of K_a and find that for 1200 EW polymer

$$R = 1.4 \pm 0.2 \text{ nm} \tag{22}$$

for $-1 < K_a/K_s < 0$. This value is in agreement with the value of 1.2–1.3 nm deduced from water transport experiments.[2] The change in free energy that results from the formation of the channel is only −11 J/cm^3; thus our elastic theory suggests the channels are continually forming and unforming at ambient temperatures. This is consistent with the previously proposed cluster–network model.

V. Conclusion

We have derived a semiphenomenological expression for the diameter of ionic clusters in ionomers and demonstrated that this expression correctly describes the variation in cluster diameter in one perfluorinated ionomer with water content, equivalent weight, and cation form. We find the cluster diameter is dominated by a balance between hydrophilic surface interactions with the ion exchange sites and the energy of elastic deformation. The model also predicts that short channels connecting adjacent clusters are thermodynamically stable, in support of the cluster–network model proposed by us earlier. The current elastic theory should generally apply to other ionomers, including hydrocarbon analogues and a comparison of the phenomenological parameters K_s and K_1 for various ionomers should be instructive and interesting.

References and Notes

(1) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.
(2) Gierke, T. D. 152nd Meeting of the Electrochemical Society, Extended Abstracts, Atlanta, Ga., 1977, Abstract No. 438. *J. Electrochem. Soc.* **1977**, *124*, 319C.
(3) Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977.
(4) Yeo, S. C.; Eisenberg, A. *J. Appl. Polym. Sci.* **1977**, *21*, 875.
(5) Ceynowa, J. *Polymer* **1978**, *19*, 73.
(6) Heitner-Wirguin, C. *Polymer* **1979**, *20*, 371.
(7) Hodge, I. M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 289.
(8) Heitner-Wirguin, C.; Bauminger, E. R.; Levy, A.; Labensky de Kanter, F.; Ofer, S. *Polymer* **1980**, *21*, 1327.
(9) Yeager, H. L. Kipling, B. *J. Phys. Chem.* **1979**, *83*, 1836.
(10) Will, F. G. *J. Electrochem. Soc.* **1979**, *126*, 36.
(11) Lopez, M.; Kipling, B.; Yeager, H. L. *Anal. Chem.* **1977**, *49*, 629.
(12) Hsu, W. Y.; Barkley, J. R.; Meakin, P. *Macromolecules* **1980**, *13*, 198.
(13) Grot, W. G. F.; Munn, C. E.; Walmsley, P. N. 141st Meeting of the Electrochemical Society, Houston, Texas, May 1972, Abstract No. 154. *J. Electrochem. Soc.* **1972**, *119*, 108C.
(14) Leitz, F. B.; Accomazzo, M. A.; Michalek, S. A. 141st Meeting of the Electrochemical Society, Houston, Texas, May 1972, Abstract No. 150. *J. Electrochem. Soc.* **1972**, *119*, 108C.
(15) Yeo, R. S.; McBreen, J. *J. Electrochem. Soc.* **1979**, *126*, 1682.
(16) Olah, G. A.; Kaspi, J. *Nouv. J. Chim.* **1978**, *2*, 531, 583.
(17) Olah, G. A.; Keumi, T.; Meidar, D. *Synthesis* **1978**, 929.
(18) Olah, G. A.; Kaspi, J.; Bukala, J. *J. Org. Chem.* **1977**, *42*, 4187.
(19) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 6642.
(20) Mauritz, K. A.; Hora, C. J.; Hopfinger, A. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19*, 324.
(21) Hopfinger, A. J.; Mauritz, K. A. Hora, C. J. 152nd Meeting of the Electrochemical Society, Atlanta, Ga., Oct 1977 Abstract No. 439. *J. Electrochem. Soc.* **1977**, *124*, 319C.
(22) Hopfinger, A. J., private communication.
(23) Fedors, R. F. *Polymer* **1980**, *21*, 207.
(24) Varga, O. H. "Stress-Strain Behavior of Elastic Materials"; Interscience: New York, 1966; pp 152–155.
(25) The dependence of the tensile modulus, $G(c)$, on the water content of swollen polymer I can be derived theoretically from an effective medium theory of a random composite (Hsu, W. Y.; Giri, M.; Ikeda, R. M., to be published). At room temperature and 1200 EW and for the water uptake listed in Tables III–VI, the theoretical results can be fitted to eq 14 with $G_0 = 275$ J/cm^3, $\alpha = 0.0331$, and a correlation coefficient of −0.99996. These numbers compare favorably with Munn's empirical values reported in ref 13 and also quoted in the text. The only input to the calculation is the known shear and bulk modulii of the dry polymer I and water and the water content. There is no adjustable parameter and details will be reported in a forthcoming paper.
(26) Stillinger, F. H. *Adv. Chem. Phys.* **1975**, *31*, 1–102.
(27) Munn, G. E., unpublished results.
(28) (a) Falk, W. *Can. J. Chem.* **1980**, *58*, 1495. (b) Falk, W. "Perfluorinated Ionomer Membranes", to be published in *ACS Symp. Ser.*

Properties of Low Molecular Weight Block Copolymers. 1. Differential Scanning Calorimetry of Styrene–Dimethylsiloxane Diblock Copolymers[1]

Sonja Krause,* Magdy Iskandar,[2] and Mohammad Iqbal[3]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.

Received July 13, 1981

ABSTRACT: The glass transition temperature, T_g, the width of the glass transition interval, ΔT_g, and the change in specific heat at T_g, ΔC_p, were obtained by differential scanning calorimetry for both microphases in a series of phase-separated styrene–dimethylsiloxane (S–DMS) diblock copolymers and were compared with the same quantities obtained on styrene (S) and on dimethylsiloxane (DMS) homopolymers of comparable molecular weight. In S–DMS samples with S block molecular weights $\geq 3.90 \times 10^4$, the S phases had properties very similar to those of S homopolymer. At lower S block molecular weights, the S phase properties diverged from those of S homopolymers of comparable weight; large divergences occurred when the S block molecular weight was $\leq 0.82 \times 10^4$. Various interpretations of the data are considered.

