Macromolecules

Volume 3, Number 1 January–February 1970

Block Copolymers of Polydimethylsiloxane and Polystyrene

John C. Saam, David J. Gordon, and Sarah Lindsey

Polymer Research Laboratory, Dow Corning Corporation, Midland, Michigan 48640.

Received September 4, 1969

ABSTRACT: The title copolymers are prepared essentially free of the parent homopolymers by polymerizing hexamethylcyclotrisiloxane with "living" polystyrene prepared from an alkyllithium. The siloxane polymerization generates poly(styrene-b-dimethylsiloxane) without the complications of chain scission and oligomerization usually encountered in anionic polymerization of cyclosiloxanes. The AB block copolymers resemble surfactants due to the extreme differences in solubility between the two blocks. Films of the block copolymers when cast from solution show a morphology determined by the nature of the solvent and the degree to which each block is solvated.

Block copolymers of polydimethylsiloxane and polystyrene present an unusual situation where within the same molecule two segments are present which can independently show the extremes in properties characteristic of each homopolymer. Thus, the atypical properties shown by solutions and films of organic block copolymers such as poly(styrene-b-butadiene) that arise from the differing natures of the two blocks[1] should be greatly enhanced in the present systems due to the abnormally flexible nature of the polysiloxane coil[2] and its extremely low solubility parameter compared with polystyrene. The present investigation is therefore concerned with the preparation of poly(styrene-b-dimethylsiloxane). Furthermore, copolymers of sufficiently high molecular weight and purity are sought which will allow examination of this unique system without the encumbering and confusing complications arising from contamination with the parent homopolymers.

A number of approaches have been employed to prepare block[3] or graft[4] copolymers of polystyrene and polydimethylsiloxane. The most promising method takes advantage of the precise nature of "living" polystyrene systems, where the metal–carbon bonds at the ends of the chain are reported to polymerize a cyclosiloxane to give "ABA" block polymers in the molecular weight range of interest for the present investigation.[3b,c]

$$K^{+-}(C_6H_5CHCH_2)_n{}^-K^+ + 2m(Me_2SiO)_4 \longrightarrow K^{+-}(Me_2SiO)_{4m}(C_6H_5CHCH_2)_n(Me_2SiO)^-{}_{4m}K^+ \quad (1)$$

Previous work, however, affords materials unsuitable for the present investigation because of the large amounts of homopolymer obviously generated and the low yields of block copolymer obtained. The difficulty undoubtedly arises from the extensive formation of oligomers and cyclosiloxanes known to take place during siloxane polymerizations of this nature.[5]

The present approach seeks to form poly(styrene-b-dimethylsiloxane), the "AB" block copolymer, through the reaction of polystyryllithium with the more reactive hexamethylcyclotrisiloxane. The rate of propagation of the cyclosiloxane is known to exceed the rates of oligomerization or cyclization, presumably as a consequence of strain enhanced reactivity. This selectivity is especially evident when lithium bases and suitable promoters are employed for the polymerization.[6a] Lithium silanolate was recently reported to initiate sequential copolymerization of certain cyclotrisiloxanes.[6b]

Experimental Section

Reagents. Cyclohexane from Mathieson Coleman and Bell was dried over freshly baked Linde 3A Molecular Sieves. Benzene, 1000 ml, was distilled from 0.03 equiv of butyllithium prior to use. Styrene, Eastman White Label, was washed with dilute sodium hydroxide to remove any inhibitors, dried, and distilled just prior to use. Tetrahydrofuran from J. T. Baker Co. and bis(2-methoxyethyl) ether from Eastman Organic Chemicals were distilled from sodium prior to use. Hexamethylcyclotrisiloxane was used without further purification.

Preparation of Poly(styrene-b-dimethylsiloxane). Freshly distilled styrene, 80 g (0.77 mol), in 275 ml of cyclohexane was refluxed under a slow purge of pure dry nitrogen for 15 min. Further drying was effected by refluxing the solu-

---

[1] See G. E. Molau, Publication 1573, National Academy of Sciences, Washington, D. C., 1968, p 243.

