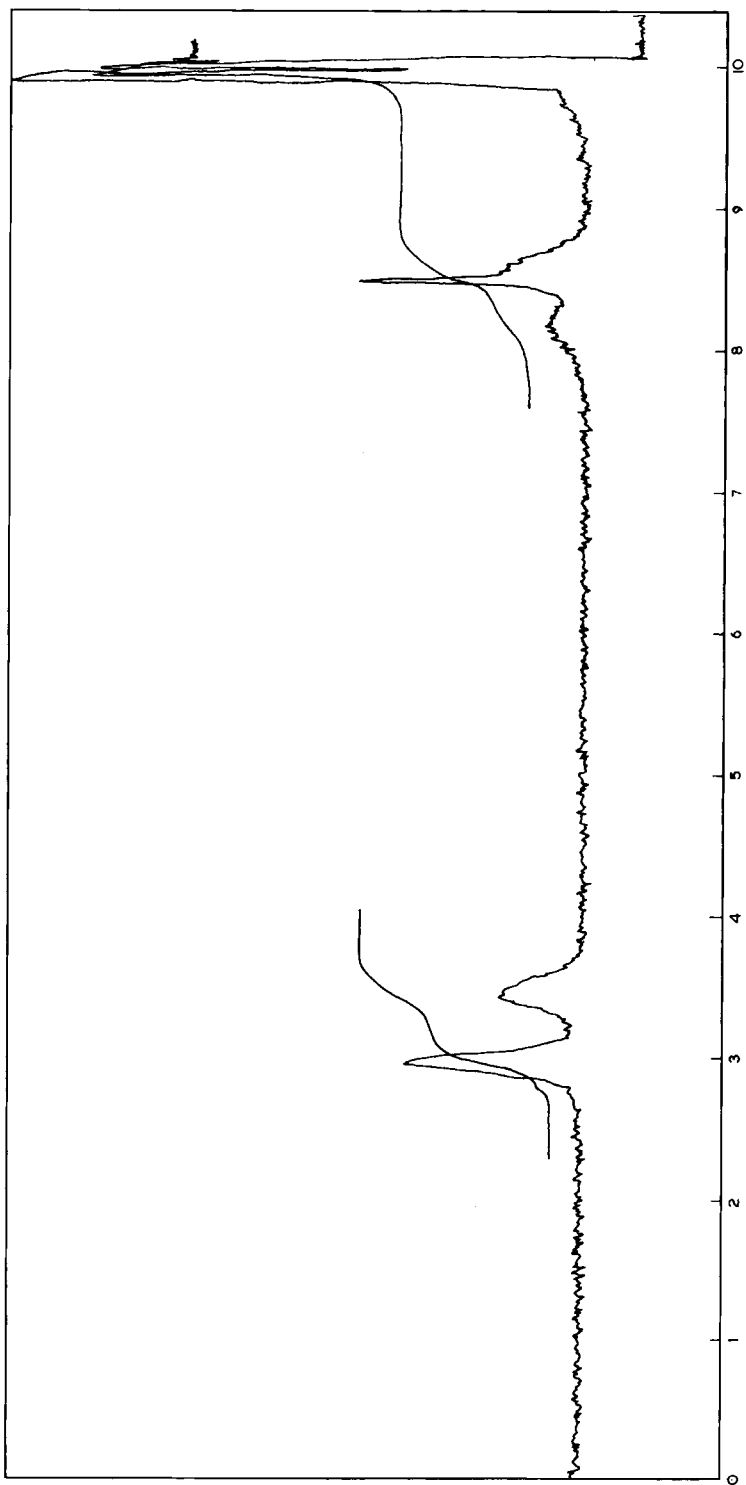
Fig. 6. Proton magnetic resonance spectrum. An external TMS standard was used.

