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G. K. Rickle^a

^a Central Research The Dow Chemical Company Midland, Michigan

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SYNTHESIS AND PROPERTIES OF POLY(STYRENE-*b*-TRIMETHYLVINYLSILANE)

G. K. RICKLE

Central Research
The Dow Chemical Company
Midland, Michigan 48674

ABSTRACT

The diblock copolymer poly(styrene-*b*-trimethylvinylsilane) was made anionically by sequential addition of the monomers. The copolymer is amphipathic and will stabilize foams consisting of nitrogen and polymer hydrocarbon solutions. The foam stabilization properties of poly(styrene-*b*-trimethylvinylsilane) are dependent upon molecular weight, composition, and concentration. The optimum diblock copolymer has \bar{M}_n in the range of 9 000-30 000, contains about 0.10 mole fraction trimethylvinylsilane, and is used at about 0.3 wt% concentration for foams consisting of nitrogen dispersed in a solution of polystyrene in styrene monomer.

INTRODUCTION

Materials that are surface active in hydrocarbon media and inert to carbanions would be desirable as foaming agents in a reaction injection molding (RIM) process [1], using anionic polymerization methods, for styrenics and dienes. Alkylsilanes have lower surface energies than most hydrocarbons [2, 3] and are inert to carbanions [4]. Thus, block copolymers containing alkylsilane and hydrocarbon segments are expected to be amphipathic and have surface activity in hydrocarbon media. One method to make such block copolymers would be to sequentially polymerize styrene and trimethylvinylsilane by an-

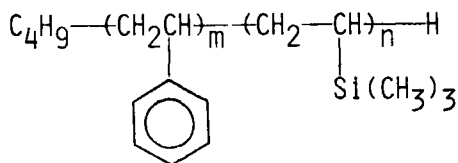


FIG. 1. The structure of poly(styrene-*b*-trimethylvinylsilane).

ionic polymerization methods. Previous work has shown the anionic polymerization of trimethylvinylsilane is self-terminating [5]. The self-termination limits the molecular weight of the poly(trimethylvinylsilane) segment and necessitates making the poly(styrene) segment first. This report describes the preparation and some properties of the block copolymer poly(styrene-*b*-trimethylvinylsilane), Fig. 1.

EXPERIMENTAL

General Procedures and Chemicals

All chemicals were purchased from commercial sources. The polymerization solvent, cyclohexane, was extracted with sulfuric acid, and the trimethylvinylsilane was distilled. Both were run through an alumina column prior to use, as were the promoter, tetrahydrofuran, and styrene monomer. The initiator, *n*-butyllithium, was used as received. Differential scanning calorimeter (DSC) thermograms were made using a Du Pont 1090 thermal analyzer interfaced to a Du Pont 910 DSC. A Varian EM-360A spectrometer was used to obtain the proton NMR spectra of poly(styrene-*b*-trimethylvinylsilane). The NMR solvent was carbon tetrachloride with dichloromethane as an internal reference. Gel permeation chromatography (GPC) was done with tetrahydrofuran eluant on a Waters Model 150C instrument containing Toyo Soda columns packed with TSK-gel.

Preparation of Poly(Styrene-*b*-Trimethylvinylsilane)

Styrene, 85 g, was added to 708.0 g of cyclohexane containing 35 μL of tetrahydrofuran. The solution was degassed and kept under a blanket of nitrogen at room temperature. The polymerization was initiated with 4.25 mL of 1.77 *N*-*n*-butyllithium in cyclohexane. After the styrene was consumed,

~1.5 h, the trimethylvinylsilane, 21.0 mL, was added and the reaction allowed to proceed for about 72 h, at which time the trimethylvinylsilane conversion was 80%. The polymerization was stopped by the addition of methanol. The cyclohexane solvent was removed by evaporation and the polymer redissolved in methylene chloride. The solution was then added to an excess of methanol, causing the polymer to precipitate. The white powder was washed and dried. The product, 97.4 g, contained 0.12 mole fraction trimethylvinylsilane and had a \bar{M}_w of 21 300 (based on GPC measurements using polystyrene calibration standards). Extraction of the polymer with pentane failed to yield any poly(trimethylvinylsilane) homopolymer. Likewise, copolymers rich in trimethylvinylsilane were completely soluble in pentane, indicating that poly(styrene) homopolymer is absent.