[2] P. J. Flory, L. Mandelkern, J. B. Kinsinger, and N. N. Schulz, *J. Amer. Chem. Soc.*, **74**, 3364 (1952).

[3] (a) G. Greber and L. Metzinger, *Makromol. Chem.*, **39**, 167 (1960); (b) M. Morton, A. A. Rembaum, and E. E. Bostick, *J. Appl. Polym. Sci.*, **8**, 2707 (1964); (c) M. Mitoh, A. Tabuse, and Y. Minoura, *Kogyo Kagaku Zasshi*, **70** (11), 1969 (1967).

[4] (a) G. Greber and E. Reese, *Makromol. Chem.*, **55**, 96 (1962); (b) Y. Minoura, M. Sundo, and Y. Enomoto, *J. Polym. Sci., Part A-1*, **6**, 979 (1969).

[5] J. B. Carmichael, D. J. Gordon, and F. J. Isackson, *J. Phys. Chem.*, **71**, **2011** (1967); M. Morton and E. E. Bostick, *J. Polym. Sci., Part A*, **2**, 523 (1964).

[6] (a) C. L. Lee, C. L. Frye, and O. K. Johannson, *Polym. Preprints*, **10** (2), 1361 (1969); (b) E. E. Bostick, U. S. Patent 3,337,496 (1967); *Polym. Preprints*, **10** (2), 877 (1969).

TABLE I

PREPARATION OF POLY(STYRENE-b-DIMETHYLSILOXANE)

Mol of BuLi $\times 10^3$	Wt, g		% yield polymer	% (wt)[a] Me_2SiO	$M_c \times 10^{-3}$	$\overline{M}_N \times 10^{-3}$	Wt % free homopolymer	
	C_8H_8	$(Me_2SiO)_3$					$(C_8H_8)_n$[b]	$(Me_2SiO)_n$[c]
28.0	140	60	96	28.4	7.14	7.06	Nil	Nil
7.0	140	60	84	29.1	28.6	30.6	Nil	Nil
5.4[d]	104	166.6	84	61.6	50.1	48.8	Nil	1.6
3.0	90	67	78	32.0	44.1[e]	47.6	1.1	Nil
3.0	90	67	80	33.0	44.7[e]	41.4	2.0	Nil
2.6[d]	80	120	91	58.7	77.0	80.0	Nil	1.9
1.0[d]	80	168	80	53.6	178.0[e]	170.0	5.0	5.9
0.66[f]	80	120	95	60.1	303	297	Nil	6.4

[a] Based on silicon analysis. [b] Determined by precipitation from cyclohexane at 0°. [c] Based on homopolymer which separates from bromobenzene solutions. [d] Silanol at the end of siloxane chain. Other examples contain Me_2SiVi at the end of siloxane chain. [e] M_c calculated on the basis of conversion of $(Me_2SiO)_3$ as indicated by silicon analysis. [f] Benzene (1 l.) instead of cyclohexane was the solvent and 20 ml of diglyme to promote the siloxane polymerization instead of THF.

