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Study of Microphase Separation in Block Copolymers of Styrene and α-Methylstyrene in the Glass Transition Region Using Quantitative Thermal Analysis

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ABSTRACT: Heat capacities of poly(α-methylstyrene) and three microphase-separated, high molecular weight block copolymers of α-methylstyrene (MS) and styrene (S) of the type MS–S and MS–S–MS have been measured. Also measured were heat capacities of polystyrene spheres of 85–868-nm diameter (temperature range 310–490 K). The data are compared to newly established heat capacities of polystyrene and poly(α-methylstyrene) from our data bank. The block copolymers have two glass transitions. The MS-block glass transition has its beginning up to 43 K lower than the homopolymer, while the S-block glass transition has its end up to 31 K higher than the homopolymer, but there is little change in the glass transition temperature proper. Polystyrene spheres show also a lowering of the beginning of the glass transition. All effects are related to the specific surface area of the microphases. Hysteresis in heat capacity at the glass transition is diminished in these block copolymers.

Introduction

Heat capacity is the key thermodynamic property of any material. Its theory is reasonably well understood and can be used in conjunction with experimental data to deduce information on molecular motion and interaction in polymers.[1] In the last 5 years a heat capacity data bank has been established by us which contains in more than 500 tables information on all published heat capacity measurements on over 100 linear macromolecules.[2] The data bank is part of the Advanced Thermal Analysis Laboratory (ATHAS). Literature and newly measured heat capacity data are being analyzed in terms of chemical structure of the polymer repeating units toward perfection of an addition scheme.[3] In particular, the additivity rules for homopolymers and copolymers in the solid and molten states, in the glass transition region, and in different chain macroconformations are investigated. In this paper we present heat capacity measurements in the glass transition region of block copolymers of α-methylstyrene (MS) and styrene (S) and the corresponding homopolymers and an analysis of additivity of block copolymer heat capacities.

The glass transition temperature can be used to characterize amorphous macromolecules. It is taken best as the temperature of half-freezing at a given cooling rate (the temperature where 50% of the change in heat capacity has occurred). The glass transition temperature can also be taken as the temperature where the linearly extrapolated enthalpies of the glass and melt intersect.[4] Note that this point of intersection of the enthalpies can be measured on cooling *or* heating but refers in both cases to the glass transition temperature which corresponds to the cooling rate of the sample. In the case of measuring the glass transition temperature by finding the temperature of half-unfreezing, reasonable results were obtained only if the sample was cooled before at a rate similar to the heating rate. When largely different heating and cooling rates are used, hysteresis effects with endothermic or exothermic peaks are observed.[5] For quantitative characterization, the heat capacity change at the glass transition temperature, ΔC_p, is needed.[6] In the present study it will be shown that the temperature of the beginning and the end of the glass transition may also be of importance for characterization.

Block copolymers have been synthesized with known sequence length and composition, and thermal analysis and electron microscopy have been used to establish the solid-state structure for several block copolymers.[7-10] Diblock and triblock copolymers show microphase separation when the different blocks are incompatible. A particular aspect of study has been the nature of the domain boundaries between the microphases. Several descriptions of phase separation in block copolymers have been given. Particularly controversial has been the assumption of pure A, pure B, and mixed interdomain regions.[11-20] Our present study reveals that for S–MS block copolymers of sufficiently high block molecular weight it is not necessary to assume a separate interdomain region to explain the thermal analysis results.

Thermal analyses have been used frequently to study the microphase separation in block copolymers [differential scanning calorimetry (DSC)[20-23] and dynamic mechanical analysis[24,25]]. Most studies were restricted to locating glass transitions; only in a few investigations has the quantitative increase in heat capacity at the glass transition, ΔC_p, been measured.[14,21,26] No heat capacity measurements on block copolymers over wider temperature ranges have been reported before in the literature. In this paper the heat capacities of the phase-separated block copolymers are calculated from the homopolymers by assuming additivity of the heat capacity of the blocks. These heat capacities are compared with the measured heat capacities and analyzed in terms of the microphase dimensions of the blocks. To further analyze the effect of microphase surfaces, we have measured heat capacities on polystyrene spheres of varying sizes. It will be shown that microphase separation can have a pronounced effect on the unfreezing of a glass such that the "normal" base-line method for ΔC_p determination may give largely erroneous values.[26]

Qualitative thermal analysis data have been reported earlier on styrene and α-methylstyrene block copolymers. Robeson et al.[25] have reported mechanical loss and shear modulus–temperature data on diblock copolymers containing 50% of each constituent (M_w = 80 000–420 000). These block copolymers are lower in molecular weight than the ones used in this research and showed one-phase behavior (one T_g). The observed glass transitions in the range 403–407 K are intermediate between the glass transition temperatures of polystyrene (373 K) and poly(α-methylstyrene) (441 K). This is in agreement with the observation of Baer,[27] who reported that triblock copolymers of polystyrene and poly(α-methylstyrene) exhibited one-phase behavior even at molecular weights above 10^5. Dunn and