Diblock copolymers with varying molecular weights and compositions were made in a similar manner, except that the amounts of initiator and monomers used were altered to give the desired molecular weight and composition.

Foam Evaluation

Polystyrene solutions, 20 wt% were made by dissolving Styron 685 brand polystyrene in styrene monomer. The viscosity of the solution was 520 cps at 23°C as measured on a Brookfield HBT viscosimeter using Spindle 3 at 20 rpm.

To determine foaming properties of the diblock copolymers, 100 g of the styrene-polystyrene solution containing 1.0 g of diblock copolymer was stirred for 20 min at 1 000 rpm under a nitrogen pressure of 100 psi in a 1-L autoclave. The pressure was released, and the dissolved nitrogen foamed the solution. The foam was immediately poured into a graduated cylinder. The foam and liquid volumes were recorded as a function of time. To correct for different volumes being measured, the data were normalized by plotting the foam expansion ratio, R , versus time. The foam expansion ratio is defined as

$$R = \frac{V_t - V_f}{V_f}, \quad (1)$$

where V_t is the volume at time t , and V_f is the volume after foam has dissipated.

The slope of R versus time plots is related to the persistence of the foam, while the R at $t = 0$, referred to as the maximum foam expansion ratio or R_{\max} , gives a measure of the foaming activity of the diblock copolymer.

RESULTS AND DISCUSSION

Molecular Weight and Composition

The kinetics will place certain limitations on the polymerization of the trimethylvinylsilane [5]. Termination reactions occur in the trimethylvinylsilane polymerization, so diblock copolymers of styrene and trimethylvinylsilane are best prepared by anionic polymerization of the styrene segment prior to the trimethylvinylsilane segment. The polymerization of the trimethylvinylsilane segment is slow; the propagation rate constant (as defined in Ref. 5) in cyclohexane at 22°C is 1.4 mL^{1/2}/(mol^{1/2}·min) unless ether promoters are present. However, ethers accelerate the termination reaction more than the propagation, so yield and molecular weight decrease as the ether concentration increases. Thus, a compromise between yield, molecular weight, and polymerization rate is necessary. However, block copolymers can be designed with different compositions and molecular weights with knowledge of the kinetics for the poly(trimethylvinylsilane) segment.

Values for \bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n for the poly(trimethylvinylsilane) segment determined from the kinetics are

$$\bar{M}_n = \frac{wM_0}{I_0} (1 - e^{-I_0k_2/k_3}), \quad (2)$$

$$\bar{M}_w = \frac{wk_2}{2k_3} M_0(1 + e^{-I_0k_2/k_3}), \quad (3)$$

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{k_2 I_0 (1 + e^{-I_0k_2/k_3})}{2k_3 (1 - e^{-I_0k_2/k_3})}, \quad (4)$$

where w is the monomer molecular weight, M_0 is the initial monomer concentration, I_0 is the initial initiator concentration, k_2 is the propagation rate constant, and k_3 is the termination rate constant.

Figure 2 contains the GPC elution profile of the poly(styrene) segment (obtained by removing a sample prior to the trimethylvinylsilane addition) of a diblock copolymer containing 0.52 mole fraction poly(styrene) and the elution profile of the resulting diblock copolymer. The elution peak of the diblock copolymer has shifted to lower elution volumes with respect to the poly(styrene) segment, as expected for the increased molecular weight of the diblock. Both the diblock copolymer and the poly(trimethylvinylsilane) segment