tion over calcium hydride for about 30 min. The solution was then transferred to a purged reactor without exposure to the atmosphere and the polymerization was initiated under a slight nitrogen pressure by introduction of 1.62 ml of a 1.6 *M* solution of butyllithium in hexane (2.6×10^{-3} mol). Cooling was required in the initial stages of the polymerization. Concurrently in a separate vessel 120 g (0.54 mol) of hexamethylcyclotrisiloxane in 350 ml of cyclohexane was dried similar to the styrene solutions. After 3–4 hr at room temperature the polymerization of styrene was complete and a 100-ml portion of the dried solution of the cyclotrisiloxane was added to the polymerization vessel without exposure to either solution to the atmosphere. After about 1 hr of stirring at 50–60° the characteristic color of the living polymer completely disappeared and the remaining solution of hexamethylcyclotrisiloxane in cyclohexane was introduced with 120 ml of THF. After refluxing and stirring for 4 hr, the originally cloudy mixture was almost clear. One portion was neutralized with 1.0 ml of vinyldimethylchlorosilane followed by 1.0 g of sodium bicarbonate to give a solution of the block polymer with a vinyl end group. The second portion was neutralized with 1.0 ml of acetic acid followed by 1.0 g of sodium bicarbonate to give a solution of the block polymer with a silanol end group. Each solution was washed with water and precipitated with methanol. The precipitates were washed with methanol several times and the residual solvent was removed at 0.1 mm at 50° for 19 hr. This gave a total of 182 g (91%) of polymer. Other details are shown in Table I.

Polymerization of Hexamethylcyclotrisiloxane with Alkyllithium. A solution of 250 g of hexamethylcyclotrisiloxane in 200 ml of cyclohexane was dried in the manner described above and 12.5 ml of a 1.6 *M* solution of butyllithium in hexane (0.020 mol) was introduced to the refluxing solution. Then 5 ml of diglyme was added and the solution was refluxed in a dry nitrogen atmosphere throughout the polymerization. Analysis by glpc of samples removed from the mixture showed that the maximum amount of tetrameric and pentameric cyclosiloxanes formed was about 1% based on the starting monomer and that the reaction was better than 90% complete after 2.5 hr. The mixture was treated with vinyldimethylchlorosilane and the polymer was isolated as described above to give 205.2 g (82% yield) of polydimethylsiloxane [M_n (glpc) = 12,400 (calcd $\overline{M}_n$ = 12,500); M_w/M_n (glpc) = 1.18].

Free polystyrene in the block polymers was estimated from the insoluble material precipitated from a solution of 1 g of the block polymer in 25 g of cyclohexane and 1.2 g of hexane. The solutions were centrifuged at 0° at 2000 rpm for 10 min. The supernatant liquid was removed and the precipitate weighed after removal of solvent. The results are shown in Table I. When the third polymer shown in Table I was deliberately blended with 10 wt % polystyrene, $\overline{M}_n$ = 100,000, this method gave a recovery of 97% of the added free polystyrene.

Free polydimethylsiloxane was estimated from the amount separated in the upper layer from dispersions of 1.25 g of block copolymer in 25 ml of bromobenzene after centrifugation at 2000 rpm for 30 min. A sample of the block polymer showing less than 2% free siloxane but containing 10 wt % of deliberately added free polydimethylsiloxane gave a minimum recovery of 90% of the added siloxane by this method.

Number average molecular weights were determined with a Mechrolab 501 membrane osmometer with 0.2, 0.4, 0.6, 0.8, and 1.0 wt % solutions of the block polymer in amyl acetate. Plots of π/c *vs.* c were linear and $\overline{M}_n$ was calculated from the intercept.

Electron micrographs were obtained with a Hitachi HS-7S electron microscope. Films were prepared by casting one drop of a 10% solution of the block copolymer on a water substrate. The films were transferred to a carbon-coated copper grid and examined in the instrument at 50 kV. Films of polystyrene examined under these conditions were transparent.

Discussion and Results

Polystyryllithium reacts with hexamethylcyclotrisiloxane in benzene or cyclohexane to give lithium dimethylsilanolate at the end of the polystyrene chain presumably by the route demonstrated for the reaction of the trimer with alkyllithium.[7] This reaction, eq 2, (where b = 1, 2, and 3), is complete when the characteristic color of the "living" polymer completely disappears.

$$Bu(C_6H_5CHCH_2)_nLi + (Me_2SiO)_3 \longrightarrow Bu(C_6H_5CHCH)_n(Me_2SiO)_bLi$$

Introduction of a promoter such as tetrahydrofuran or diglyme is necessary to polymerize the cyclosiloxane from the siloxanolate ends to generate selectively poly(styrene-b-dimethylsiloxane). The siloxane polymerization is terminated by introduction of vinyldimethylchlorosilane or acetic acid to give either Me_2SiVi or Me_2SiOH at the end of the siloxane block.