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Table I
Sample Characterization

sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	% MS (w/w)	mole fraction of MS
polystyrene	498 000		0	0
triblock MS-S-MS(25)	970 000	1.3	25	0.23
triblock MS-S-MS(45)	400 000	1.4	45	0.42
diblock S-MS(58)	1 060 000	1.14	58	0.55
poly(α-methylstyrene)	670 000	1.13	100	1.00

Krause[28] have reported that block copolymers of styrene and α-methylstyrene are homogeneous up to considerably higher molecular weights than the blends of the corresponding homopolymers. Krause et al.[22,29] have analyzed by electron microscopy[29] and thermal analysis[22] a series of phase-separated diblock and triblock copolymers of styrene and α-methylstyrene of rather high molecular weight (M_w = 400 000–1 700 000). These studies included the block copolymers used in our research. Microphase separation was inferred from the appearance of the glass transitions of polystyrene and poly(α-methylstyrene) from a two-phase structure visible by transmission electron microscopy. For most samples two glass transitions were observed. This included sample S–MS(58) of this study. For a number of other block copolymers with less than 30% of α-methylstyrene comonomer units, including MS–S–MS(25) of this study, only one glass transition in the neighborhood of the polystyrene glass transition was observed. It was noted that the glass transition of the poly(α-methylstyrene) phase seemed harder to observe by thermal analysis than the glass transition of the polystyrene phase. Thus, it was concluded that the absence of the poly(α-methylstyrene) T_g was normal even in high molecular weight samples containing less that 50% of α-methylstyrene. In this study we will show that the difficulty in observing the poly(α-methylstyrene) T_g can be associated with the lowering of the temperature of the beginning of the glass transition but not the absence of or reduction in the glass transition. For two triblock samples, including sample MS–S–MS(45) of this paper, a very broad transition was found, ranging from the T_g of polystyrene to that of poly(α-methylstyrene). It was concluded that these triblock copolymers, which are on the lower end of the molecular weight range for incompatibility, were homogeneous. We will show, however, that these triblock copolymers are phase separated, in agreement with electron microscopy,[29] and that the very broad glass transition is due to the end of the polystyrene glass transition extending to higher temperatures and the beginning of the poly(α-methylstyrene) glass transition extending to lower temperatures.

The present paper illustrates that by increasing the quantitative aspects of thermal analysis, the information gained can be increased substantially.

Experimental Section

The block copolymers of styrene (S) and α-methylstyrene (MS) were kindly donated to us by Professor S. Krause. Their detailed characterization, as reported in a recent publication,[22] is summarized in Table I. All polymers were prepared by anionic polymerization in tetrahydrofuran at 195 K, using 2-butyllithium and sodium naphthalene as initiators for S–MS and MS–S–MS block copolymers, respectively. The compositions of the copolymers listed in Table I are average compositions obtained by proton magnetic resonance and infrared spectroscopy. Molecular weight averages were obtained by gel permeation chromatography (GPC). Toluene was used as solvent and the GPC was calibrated with standard polystyrenes (PS). The molecular weight averages were calculated by assuming the calibrations for poly(α-methylstyrene) (PMS) and for the block copolymers were identical with the PS calibration.

Table II
Morphological Characterization of Samples

sample	morphology	phase dimensions, nm	surface area, 10^4 m^2 kg^{-1}
S-MS(58)	lamellar	light (PMS), 120 dark (PS), 60	1.56 3.17
MS-S-MS(45)	lamellar	light (PMS), 45 dark (PS), 75	4.17 3.81
MS-S-MS(25)	none obsd		
polystyrene-latex-085	spherical	85	6.66
polystyrene-latex-222	spherical	222	2.55
polystyrene-latex-868	spherical	868	0.65

Uniform latex spheres of emulsion-polymerized polystyrene of various sizes (0.085, 0.222, and 0.868 μm) were obtained from Ernest F. Fullam, Inc. These uniform latex spheres were used for calibration of electron microscopes. All the spheres were supplied suspended in water. The spheres were recovered by carefully vacuum drying at 310 K. Scanning electron micrographs (shown in Figure 13) were obtained to establish that vacuum drying did not fuse the latex spheres.

The morphological characterization of all samples is summarized in Table II. The data on block copolymers are taken from an electron microscopy study.[29] The block copolymers were prepared for transmission electron microscopy (TEM) by room-temperature evaporation of toluene from a 1% solution of the polymer. The solutions were cast onto a microscope slide, so that films of about 5 μm were formed after evaporation of the solvent. The phase dimensions of the microphases given in Table II are the widths of the lamellae. It is difficult to identify the light and the dark areas in the electron micrographs. To be consistent with the composition, the light areas in the electron micrographs (positives) had to be taken as α-methylstyrene and dark areas as styrene. The dimensions of polystyrene spheres were provided by the supplier.