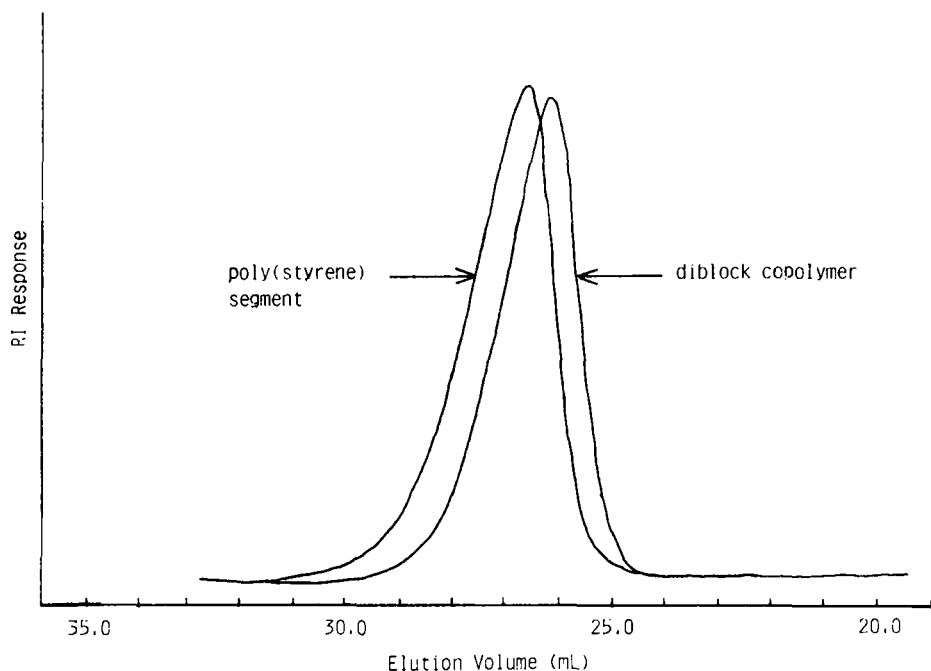


FIG. 2. The GPC elution profile of a diblock copolymer and its poly(styrene) segment. The diblock copolymer contains 0.52 mole fraction poly(styrene).

molecular weight can be determined from the poly(styrene) segment molecular weight and the diblock copolymer composition.

The composition of the copolymer was readily determined by proton NMR; the silane methyl hydrogens show an absorption centered at 0.2 ppm. The aromatic hydrogens from poly(styrene) give broad peaks at 6.6 and 7.0 ppm. The methylene and methine hydrogens from both the poly(styrene) and poly(trimethylvinylsilane) blocks show broad peaks at 1.1 and 1.6 ppm. The ratio of aromatic to methyl hydrogens is used to determine the composition of the copolymer. Figure 3 is the proton NMR spectrum for poly(styrene-*b*-trimethylvinylsilane) having \bar{M}_n of 41 600 and 0.52 mole fraction styrene. Generally, the observed molecular weight of the poly(trimethylvinylsilane) segment is higher than the calculated theoretical value, probably due to some polystyryl anion termination occurring when the trimethylvinylsilane is added.