Introduction

Recently, we[4] reported a comparison of the glass transition temperatures (T_g's) of the styrene (S) microphases in styrene–dimethylsiloxane (S–DMS) diblock copolymers, in styrene–isoprene diblock and triblock copolymers, and in styrene–ethylene oxide diblock and triblock copolymers. In that work, it appeared that the magnitudes of the T_g's of the S microphases in all these systems were approximately the same as long as S microphases made up of equal molecular weight blocks were compared. We concluded, therefore, that the chemical nature of the other block or blocks that are attached to the styrene blocks has no effect

0024-9297/82/2215-0105$01.25/0

on the T_g of the styrene microphase unless the molecular weight and composition of the block copolymer are near those at which microphase separation no longer takes place. That work also led to the conclusion that the phase boundaries are probably sharp in most phase-separated block copolymers.[5]

One major problem with our comparison of the T_g's of the S microphases in different copolymers was the fact that the data had been obtained by different workers in different laboratories with different differential thermal analyzers and differential scanning calorimeters. The aim of the present work was to obtain data on different types of styrene-containing block copolymers on a single set of instruments in the same laboratory. This paper deals with the differential scanning calorimetry (DSC) of S–DMS diblock copolymers; the next three papers will deal with the DSC of styrene–butadiene block copolymers and with refractive index vs. temperature measurements on many of these samples.

Experimental Section

Polystyrene (PS). Anionically polymerized standard polystyrene samples with molecular weights ranging from 600 to 1.8 × 10^6 were purchased from the ARRO Chemical Co., Joliet, Ill.; all samples had $\bar{M}_w/\bar{M}_n \leq 1.1$.

Monomers. All distillations, manipulations, and polymerizations were done under dry, O_2-free N_2, unless otherwise stated. Hexamethylcyclotrisiloxane (D_3), from the Silicone Products Division, General Electric Co., was purified by refluxing a 50% solution in benzene overnight over CaH_2; distillation was carried out under dry, O_2-free N_2, and the fraction boiling at 134 °C was used for polymerization. Styrene, from Matheson Coleman and Bell, was first washed with 10% NaOH to remove inhibitor and then washed with water, dried over CaH_2, and purified by reduced-pressure distillation just prior to use.

Solvents and Initiators. Cyclohexane, *n*-hexane, and *n*-pentane were treated with concentrated H_2SO_4, washed with water, and dried over $LiAlH_4$. Tetrahydrofuran (THF) and diglyme were distilled once and twice, respectively, over Na metal and were then distilled over $LiAlH_4$. These solvents were stored over prebaked Linde molecular sieves, Type 3A, and degassed before use. *sec*-Butyllithium was prepared by reacting 2-chlorobutane with Li metal in *n*-pentane following the method of Bryce-Smith and Turner.[6] The *n*-pentane was evaporated under vacuum and replaced by *n*-hexane. The concentration was estimated by the Gilman et al.[7] double-titration method.

Poly(dimethylsiloxane) (PDMS). *sec*-Butyllithium solution was injected into a dried solution of D_3 in toluene at room temperature. After 3 h of magnetic stirring, enough diglyme to form a 6% (v/v) solution was injected and the polymerization was allowed to proceed at 55 °C for 2–3 h and terminated, at ~50–75% conversion, by chlorotrimethylsilane, followed[9] by $NaHCO_3$. The polymer was precipitated with excess CH_3OH and dried to constant weight at 50 °C in a vacuum oven.

Poly(styrene-*b*-dimethylsiloxane) (S–DMS). The method of Saam et al.[8] was slightly modified as follows. Ten to fifteen percent solutions of styrene and of D_3 were prepared in cyclohexane and dried over Linde molecular sieves, Type 3A, for at least 24 h. The styrene solution was then dried and degassed over CaH_2 and transferred to the polymerization flask. *sec*-Butyllithium was added with stirring under slight N_2 pressure, and, 4–5 h later, enough THF was injected[9] to form a ~0.1 M solution. After this, D_3 solution that had been refluxed over CaH_2 for 0.5 h was added. After ~30–45 min, the characteristic color of the polystyryl anion virtually disappeared and enough diglyme was injected to make a 6–8 vol % solution. The reaction was terminated after ~50–70% conversion by chlorotrimethylsilane, followed[9] by $NaHCO_3$. The polymer was precipitated with excess methanol; it was then washed 3 times with methanol and dried to constant weight at 50 °C in a vacuum oven.

All S–DMS samples prepared as above are designated I in this work. Other samples, designated R, were prepared and characterized by Zilliox, Roovers, and Bywater[9] and were kindly sent to us by J. E. L. Roovers. Two more samples, designated D, were kindly given to us by J. W. Dean, Silicone Products Division, General Electric Co.

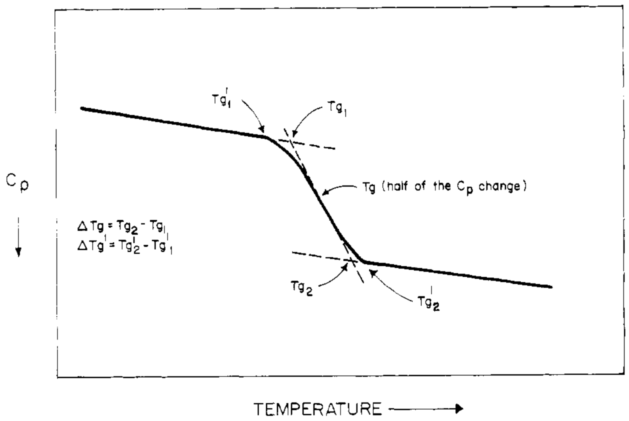

Figure 1. Definitions of various characteristic temperatures associated with the glass transition as obtained from a typical thermogram from a Du Pont 990 thermal analyzer, DSC mode.