Analysis by glpc during and immediately after

---

(7) C. L. Frye, R. M. Salinger, J. M. Klosowski, and T. DeYoung, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, M 152.

formation of the siloxane block in several runs shows that only 0.5–1% of tetrameric or higher cyclosiloxanes form based on the siloxane monomer consumed and that the styrene is almost completely polymerized. Use of butyllithium instead of polystyryllithium under comparable conditions gives a more readily analyzed polymer and further illustrates that the siloxane polymerization is free of complicating side reactions. Obtained from this experiment are good yields of polydimethylsiloxane where $\bar{M}_w/\bar{M}_n$ approaches unity and little or no oligomeric siloxanes are formed.

The ratio of the total weight of monomers consumed to the number of moles of butyllithium used in initiation is the calculated molecular weight of the block copolymers, M_c. Table I shows several examples of good agreement of M_c with measured values of $\bar{M}_n$ and establishes a constant number of growing chain ends during the copolymerization. The absence of random termination, initiation, and oligomerization is also reflected in the small amounts of homopolymer found in the copolymers shown in Table I. The absence of appreciable randomization in the siloxane polymerization thus allows formation of block polymers of predetermined molecular weight and composition where purification by laborious fractionation or precipitation procedures is unnecessary. A typical example of the polymerization procedure is illustrated in the Experimental Section.

Properties in Solution. Dilute solutions of the block copolymers of polystyrene and polydimethylsiloxane are clear in toluene, a good solvent for both blocks, whereas the corresponding homopolymers mixed at comparable concentrations give two-phase systems. Higher concentrations of block copolymer tend to give solutions which are thixotropic and, particularly with the higher molecular weight species, iridescent. This indicates an orientation of the solute similar to that noted in solutions of polystyrene–polybutadiene block copolymers.[8]

Addition of equal volumes of decamethyltetrasiloxane, a precipitant for polystyrene but a very good solvent for polydimethylsiloxane, to solutions of the block copolymer in toluene fails to induce any precipitation or visible phase formation. Instead the mixture remains almost clear and assumes an iridescent bluish tinge indicative of small colloidal particles. With cyclohexane, also a selective solvent for polydimethylsiloxane, similar phenomena occur. Colloids are also noted in bromobenzene but in this case the solvent is good for polystyrene but very poor for polydimethylsiloxane.

An abrupt increase in the viscosity of solutions of block copolymer in cyclohexane is noted as concentrations are increased over about 5 g/dl (Figure 1). Beyond this concentration a blue color is apparent and the viscosity increases until the solution becomes thixotropic at about 15–20 g/dl. The phenomena appear reversible as dilution of the thickened sol causes a return to lower viscosity. Such behavior is typical of nonionic surfactants at their critical micelle concentration where molecules of solute extensively aggregate. This is interpreted in the present system as preferential solvation of the siloxane blocks with simultaneous collapse and aggregation of the less solvated polystyrene blocks to form micelles.[1,9] The more solvated blocks of polydimethylsiloxane thus hold the multimolecular micelles in suspension to give greatly increased viscosities.

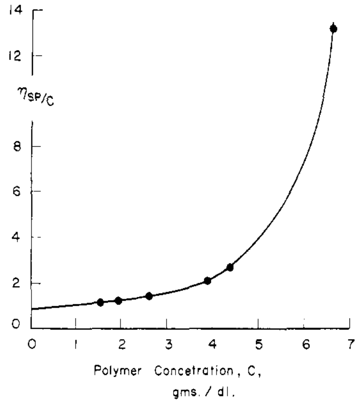

Figure 1. Effect of concentration on reduced viscosity at 25° of solutions in cyclohexane of a 37/63 polystyrene–polydimethylsiloxane block copolymer of M_n = 170 × 10^3.