TABLE III
Protons Chemical Shifts of Polymers and their Chemical Composition

| Polymer | Chemical Shift Value | | | | | Dimethyl silicon protons | Mole fraction $(Me_2SiO)_n$ calc from NMR |
	Meta and para phenyl protons	Ortho phenyl protons	Methine protons	Methylene protons			
Polystyrene	2.85	3.35	8.1	8.5		—	—
Poly(DMS-b-St-b-DMS)							
A	2.83	3.30	8.1	8.48		9.85	0.522
B	2.83	3.30	8.1	8.50		9.80	0.545
C	2.83	3.30	8.1	8.50		9.80	0.613

Fig. 7. Thermal aging of block copolymer in air (°C) (1) 150, (2) 200, (3) 300.

Mole fractions of dimethylsiloxane units X in block copolymers were obtained from the resonance spectra using the relation

$$X = 5A_{DM}/(6 A_{St} + 5 A_{DM})$$

where A_{DM} is the area of the dimethylsiloxy signal and A_{St} is the area of the phenyl protons. The calculated values are in close agreement with the gravimetric results which will be obvious from Table III.

EFFECT OF THERMAL AGING OF POLY(DMS-*b*-St-*b*-DMS)

Thermal decomposition and loss in weight observed on heating the styrene–siloxane block copolymer in air at 150, 200, and 300°C are shown in Figure 7. It is evident that at 200 and 300°C, the degradation rates varied considerably. This loss in weight in polymer would lead to (1) depolymerization or reversion to low-molecular-weight cyclic siloxane; and (2) hydrolytic scission at siloxane bonds in the main chain.

The cyclic degradation products formation resulting from Si—O bonds fracture[20] in the presence of terminal groups, e.g., Si—OH can be described as follows:

in which Me = CH_3. At 300°C the loss in weight of the polystyrene segment may be a consequence of the chain scission.

References

1. A. Noshay and J. E. McGrath, *Block Copolymers,* Academic, New York, 1977.

2. S. L. Aggarwal and R. A. Livigni, *Polym. Eng. Sci.,* **17,** 498 (1977).

3. M. Szwarc, *Nature,* **178,** 1168 (1956).

4. J. C. Saam and W. G. Fearon, Ger. Pat. 2142594, CA 77, 20367t (1972).

5. P. Bajaj, G. N. Babu, D. N. Khanna, and S. K. Varshney, *J. Appl. Polym. Sci.,* **23,** 3505 (1979).

6. J. C. Saam, D. J. Gordon, and S. Lindsay, *Macromolecules,* **3,** 1 (1970).

7. J. W. Dean, *J. Polym. Sci. Polym. Lett. Ed.,* **8,** 677 (1970).

8. M. Morton, Y. Kesten, and L. J. Fetters, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* **26,** 113 (1975).

9. A. Marsiat and Y. Gallat, *Makromol. Chem.,* **176,** 1641 (1975).

10. M. Morton, A. A. Rembaum, and E. E. Bostick, *J. Appl. Polym. Sci.,* **8,** 2707 (1964).

11. P. Bajaj, S. K. Varshney, and A. Misra, *J. Polym. Sci. Polym. Chem. Ed.,* **18,** 295 (1980).

12. D. G. Anderson and K. E. Isakson, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.,* **10,** 1190 (1969).

13. P. Bajaj, D. N. Khanna, and G. N. Babu, *Eur. Polym. J.,* **15,** 1083 (1979).

14. C. L. Lee, C. L. Frye, and O. K. Johannson, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.,* **10,** 1361 (1969).

15. W. G. Davies and D. P. Jones, *Ind. Eng. Chem. Prod. Res. Dev.,* **10,** 168 (1971).

16. J. C. Saam, A. H. Ward, and F. W. G. Fearon, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.,* **13,** 524 (1972).

17. T. Onishi and S. Krimm, *J. Appl. Phys.,* **32,** 2320 (1961).

18. F. A. Bovey, *Polymer Conformation and Configuration,* Academic, New York, 1969.

19. T. Uryu, T. Seki, T. Kawamura, A. Funamoto, and K. Matsuzaki, *J. Polym. Sci. Polym. Chem. Ed.,* **14,** 3035 (1976).

20. YU A. Aleksandrova, T. S. Kikitina, and A. N. Pravednikav, *Vysokomol. Soedin. Ser. A,* **10,** 1078 (1968).