Characterization. $\bar{M}_n$ values for some polymers were determined[10] with a Model 232A vapor pressure osmometer, Wescan Instruments Inc., and for others with either a Mechrolab Model 501 high-speed membrane osmometer (no longer on the market) or a Knauer membrane osmometer, Utopia Instrument Co., Joliet, Ill. Apparent molecular weight distributions were determined with a Waters Associates Anaprep gel permeation chromatograph run in the analytical mode at room temperature with a 1 mL/min flow rate. The exclusion limits of the five columns used ranged from 2 × 10^3 to 7 × 10^5 Å; the pressure was 100 psi and the flow time was ~ 4 h. The columns were calibrated by using standard PS samples in distilled toluene, and, in most cases, it was assumed that the PS calibration held for both PDMS and S–DMS. It has been shown[10] that the absolute error in $\bar{M}_n$ averages is about -6% for S–DMS and for PDMS samples using this procedure. Since our set of columns allowed considerable boundary spreading for the lowest molecular weight samples,[10] a method developed by Osterhoudt and Ray[11] was used to correct $\bar{M}_w/\bar{M}_n$ values for some of the samples.

Average compositions of the S–DMS samples were obtained with a Varian T-60A proton nuclear magnetic resonance spectrometer. Homopolymer mixtures in CCl_4 were used to calibrate the instrument; the area under the phenyl peak of styrene at 6–8-ppm chemical shift was compared with that under the CH_3 peak of DMS at ~0-ppm chemical shift. Spectrograde dioxane, 4.8–5.0-ppm chemical shift, was used as a reference.

Differential Scanning Calorimetry (DSC). All work was done on a Du Pont thermal analyzer, Model 990, run in the DSC mode, in the laboratory of Professor B. Wunderlich. The temperature axis of the DSC instrument was calibrated from 193 to 693 K with six different standards; the standard deviation was about ±1.3 K over this temperature range. The specific heat axis was then calibrated by using sapphire (Al_2O_3). Most polymer samples weighed 15–39 mg except for a few duplicate runs with 50-mg sample weights and were run at equal heating and cooling rates, 10 K min^{-1}, under a constant stream of N_2; the first heat of each sample was discarded for this work unless data on a quenched sample were desired, and all data were obtained during the heating part of the cycle. Figure 1 shows the definitions of the quantities T_{g_1}', T_{g_1}, T_g, T_{g_2}, and T_{g_2}' that we report in this work. The change in heat capacity at T_g was calculated from the vertical distance between the two extrapolated base lines at T_g. The width of the glass transition region can be taken either as $\Delta T_g = T_{g_2} - T_{g_1}$ or as $\Delta T_g' = T_{g_2}' - T_{g_1}'$. Although $\Delta T_g'$ seems to be a more reasonable definition for the width of the glass transition than ΔT_g, it is much more subjective and variable and will not be used in the discussion. Since, however, questions may arise about this point, we are reporting both T_{g_2}' and T_{g_1}' under Results.

Results

Table I gives the characterization and thermal data of the standard PS samples. The thermal data were obtained from a single run, never the first heating, on each sample.

Table I
PS Data

sample	nominal mol wt × 10^{-4}	$\overline{M}_n \times 10^{-4}$	T_g, K	T_{g_1}, K	$T_{g_2} = T_{g_2}'$, K	T_{g_1}', K	ΔC_p, J g^{-1} K^{-1}
PS1	0.06		259	255	261	247	0.285
PS2	0.09		307	300	310	287	0.285
PS3	0.20	0.20[a]	331	328	334	320	0.285
PS4	0.40	0.34[a]	347	344	350	338	0.276
PS5	1.03	0.99[a]	368	366	371	359	0.293
PS6	2.04	2.06[a]	373	369	375	364	0.305
PS7	5.10	5.02[b]	377	374	379	369	0.288
PS8	10.0	10.0[b]	378	375	380	370	0.280
PS9	20.0	19.9[b]	378	375	381	370	0.293
PS10	180	150[b]	378	377	381	370	0.293

[a] Using vapor pressure osmometry. [b] Using membrane osmometry.

Table II
PDMS Data

sample	$\overline{M}_n \times 10^{-4}$ (GPC)	$\overline{M}_w/\overline{M}_n$ (GPC)	T_g, K	T_{g_1}, K	$T_{g_2} = T_{g_2}'$, K	T_{g_1}', K	no. of runs
PDMS1	0.50	1.16	149	148	150	144	1
PDMS2	2.43	1.21	150 ± 0.5	148 ± 0.5	150 ± 0.5	147 ± 1	2
PDMS3	8.41	1.19	150 ± 0.5	149 ± 0.5	151 ± 0.5	145 ± 0.5	2

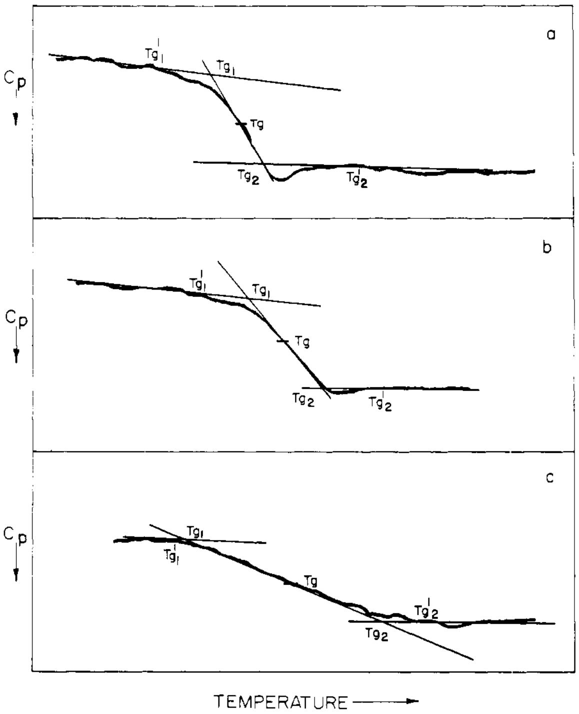

Figure 2. Some typical thermograms. The temperature scale is the same for these thermograms, but the curves have been shifted as if the three samples had comparable T_g's. (a) PS, $\overline{M}_n^S = 2.04 \times 10^4$. (b) A high molecular weight S microphase, $\overline{M}_n^S = 28.2 \times 10^4$. (c) A low molecular weight S microphase, $\overline{M}_n^S = 0.141 \times 10^4$.