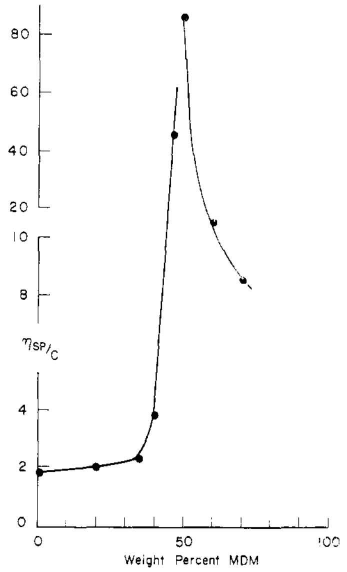

Figure 2. Effect of changing the composition of solvent on reduced viscosity at 25.0° of the same copolmer in Figure 1 in solutions of MDM–toluene. The concentration of copolymer in each solution is 4.2 g/dl.

A critical micelle point is also approached by changing the composition of the solvent in toluene–octamethyltrisiloxane (MDM) solutions while holding constant the concentration of block copolymer. This is seen in Figure 2 where little change in solution viscosity is observed until about 40 wt % MDM is present. Here, as in the case with cyclohexane, the viscosity abruptly increases to extremely high values. Prior to this point the solutions are fairly clear but at the higher levels of MDM the solutions become iridescent blue to bluish white. Further increase in the amount of MDM causes a reduction in viscosity until the level of MDM is about 70% where solid gellike particles form. Be-

---

(8) E. Vanzo, *J. Polym. Sci., Part A-1*, 4, 1727 (1966).

(9) (a) F. M. Merrett, *J. Polym. Sci.*, 24, 467 (1957); (b) Y. Gallot, E. Franta, P. Remp, and H. Benoit, *ibid., Part C*, 4, 473 (1963).

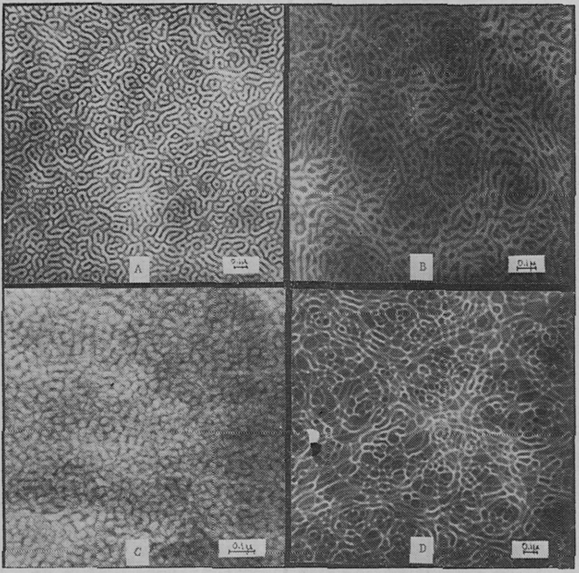

Figure 3. Electron micrographs of thin films of poly(styrene-b-dimethylsiloxane) cast from various solvents: A, cast from toluene, 33 mol % polystyrene, $\bar{M}_n = 48.8 \times 10^3$; B, cast from toluene, 60 mol % polystyrene, $\bar{M}_n = 47.6 \times 10^3$; C, cast from cyclohexane, same block copolymer as in A; D, cast from bromobenzene, same block polymer as in A.

yond this point the system is partially gelled and impossible to measure. Addition of more toluene redissolves the gel.