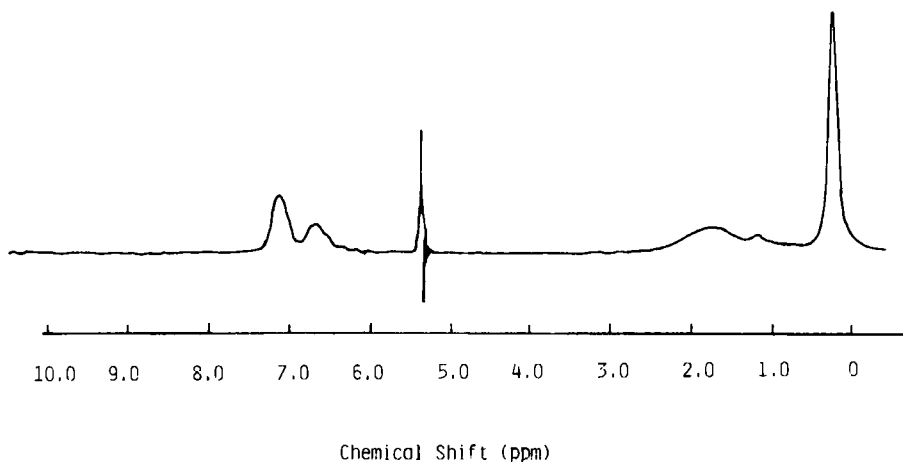


FIG. 3. The proton NMR spectrum of poly(styrene-*b*-trimethylvinylsilane). The peak at ~ 5.4 ppm is due to the internal standard, dichloromethane.

The GPC diblock copolymer molecular weight, based on poly(styrene) calibration standards, is low, indicating that the poly(trimethylvinylsilane) segment coil is more contracted in tetrahydrofuran than poly(styrene) as shown in Table 1, which summarizes the molecular weight data of several diblock copolymers.

DSC Measurements

The DSC thermogram for poly(styrene-*b*-trimethylvinylsilane) of \bar{M}_n 41 600 and 0.52 mole fraction styrene is shown in Figure 4. At the heating rate of $10^\circ\text{C}/\text{min}$, two transitions were detected, one at 100°C , the other at 175°C . The 100°C transition agrees with the T_g reported for poly(styrene) [6], while the 175°C transition corresponds to the T_g reported for poly(trimethylvinylsilane) [7].

Foaming Properties

The foaming properties of poly(styrene-*b*-trimethylvinylsilane) are dependent upon concentration, composition, and molecular weight. Figure 5, Curve 1, shows how the foaming activity rises and levels off at a trimethylvinylsilane content of 0.40 mole fraction. At higher \bar{M}_n (Fig. 5 Curve 2), the foaming ac-

TABLE 1. Molecular Weight Data for Poly(styrene-*b*-trimethylsilane)

| Styrene mole fraction | 0.91 | 0.89 | 0.67 | 0.62 | 0.60 | 0.59 | 0.57 | 0.52 |
|-----------------------------------|-------|--------|--------|-------|-------|--------|--------|--------|
| Polystyrene segment: | | | | | | | | |
| \bar{M}_n | 2 350 | 15 600 | 6 900 | 1 490 | 2 560 | 10 900 | 8 580 | 21 600 |
| \bar{M}_w | 3 100 | 19 300 | 7 900 | 1 830 | 2 910 | 12 800 | 10 800 | 32 300 |
| Polytrimethylvinylsilane segment: | | | | | | | | |
| \bar{M}_n obs | 232 | 1 930 | 3 400 | 914 | 1 710 | 7 560 | 6 470 | 20 000 |
| \bar{M}_w obs | 309 | 2 390 | 3 900 | 1 120 | 1 940 | 8 920 | 8 190 | 29 900 |
| \bar{M}_n calc | NA | 1 720 | NA | NA | 1 720 | 7 300 | 5 760 | 18 800 |
| \bar{M}_w calc | NA | 1 930 | NA | NA | 1 840 | 7 720 | 6 570 | 21 000 |
| Diblock copolymer: | | | | | | | | |
| Actual \bar{M}_n | 2 580 | 17 600 | 10 300 | 2 400 | 4 270 | 18 400 | 15 100 | 41 600 |
| GPC \bar{M}_n | 2 530 | 16 600 | 8 780 | 2 360 | 3 980 | 16 300 | 12 300 | 33 700 |