Table III
S-DMS Diblock Copolymer Characterization

sample	$\overline{M}_n \times 10^{-4}$ (OSM)	$\overline{M}_n \times 10^{-4}$ (GPC)	$\overline{M}_w \times 10^{-4}$ (GPC)	$\overline{M}_w/\overline{M}_n$ (GPC)	[S], wt % (NMR)
I23	0.329	0.271	0.395	1.46	86
I24		0.388	0.523	1.35	86
I25		0.394	0.548	1.39	78
I22	0.38	0.440	0.554	1.26	32
I26		0.732	0.90	1.23	79
I15	0.96	0.88	0.98	1.11	59
I28		1.54	1.71	1.11	24
R13		1.51	1.60	1.06	54[a]
D2	1.90	1.83	2.30	1.26	84[a]
I29		2.19	2.50	1.14	29
D1	2.08	2.00	2.60	1.32	88
R14	3.67	3.09	3.40	1.10	57[a]
R15		8.3	10.0	1.20	47[a]
R5		15.6	18.5	1.19	74[a]
R8		17.5	20.3	1.16	60[a]
R25		42.7	49.2	1.15	66[a]
R26		54.8	62.0	1.31	58[a]

[a] As given by the supplier.

Figure 2a shows a typical PS thermogram; each PS thermogram had a hysteresis peak in spite of our ostensibly equal heating and cooling rates. Table II shows the characterization and thermal data on three PDMS samples. All three of the PDMS thermograms showed crystallization and melting peaks above T_g, with the area under the melting peak somewhat greater than that under the crystallization peak; this indicates that some of the polymer had crystallized while cooling so that ΔC_p could not be calculated directly from the vertical change in the thermogram at T_g (see Figure 1). Various attempts were made to estimate the amount of PDMS that had crystallized during cooling, but these were not very successful because it was difficult to find the base line near the crystallization and melting peaks.

Table III shows characterization data on the S–DMS samples, Table IV shows the thermal properties of the S microphases in these block copolymers, and Table V shows the thermal properties of the DMS microphases. The limits of error shown in Tables IV and V are mean deviations. The number of runs used for the calculations varied for each sample and are given in Tables IV and V. The samples that are missing from Table V are those containing <22% DMS with DMS block molecular weights such that the DMS microphases crystallized under our conditions; this made it impossible to extract glass transition data from the DSC curves. The samples in Table V which have missing ΔC_p values are those with >22% DMS and DMS molecular weights high enough so that crystallization and melting peaks, as well as the glass transition, were observed. Estimates of the percent crystalline material present below T_g were as difficult for these samples as they were for the PDMS homopolymers.

Discussion

Homopolymers. The T_g data on anionically polymerized PS standard samples shown in Table I are in rea-

Table IV
Thermal Properties of the S Block in S-DMS Diblock Copolymers

sample	$\bar{M}_n^{S}$ × 10^{-4}	[S], wt %	T_g, K	T_{g_1}, K	T_{g_2}, K	T_{g_1}', K	T_{g_2}', K	ΔC_p, J g^{-1} K^{-1}	no. of runs	ΔT_g, K
I22	0.141	32	317 ± 4	292 ± 7	332 ± 7	292 ± 7	335 ± 1	0.22 ± 0.02	5	40 ± 10
I23	0.233	86	317 ± 1	308 ± 1	329 ± 5	297 ± 2	330 ± 6	0.36 ± 0.02	7	21 ± 6
I25	0.307	78	323 ± 0.5	313 ± 2	332 ± 0.5	303 ± 2	332 ± 1	0.42 ± 0.01	4	19 ± 3
I24	0.334	86	322 ± 0.5	312 ± 1	330 ± 0.5	299 ± 2	350 ± 11	0.44 ± 0.02	4	52 ± 22
I28	0.370	24	324 ± 2	298 ± 1	334 ± 2	298 ± 1	348 ± 2	0.51 ± 0.03	2	36 ± 3
			322 ± 8	297 ± 1	332 ± 2	297 ± 1	348 ± 12	0.35 ± 0.02[a]	2	35 ± 3
I15	0.519	59	320 ± 9	290 ± 12	342 ± 10	278 ± 24	350 ± 11	0.43 ± 0.14	6	52 ± 22
I26	0.58	79	346 ± 3	332 ± 7	354 ± 1	316 ± 16	354 ± 1	0.20 ± 0.02	6	52 ± 22
			348	335	356	317	358	0.18[a]	1	21
I29	0.63	29	335	304	360	304	367	0.55	1	56
R13	0.82	54	358 ± 4	342 ± 4	370 ± 2	314 ± 8	371 ± 1	0.22 ± 0.08	2	28 ± 6
D2	1.54	84	370 ± 1	357 ± 2	381 ± 3	337 ± 11	381 ± 3	0.28 ± 0.01	4	24 ± 5
R14	1.76	57	374 ± 0.5	368 ± 3	382 ± 2	360 ± 4	383 ± 0.5	0.18 ± 0.02	4	14 ± 5
D1	1.76	88	370 ± 0.5	361 ± 2	378 ± 3	340 ± 4	379 ± 2	0.27 ± 0.02	5	17 ± 5
R15	3.90	47	377 ± 0.5	371 ± 4	384 ± 3	358 ± 10	383 ± 3	0.28 ± 0.02	3	13 ± 7
R8	10.5	60	378 ± 0.5	374 ± 0.5	384 ± 2	366 ± 2	384 ± 3	0.28 ± 0.04	3	10 ± 3
R5	11.5	74	379 ± 0.5	373 ± 2	384 ± 2	354 ± 14	384 ± 2	0.42 ± 0.16	2	11 ± 4
R25	28.2	66	376	373	382	366	382	0.31	1	9
R26	31.8	58	378 ± 0.5	372 ± 2	384 ± 2	362 ± 2	384 ± 2	0.33 ± 0.01	2	12 ± 4

[a] Quenched and heated to ~450 K in an oven; then the Al pan was dropped into liquid nitrogen.