A reversible formation of micelles similar to that in cyclohexane is postulated. A difference, however, is that the cores of polystyrene within the micelles are solvated only with toluene but the exterior blocks of polydimethylsiloxane are solvated with MDM as well as toluene. The MDM tends to solvate strongly the siloxane blocks but not the styrene blocks. Thus, first the viscosity increases after the critical point where the less solvated blocks of polystyrene aggregate, but as the solvation of the siloxane exterior disproportionately increases with increasing MDM, some disassociation can take place to give fewer and smaller micelles. This would give a maximum in viscosity with increasing MDM. The intrinsic viscosity of these solutions gradually increases from 0.8 to 1.2 dl/g as the amount of MDM is increased to 90 wt % in the solvent. This can result from molecular associations in dilute solution but the preferred interpretation is that increased overall chain dimensions result from the disproportionately increased solvation of the siloxane blocks as the amount of MDM increases.

Properties of Films. The texture of films of the block copolymers obtained from evaporation of their solutions depends on the solvent and reflects to some extent the nature of the molecular associations in solution. Thus, from bromobenzene, a selective solvent for polystyrene, hard brittle films form but the same block copolymer from cyclohexane or toluene–MDM gives soft rubbery films. The phenomena are reminiscent of those seen in the poly (methyl methacrylate)–rubber graft copolymers.[9a] Thin films of the block copolymers tend to be iridescent.

Electron photomicrographs of very thin films cast from toluene, Figure 3A, show oriented structures where the polystyrene blocks have agglomerated to form white spaghetti-like microphases. These phases are 282 ± 15 Å in diameter which corresponds to twice the calculated distance of the most remote chain atom in the unperturbed polystyrene block from one of its chain ends, $1.4r_0 = 124$ Å.[10] The blocks of polydimethylsiloxane in Figure 3A are present in the greater amount and appear as the black continuous phase. The minimum width of this phase or the closest approach between polystyrene phases is uniformly 170 ± 20 Å. This corresponds closely to the calculated distance of the most remote chain atom in the unperturbed polysiloxane block from one of its ends, $1.4r_0 = 169$ Å. This uniform spacing is particularly evident in the situation where some polydimethylsiloxane is entrapped within a polystyrene phase. An apparent phase inversion is seen in Figure 3B where the polystyrene blocks are now present in the greater amount. The white polystyrene phase is now continuous and the width of the discontinuous dark regions of polydimethylsiloxane, 231 ± 37 Å, is roughly twice the calculated $1.4r_0 = 124$ Å.

The structures in Figure 3A and 3B appear to be a variant of the rodlike structures reported by Matsuo, *et al.*[11] The blocks in the discontinuous phase are pictured as aligning themselves as random coils more or less in double rows on a given plane. A number of such rows would compose a rodlike phase. The distance between the rodlike structures might be expected to be limited by the chain dimensions of the block in the continuous phase. The present materials are unique in that well-defined phase separations appear at roughly one-tenth of the molecular weight for such separations with the styrene–butadiene block copolymers. This is ascribed to the greater differences in solubility between polydimethylsiloxane and polystyrene blocks.

A different orientation is apparent when films of the block polymer are cast from solutions where one of the blocks is preferentially solvated. This is seen in Figure 3C which is an electron micrograph of a film of the same polymer shown in Figure 3A but cast from a solution of cyclohexane. Cell-like structures are apparent where dark areas of polydimethylsiloxane surround the lighter areas of polystyrene. The micellar structures can form as the solvent is removed and the more weakly solvated blocks of polystyrene preferentially aggregate by the same mechanism which causes the abrupt changes in viscosity noted in Figure 1. The electron micrograph shown in Figure 3D is the same polymer cast from bromobenzene. In this case, the solvent is very poor for polydimethylsiloxane and the tendency is reversed from Figure 3C. These changes in cellular structure explain the differences in texture of films cast from different selective solvents and reflect the aggregated structures in solution.

Acknowledgment. The authors are indebted to L. A. Hulce and the late N. Plics who prepared the electron micrographs.

---

(10) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains, High Polymer Series," Vol. XVII, Interscience Publishers, New York, N. Y., 1963, p 181.

(11) M. Matsuo, S. Sagae, and H. Asai, *Polymer*, **10** (2), 79 (1969).