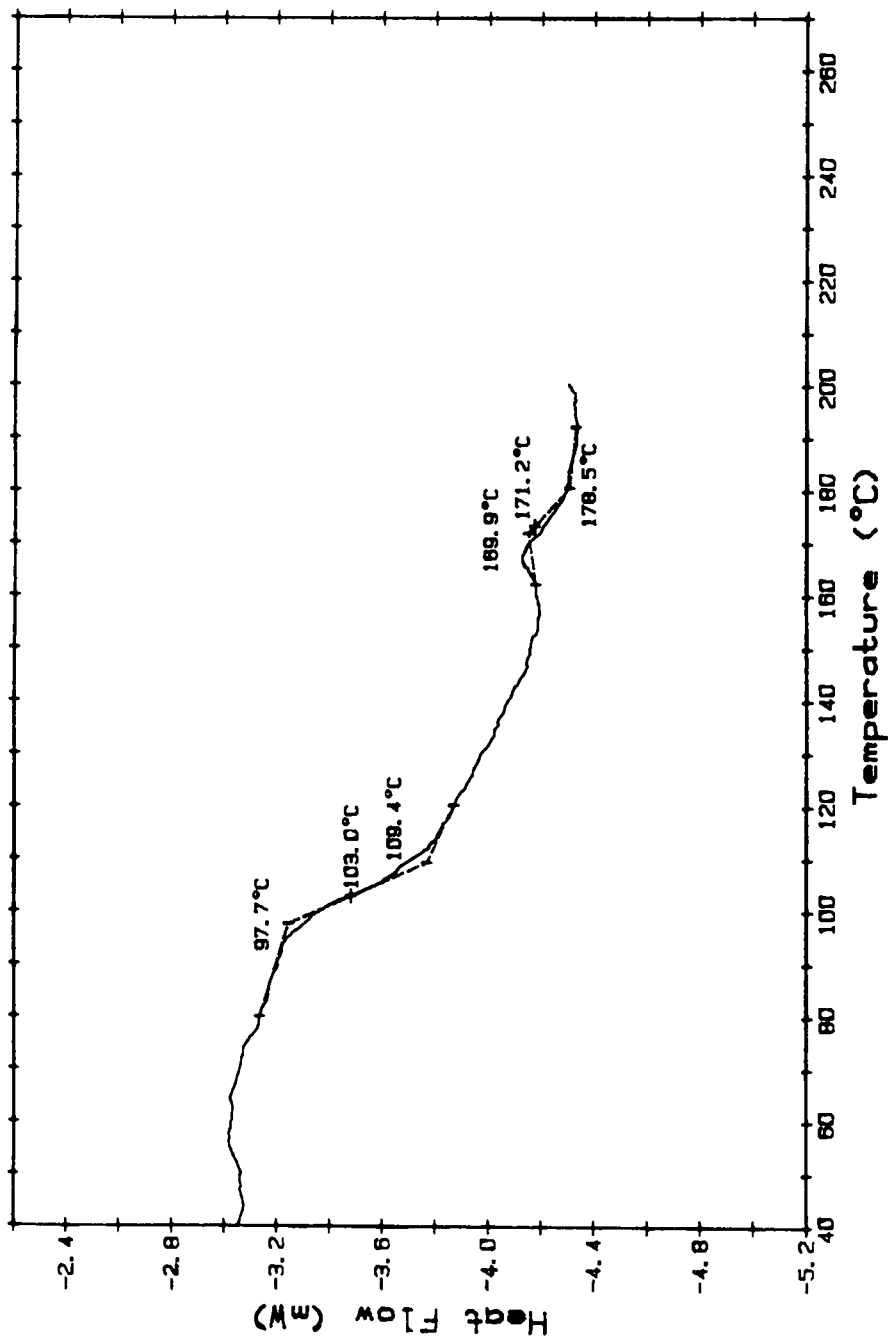


FIG. 4. The DSC thermogram for poly(styrene-*b*-trimethylvinylsilane) of \bar{M}_n 41,600 and 0.52 mole fraction styrene. The sample size was 13.31 mg and the heating rate was 10°C/min.