Table V
Thermal Properties of the DMS Block in S-DMS Diblock Copolymers

sample	$\bar{M}_n^{DMS}$ × 10^{-4}	[DMS], wt %	T_g, K	T_{g_1}, K	T_{g_2}, K	T_{g_1}', K	T_{g_2}', K	ΔC_p, J g^{-1} K^{-1}	no. of runs
D1	0.24	12.1	160 ± 5	157 ± 4	162 ± 5	157 ± 4	162 ± 5	0.63 ± 0.04	4
D2	0.29	16.1	148 ± 0.5	142 ± 2	151 ± 1	143 ± 3	151 ± 1	0.59[a]	2
I22	0.30	68	155 ± 2	151 ± 0.5	158 ± 2	151 ± 0.5	163 ± 2	0.56 ± 0.14	4
I15	0.36	41	152 ± 1	148 ± 0.5	154 ± 2	148 ± 0.5	160 ± 2	0.66 ± 0.18	6
R13	0.69	46	152	149	155	149	158		1
I28	1.17	76	157 ± 0.5	154 ± 0.5	161 ± 0.5	154 ± 0.5	181 ± 4	0.46 ± 0.01	2
R14	1.33	43	158 ± 0.5	153 ± 2	161 ± 0.5	152 ± 2	161 ± 0.5		3
I29	1.56	71	187	177	197	172	207	0.22[b]	1
			154 ± 0.5	149 ± 1	157 ± 0.5	149 ± 1	162 ± 4		3
R5	4.1	26	148	140	152	140	152		1
R15	4.4	53	141 ± 4	146 ± 6	153 ± 5	146 ± 6	153 ± 5		3
R8	7.0	40	155 ± 3	151 ± 2	157 ± 2	141 ± 5	158 ± 0.5		2
R25	14.5	33.5	150 ± 0.5	150 ± 0.5	152 ± 0.5	150 ± 0.5	152 ± 0.5		2
R26	23.0	42	150 ± 1	148 ± 1	153 ± 2	148 ± 1	153 ± 2		2

[a] ΔC_p calculated from a single run. [b] Sample was quenched in liquid nitrogen from 450 °C.

sonable agreement with those obtained by other workers using different DSC or differential thermal analysis equipment and, generally, heating and/or cooling rates different from those used in this work.[13-16] The ΔT_g for these samples was 6 ± 1 K (the error is the mean deviation) under our conditions; this value is given as a basis for comparison with the data obtained for S microphases in various block copolymers using the same heating and cooling rates. We do not attribute any theoretical significance to the observed ΔT_g of these PS standards. The ΔC_p obtained for the PS standards in this work was 0.288 ± 0.006 J g^{-1} K^{-1} (mean deviation). This value is in good agreement with literature values, 0.296,[17] 0.282 ± 0.006,[18] 0.31,[19] and 0.295[20] J g^{-1} K^{-1}, also obtained by DSC. It is somewhat surprising that the ΔC_p in this work did not change even for the lowest molecular weight oligomers (mol wt 600).

In contrast to the data on PS, the T_g of PDMS was ~150 K, independent of molecular weight for the three samples studied in this work; similar results were obtained by Cowie and McEwen,[21] who found, using DSC extrapolated to infinitely slow heating rates, that T_g = 148 K for PDMS with $\bar{M}_n > 2400$. At a heating rate of 10 K min^{-1}, the same as the one used in this work, a sample with $\bar{M}_n$ = 2.7 × 10^4 had T_g = 149 K, in excellent agreement with our value. Adachi et al.[22] obtained T_g = 148 K by DSC at an unknown heating rate on a sample of PDMS that had been cooled at 40 K min^{-1}. The ΔT_g values of our three samples were all 2 K, much smaller than those of PS. It is interesting to note, however, that $\Delta T_g/T_g$ is similar for the two polymers, 0.013 and 0.016 for PDMS and PS, respectively.

Block Copolymer Characterization. Since $\bar{M}_n$ values, when obtained by osmometry, were very close to those calculated from GPC, all the $\bar{M}_n$ values obtained from GPC were assumed correct and are used in the figures. All GPC data given were obtained in this laboratory; in general, these data were in good agreement with those of the suppliers of the D and R samples.

Properties of S Microphases. The variation of T_g and ΔT_g with S molecular weight in S-DMS diblock copolymers and with PS molecular weight in the standard homopolymers for block and homopolymer molecular weights <2.5 × 10^4 is shown in Figure 3. On that figure, horizontal bars designate T_g and vertical bars designate the range from T_{g_1} to T_{g_2} for each homopolymer or S microphase. The symbol $\bar{M}_n^S$ designates the $\bar{M}_n$ of each S block or PS sample. The curve is drawn through the PS T_g's. If the curve on Figure 3 had been continued to $\bar{M}_n^S$ = 3.18 × 10^5, the highest S block molecular weight investigated, the trend that starts on Figure 3 above $\bar{M}_n^S$ = 1.5 × 10^4 would be seen to continue; that is, for all S-DMS

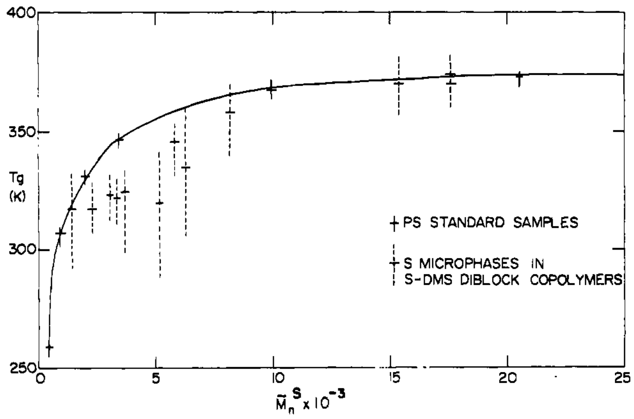

Figure 3. T_g vs. $\bar{M}_n^S$ of PS and of S microphases up to $\bar{M}_n^S = 2.5 \times 10^4$. Vertical bars represent ΔT_g.

samples with $\bar{M}_n^S > 1.5 \times 10^4$, T_g is consistent with that for PS standard samples of comparable molecular weight but ΔT_g is greater than the 6 ± 1 K found for the PS samples. For the five S–DMS samples with $\bar{M}_n^S > 2.5 \times 10^4$, the average value of ΔT_g is 11 K, about twice the PS value. The same five samples have ΔC_p values consistent with those of the PS samples. Therefore, the S microphases with $\bar{M}_n^S \geq 3.90 \times 10^4$ have T_g and ΔC_p very close to those of PS samples whose $\bar{M}_n^S$ is similar, but the ΔT_g of the S microphases is about twice that of the PS standards. This ΔT_g increase is the only noticeable different between the DSC data on PS and on these high molecular weight S microphases. Tables I and IV show that the increase in the ΔT_g of these S microphases arises both from a lowering of T_{g_1} and from an increase of T_{g_2} for these microphases relative to PS values. Logically, the increase in the ΔT_g of the S microphases cannot be ascribed to admixed DMS in an interfacial region although this would explain the lowering of T_{g_1} because, within experimental error, the ΔC_p's of these high molecular weight microphases are equal to those of PS and thus indicate that all the S segments, with no need for admixed DMS segments, are present in the S microphases.