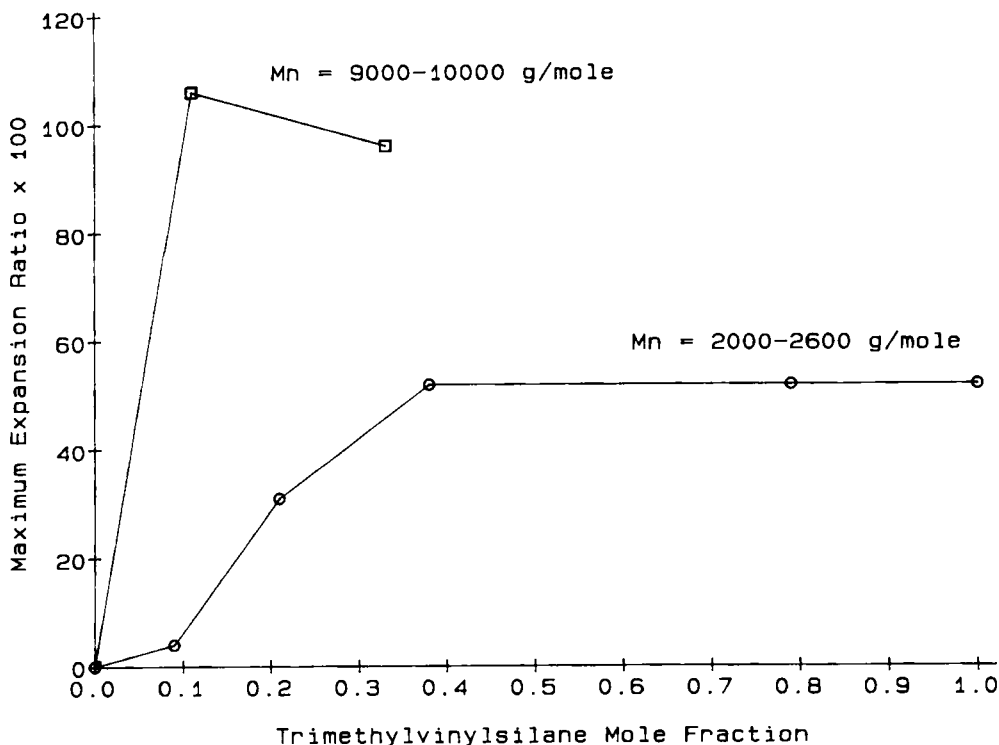


FIG. 5. Graph of maximum expansion ratio versus trimethylvinylsilane mole fraction for diblock copolymers with \bar{M}_n (GPC) = 2000-2600 (Curve 1) and with \bar{M}_n (GPC) = 9000-10,000 (Curve 2).

tivity has plateaued at or before 0.10 mole fraction trimethylvinylsilane and at a much higher level of activity. The foaming activity is also dependent upon molecular weight. At very low and at high molecular weights the activity drops (Table 2). Thus, for block copolymers containing 0.10 mole fraction trimethylvinylsilane, a poly(trimethylvinylsilane) segment of about 1000 g/mol is required for good activity.

The size of the poly(styrene) segment is also important. Table 3 shows the effect of increasing poly(styrene) segment size on foaming activity when the poly(trimethylvinylsilane) segment length is held constant. A maximum in foaming activity occurs around poly(styrene) segment sizes of 10 000 g/mol.

TABLE 2. The Effect of Molecular Weight on R_{\max} for Poly(Styrene-*b*-Trimethylvinylsilane) containing 0.90 mole Fraction Styrene

| GPC peak molecular weight | R_{\max} |
|---------------------------|------------|
| 3 280 | 0.04 |
| 7 480 | 1.06 |
| 12 400 | 0.88 |
| 24 200 | 0.88 |
| 56 100 | 0.28 |

TABLE 3. The Effect of Poly(Styrene) Segment \bar{M}_n on R_{\max} for Poly-(Styrene-*b*-Trimethylvinylsilane) having a Poly(Trimethylvinylsilane) Segment of 2 000 g/mol

| Poly(styrene) segment \bar{M}_n | R_{\max} |
|-----------------------------------|------------|
| 0 | 0.52 |
| 2 560 | 0.55 |
| 6 530 | 0.96 |
| 15 600 | 0.88 |
| 42 900 | 0.28 |

Figure 6 is a graph of R_{\max} versus poly(styrene-*b*-trimethylvinylsilane) concentration. R_{\max} rises very rapidly as the diblock copolymer loading increases before leveling out at a diblock copolymer concentration of 0.3 wt%.