An increase of ΔT_g of S and of α-methylstyrene, MS, microphases in high molecular weight, 4×10^5 to 10^6, diblock and triblock copolymers of S with MS was observed by Gaur and Wunderlich;[20] they ascribed this to an effect of the large surface areas between the microphases. The effect noted by Gaur and Wunderlich[20] was much larger than the one seen in this work; the T_g of the MS microphases was extremely diffuse as noted in the same samples earlier by Krause et al.,[23] even though these samples had MS blocks with molecular weights $\geq 2 \times 10^5$. Therefore, although it seems as if microphases have greater ΔT_g's in DSC measurements than the corresponding homopolymers, this effect appears to differ in magnitude for chemically different microphases. It appears to be much greater for MS microphases than for S microphases.

As seen in Figure 3, the T_g's of the S microphases do not decrease noticeably below those of comparable molecular weight PS samples until the S block molecular weight is $\leq 0.82 \times 10^4$. However, the T_g of the lowest molecular weight S microphase, 0.141×10^4, is again comparable with that of PS of comparable molecular weight. Concomitant with the decrease of T_g of these low molecular weight S microphases, there is a further increase of ΔT_g and a change of ΔC_p away from the homopolymer value (see Figure 4). For some S microphases, ΔC_p is greater than the PS value, and for others it is less. A lowered ΔC_p for S microphases of low molecular weight has also been noted by Morêse-Séguêla et al.[19] and by Cowie et al.[24] Morêse-Séguêla et al.[19] studied styrene–isoprene, S–I, diblock copolymers of about 50/50 (w/w) composition, with S block molecular weights from 0.14×10^4 to 0.63×10^4; all their S microphase T_g's were below those of homopolymers of comparable molecular weight and all their S microphase ΔC_p's were below that of PS. From these data and from ^{13}C NMR line width measurements, these authors concluded that there were strong dynamical interactions at the microphase interface between the chains in the two microphases and that these interactions were responsible for the lowering of T_g and of ΔC_p. Cowie et al.[24] studied Kraton G-1650, a styrene–(ethene-*co*-butene)–styrene triblock copolymer with a molecular weight of 10^4 per S block and also found a lower ΔC_p for the S microphase than that of PS; they did not calculate T_g because their thermograms appeared to exhibit two steps near the S microphase T_g. These workers indicated that their lower ΔC_p in the block copolymer showed that not all of the S segments took part in the S glass transition process but they were not certain whether this implies interfacial volumes or other mixed phases.

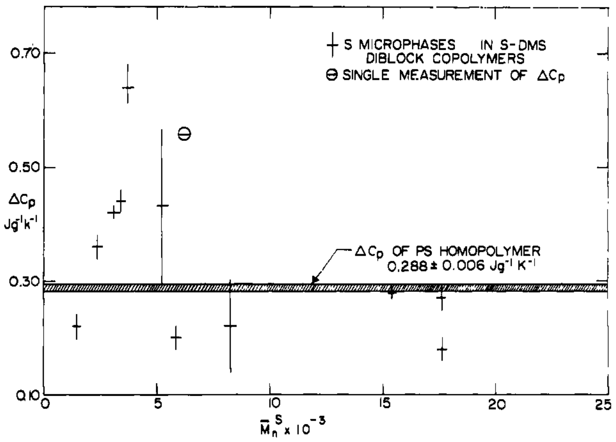

Figure 4. ΔC_p vs. $\bar{M}_n^S$ of PS and of S microphases up to $\bar{M}_n^S = 2.5 \times 10^4$. Vertical bars represent mean deviations.

Since many of our low molecular weight S microphases had elevated ΔC_p values (although others had lowered ΔC_p values), one could speculate that those S microphases that had elevated ΔC_p values probably contained admixed DMS segments. It is interesting to note that the lowest molecular weight S microphase studied, which had a T_g comparable to that of PS of equal moelcular weight, had a lowered ΔC_p. It is hard to tell whether this single observation is significant. The fact that some of our low molecular weight S microphases had lowered ΔC_p's indicates that admixing of DMS segments, if the speculation above is correct, is not the only thing that happens to affect ΔC_p. There should definitely be an effect from the connectedness of the S with the DMS blocks across the interface between microphases; this could be either a dynamical interaction as proposed by Morêse-Séguêla et al.[19] or a general effect caused by the large specific surface area between microphases as proposed by Gaur and Wunderlich.[20]

The S microphases in our S–DMS block copolymers can be divided into three groups. The high molecular weight group, $\bar{M}_n^S \geq 3.90 \times 10^4$, in which the S microphases have T_g and ΔC_p equal to those of PS of comparable molecular weight but in which ΔT_g is about double that of PS; the low molecular weight group, $\bar{M}_n^S \leq 0.82 \times 10^4$, in which the S microphases have T_g lower than that of PS of comparable molecular weight, ΔT_g's all greater than those of the high molecular weight group, and ΔC_p's either larger or smaller than that of PS; and an intermediate molecular weight group in which the changes in properties from the high to the low molecular weight group are somewhat sporadic and gradual. There are no trends with percent composition; this implies that T_{g_1}, ΔT_g, and ΔC_p of low molecular weight S microphases in S–DMS block copolymers do not vary appreciably with morphology. Since our copolymers vary between 24 and 86% S by weight, equilibrium morphologies that vary from spherical or cylindrical inclusions of S in a DMS matrix to alternate lamellae of S and DMS to cylindrical or spherical inclusions of DMS in an S matrix are to be expected in our block copolymers. We did not observe morphology directly since we did not succeed in microtoming our samples for electron microscopy, even at low temperatures.

Samples R13, R15, and R8 were also studied in the form of films obtained from cyclohexane and from butanone solutions of the polymers. The results indicate that this treatment did not change T_g outside of experimental error but that ΔT_g decreased and all ΔC_p's were less than that of PS. These preliminary experiments indicate that ΔT_g and ΔC_p change after major changes in sample pretreatment but that T_g changes very little. Quenching a sample from 450 K did not affect the thermal properties of the S microphases.

Properties of DMS Microphases. Table V shows data on the glass transitions of all the DMS microphases for which such data could be observed. The four samples for which no data are given in Table V are those which contained ≤22 wt % DMS. Values of ΔC_p are shown only for those DMS microphases which were 100% amorphous; for samples that were not quenched in liquid N_2, this included only samples with $\bar{M}_n^{\mathrm{DMS}} \leq 1.17 \times 10^4$. It was possible to obtain the DMS microphase of sample I29, with $\bar{M}_n^{\mathrm{DMS}} = 1.56 \times 10^4$, 100% amorphous by quenching this sample in liquid N_2; the sample, however, had an abnormally high T_g, 187 K, after quenching. One could therefore speculate that this DMS microphase was very different from that in a normally (10 K min^{-1}) cooled sample, perhaps containing admixed S segments. The ΔC_p values of the nonquenched 100% amorphous DMS microphases average 0.57 J g^{-1} K^{-1}. This is somewhat greater than the value 0.50 J g^{-1} K^{-1} found by Godovskii et al;[12] the difference between the two values may not, however, be significant. At any rate, especially in the case of samples D1, D2, I22, and I15, our ΔC_p data indicate that all the DMS segments were present in the DMS microphases and contributed to ΔC_p. One might speculate on the presence of some S segments in the microphases since some of them had slightly elevated T_g values as well as slightly elevated ΔC_p values. All but sample D2 among the five samples under discussion have T_g values somewhat higher than the 150 K of our PDMS homopolymers. The DMS glass transitions of the amorphous DMS microphases were broadened relative to those of PDMS, just like the glass transitions of the S microphases were broadened relative to those of PS. The average ΔT_g of these DMS microphases is 7 K, while the ΔT_g of PDMS is 2 K under our conditions. The T_g and the ΔT_g values obtained for the higher molecular weight, partly crystalline PDMS microphases are comparable to those of the 100% amorphous DMS microphases; one may note that the T_g values of the two highest molecular weight DMS microphases are equal to that of PDMS, and the ΔT_g values of these microphases are somewhat lower than those of the lower molecular weight DMS microphases.

It was stated above that the DMS microphase ΔC_p values of samples D1, D2, I22, I15, and probably I28 indicate that all the DMS segments are in the DMS microphases in these samples. Table IV shows that the ΔC_p of the S microphase in samples D1, D2, and I22 is equal to or less than that of PS, indicating that no admixture of DMS segments is necessary to explain these S microphase ΔC_p's. Samples I15 and I28, however, have elevated S microphase ΔC_p values, so that admixing of DMS segments into these S microphases was postulated. The ΔC_p of the S microphase of sample I15 had a large enough experimental error that the PS ΔC_p actually falls within its range. The data of sample I28, however, are hard to explain; it may be possible for some DMS segments close to the microphase interfaces to migrate back and forth between the DMS and S microphases as the temperature changes between the T_g's of the two microphases. This could also happen in the other block copolymer samples; some of the other effects on ΔC_p could obscure the effects of DMS migration in many of the samples.

It was stated above and it can be seen in Table V that T_g values of many DMS microphases, especially with $\bar{M}_n^{\mathrm{DMS}} \leq 1.56 \times 10^4$, are somewhat greater than that of PDMS. This is the opposite of the T_g depression, with respect to PS, found for low molecular weight S microphases with $\bar{M}_n^{\mathrm{S}} \leq 0.82 \times 10^4$. This general phenomenon in block copolymers, of a depression of the T_g of the harder microphase, the one with the higher T_g, vs. an elevation of the T_g of the softer microphase, the one with the lower T_g, has been noted by others.[19,25,26] Kraus and Rollmann,[25] using dynamic mechanical techniques, found a slight increase in the T_g of the softer microphase (isoprene or butadiene) loss maximum as the molecular weights of these blocks in triblock copolymers with S decreased to just below 10^4. Robinson and White,[26] using DSC on styrene–isoprene triblock copolymers, also found an increase in the T_g of the isoprene microphases over and above that of polyisoprene homopolymer of similar microstructure. These authors, however, found the largest increase in T_g, about 3 °C, when the isoprene blocks had molecular weights from 5×10^4 to 10×10^4; as the isoprene block molecular weights decreased to about 1.4×10^4, their T_g decreased almost to that of pure polyisoprene. Morèse-Séguéla et al.,[19] on the other hand, in a DSC study of styrene–isoprene diblock copolymers, found not only that the T_g of the isoprene microphases was higher than that of polyisoprene homopolymer but also that the microphase T_g increased with decreasing isoprene block molecular weight. In most of their samples, the ΔC_p of the isoprene microphase was equal to that of homopolymer with the exception of their lowest molecular weight sample, for which an increased ΔC_p was found. In this sample, the investigators therefore postulated extensive mixing of S segments into the isoprene microphase. Robinson and White[26] felt that it was the presence of the stiffer S blocks in their styrene–isoprene block copolymers that raised the T_g of the isoprene microphases above that of polyisoprene. In a similar vein, Morèse-Séguéla et al.[19] postulated that strong dynamical interactions with segments of the hard S phase raised the T_g's of their isoprene microphases.

A careful analysis of the composite nature of microphase-separated block copolymers reveals an additional influence on the T_g of the soft phase, namely, the presence of a thermal stress field in the samples at temperatures below the T_g of the hard phase and especially below the T_g of the soft phase. This thermal stress field is caused by the unequal coefficients of thermal expansion of the two phases and will be quite diffeent depending on whether the hard phase is an inclusion in a matrix of the soft phase or the soft phase is an inclusion in a matrix of the hard phase or the hard and soft phases have a lamellar morphology. Rubber-modified glassy plastics such as high-impact polystyrene have soft inclusions in a hard matrix; these have been studied by Paterno,[27] who found that the dilatational stresses around the rubber particles should and do lead to a small decrease in T_g of these particles. His work also indicates that an increase of T_g of the soft microphase should be expected when this phase comprises the matrix rather than the inclusions. Looking at the first five samples in Table V, those with 100% amorphous DMS microphases, one may note that the two with such high DMS content that this should be the matrix have elevated DMS microphase T_g values (samples I22 and I28), while only one of the two samples with such a low DMS content that this should be the inclusion in an S matrix has a lowered DMS microphase T_g value (sample D2) while the other has an elevated DMS microphase T_g value (sample D1). We offer no explanation for the data on sample D1. The other data are compatible with Paterno's calculations using thermal stresses.