SUMMARY

The diblock copolymer poly(styrene-*b*-trimethylvinylsilane) is readily made by sequentially and anionically polymerizing styrene and trimethylvinylsilane. Kinetics place limitations upon the length of the poly(trimethylvinylsilane)

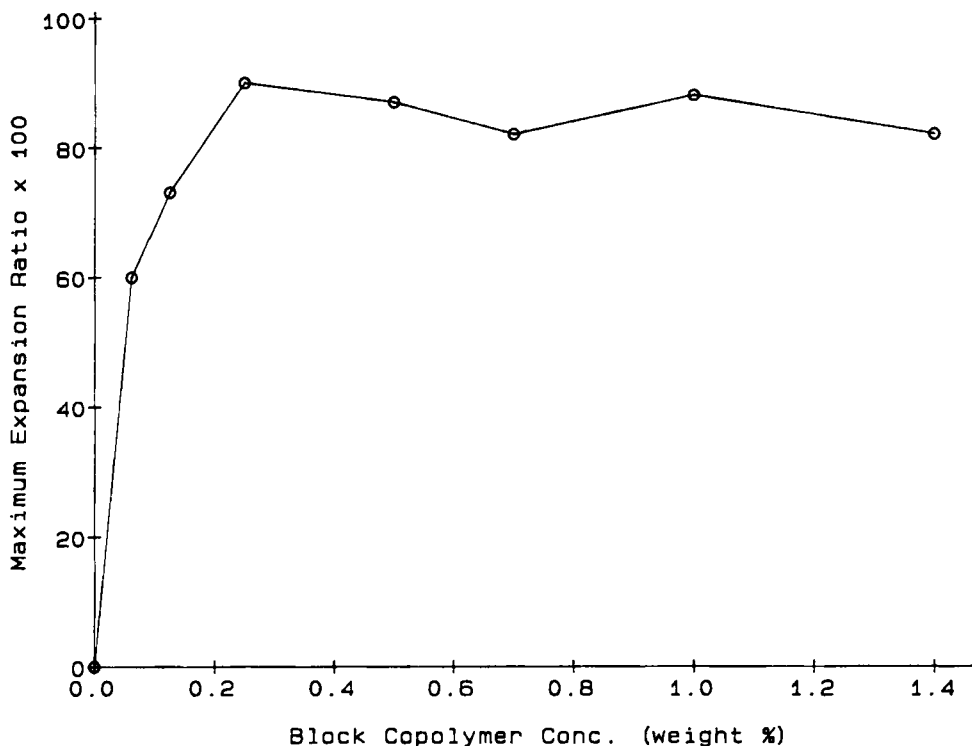


FIG. 6. Graph of maximum expansion ratio versus block copolymer concentration for poly(styrene-*b*-trimethylvinylsilane) of \bar{M}_n 17,600 and 0.89 mole fraction poly(styrene).

segment and conversion of trimethylvinylsilane monomer due to a termination reaction. Two transitions are observed in DSC thermograms indicating that the poly(styrene) and poly(trimethylvinylsilane) segments reside in separate domains. The amphiphathic nature of the diblock copolymer is revealed from molecular weight and GPC data, which show that the poly(styrene) segment is more lyophilic in tetrahydrofuran than the poly(trimethylvinylsilane) segment. The foaming properties of the diblock copolymer were found to depend upon composition, molecular weight, and concentration. Typically, concentrations of 0.3 wt% of a diblock copolymer having \bar{M}_n in the range 9 000-30 000 and 0.10 mole fraction styrene stabilized fine-celled

foams of nitrogen and polystyrene-styrene solutions. Both the foaming properties and inertness to carbanions make poly(styrene-*b*-trimethylvinylsilane) a good candidate as a foaming agent in an anionic poly(styrene) RIM process.

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