Explanations for T_g's of S Microphases. Others besides those already noted[19,21] have observed the lowering of the T_g's of low molecular weight S microphases below the T_g's of PS samples of comparable molecular weight.[16,25,26,28-30] Various of these other authors attributed this T_g lowering to mixing of segments of the soft phase into the S microphase, either throughout the S microphase or only near the interface between microphases. It has always been relatively simple, therefore, to find a hypothesis to explain the T_g lowering in low molecular weight S microphases. It is much harder to find an explanation for another of our observations, namely, that the T_g's of our higher S block molecular weight microphases (S block molecular weight $\geq 1.54 \times 10^4$; see Figure 3 and Table IV) are exactly comparable to those of PS samples of comparable molecular weight even when the T_g of PS has begun to drop below that of high molecular weight PS! If one accepts the usual explanation for the decrease in T_g of low molecular weight PS below that of high molecular weight PS, namely, that the higher concentration of chain ends in lower molecular weight PS contributes a higher concentration of free volume in those samples which then causes a decrease in their T_g values, then there is no explanation for the correspondence of these PS T_g values with those of our S microphases of comparable molecular weight. After all, each PS molecule has two free chain ends while each S block has only one free chain end; the other end of each S block is attached to a DMS block by a chemical bond. Although the DMS block is quite rubbery at the temperature at which the glass transition of the S block starts, nevertheless the S unit which is attached to the DMS block is hardly a free chain end. It should not contribute exactly the same free volume to the S microphase as is contributed by a free chain end but perhaps it does. Alternatively, the free volume theory may not be enough to explain the observations on these samples.

Acknowledgment. We thank the National Science Foundation, Polymers Program, for support of this work (Grants DMR76-19488 and DMR78-20772), and S.K. thanks the National Institutes of Health for a Research Career Award for part of the period in which this work was done. We thank B. Wunderlich for the use of the Du Pont 990 thermal analyzer, Y. S. Kim for the osmometric data and for much of the GPC data, and J. W. Dean, Silicone Products Division, the General Electric Co., and J. E. L. Roovers, National Research Council of Canada, for some of the S-DMS samples used in this work. Special thanks are given to J. Armstrong of Utopia Instrument Co., Joliet, Ill., for giving us the Knauer membrane osmometer.

References and Notes

(1) Taken, in part, from data obtained by M. Iskandar, in partial fulfillment of the requirements for the Ph.D. degree at Rensselaer Polytechnic Institute.
(2) Present address: Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va., 24061.
(3) Present address: 3M Co., St. Paul, Minn. 55144.
(4) Krause, S.; Iskandar, M. *Adv. Chem. Ser.* **1979**, *No. 176*, 205.
(5) Krause, S. *Macromolecules* **1978**, *11*, 1288.
(6) Bryce-Smith, D.; Turner, E. E. *J. Chem. Soc.* **1953**, 861.
(7) Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.
(8) Saam, J. C.; Gordon, D. J.; Lindsay, S. *Macromolecules* **1970**, *3*, 1.
(9) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.
(10) Kim, Y. S. M.S. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 1979.
(11) Osterhoudt, H. W.; Ray, L. N., Jr. *J. Polym. Sci., Part C* **1968**, *21*, 5.
(12) Godovskii, Y. K.; Levin, V. Y.; Slonimskii, G. L.; Zhdandov, A. A.; Adrianov, K. A. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 2444. *Polym. Sci. USSR (Engl. Transl.)* **1969**, *11*, 2778. Godovskii, Y. K.; Dubovik, I. I.; Papkov, V. S.; Valetskii, P. M.; Dolgoplosk, S. B.; Slonimskii, G. L.; Vinogradova, S. V.; Korshak, V. V. *Dokl. Akad. Nauk SSSR* **1977**, *232*, 105.
(13) Cowie, J. M. G. *Eur. Polym. J.* **1975**, *11*, 297.
(14) Wall, L. A.; Roestamsjah; Aldridge, M. H. *J. Res. Natl. Bur. Stand., Sect. A* **1974**, *78*, 447.
(15) Rietach, F.; Daveloose, D.; Froehlich, D. *Polymer* **1976**, *17*, 859.
(16) Toporowski, P. M.; Roovers, J. E. L. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2233.
(17) Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Phys. Chem.* **1965**, *69*, 2657.
(18) Bair, H. E. *Polym. Eng. Sci.* **1970**, *10*, 247.
(19) Morèse-Séguéla, B.; St. Jacques, M.; Renaud, J. M.; Prud'homme, J. *Macromolecules* **1980**, *13*, 100.
(20) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 1618.
(21) Cowie, J. M. G.; McEwen, I. J. *Polymer* **1973**, *14*, 423.
(22) Adachi, H.; Adachi, K.; Ishida, Y.; Kotaka, T. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 851.
(23) Krause, S.; Dunn, D. J.; Seyed-Mozzaffari, A.; Biswas, A. M. *Macromolecules* **1977**, *10*, 786.
(24) Cowie, J. M. G.; Lath, D.; McEwen, I. J. *Macromolecules* **1979**, *12*, 52.
(25) Kraus, G.; Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1133.
(26) Robinson, R. A.; White, E. F. T. In "Block Polymers"; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 123.
(27) Paterno, J. J. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y., 1970.
(28) Kraus, G.; Childers, C. W.; Gruver, J. T. *J. Appl. Polym. Sci.* **1967**, *11*, 1581.
(29) Childers, C. W.; Kraus, G. *Rubber Chem. Technol.* **1967**, *40*, 1183.
(30) O'Malley, J. J.; Crystal, R. C.; Erhardt, P. F. In "Block Polymers"; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 163.