A computer-interfaced differential scanning calorimeter (Perkin-Elmer DSC-2) was used for heat capacity measurements. An enclosed, air-cooled refrigeration unit (Perkin-Elmer Intracooler II) was attached to the DSC cell for controlled cooling to subambient temperatures. Continuous transformation of the output amplitudes into digital form was accomplished through an analog–digital converter. The digital output range is 0–10 000 and was made to correspond to the full-scale deflection of the DSC recorder. The data points were sampled every 1.25 s. Calculation of heat capacities from reference measurements (on Al_2O_3), base-line measurements, and sample measurements was done by a Hewlett-Packard 9821A calculator. The details of the equipment, calibration, and programming have been reported earlier.[30] The accuracy of the heat capacity measurements is estimated to be better than 1%.

Nonhermetically sealed aluminum pans were used for DSC measurements to accommodate larger amounts of sample (20–25 mg). For heat capacity measurements, the samples were introduced into the DSC at 310 K and quickly heated above the glass transitions (to 470 K). This was followed by cooling to 300 K at 20 K min^{-1} and measurement from 300 to 490 K, using a heating rate of 20 K min^{-1} and range sensitivity of 8–20 mJ s^{-1}. It is assumed that no significant morphological changes in our block copolymer samples have occurred due to the thermal pretreatment so that we may correlate the thermal analysis results with the electron microscopic observations. This assumption appears reasonable since the phase structure is largely set by the chemical structure of the molecules (composition and block lengths) and not by the thermal history. All our samples had sufficiently high molecular weight poly(α-methylstyrene) sequences that is not

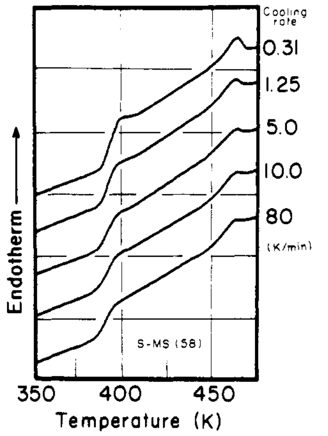

Figure 1. Glass transition endothermic hysteresis peaks on differential scanning calorimetry in S-MS(58) diblock copolymer. Heating rate 40 K/min, cooled at the indicated cooling rates.

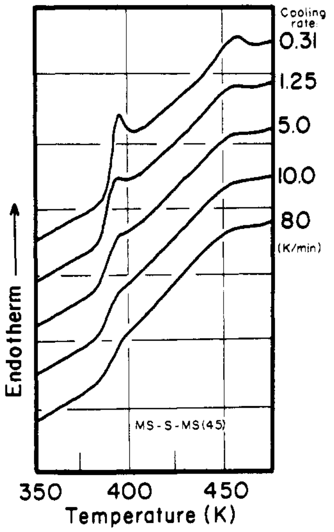

Figure 2. Glass transition endothermic hysteresis peaks on differential scanning calorimetry in MS-S-MS(45) triblock copolymer. Heating rate 40 K/min, cooled at the indicated cooling rates.

expected that in the complete thermal cycling compatibility was ever achieved.

The special cooling and heating conditions for hysteresis studies are given in the text and figures.

Results

In preliminary analyses we tried to enhance the glass transition by inducing hysteresis effects.[5] The samples were cooled in the DSC cell at various cooling rates (0.31–80 K min^{-1}) through the glass transition region, followed by heating at 40 K min^{-1}. Heating a sample at a rate faster than the cooling rate causes the appearance of an endothermic glass transition peak. The hysteresis curves for the three analyzed block copolymers are shown in Figures 1–3. The hysteresis at the polystyrene glass transition is more apparent than at the poly(α-methylstyrene) glass transition. As the cooling rate is decreased, the hysteresis peak for poly(α-methylstyrene) is more easily recognizable. This establishes that all the block copolymer samples used in this study have two glass transitions, contrary to the earlier thermal analysis observation on the same samples.[22] Qualitative thermal analysis, making use of the hysteresis phenomena, allowed thus the confirmation of microphase separation, proven already by electron microscopy.[29] It furthermore indicated that it may be more difficult than expected to establish glass transitions in multicomponent multiphase polymers. Inducing a hysteresis effect was also found to be helpful in establishing glass transitions of some polystyrene and poly(oxy-2,6-dimethyl-3-bromophenylene) blends.[31] Studies on blends of polystyrene and poly(α-methylstyrene), which may also phase separate, are in progress to establish the effects of inducing hysteresis.

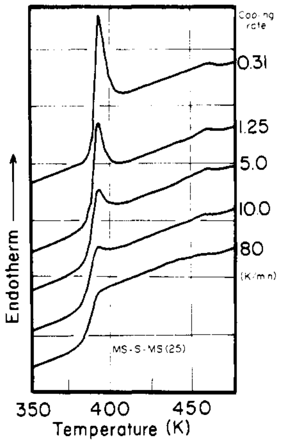

Figure 3. Glass transition endothermic hysteresis peaks on differential scanning calorimetry in MS-S-MS(25) triblock copolymer. Heating rate 40 K/min, cooled at the indicated cooling rates.

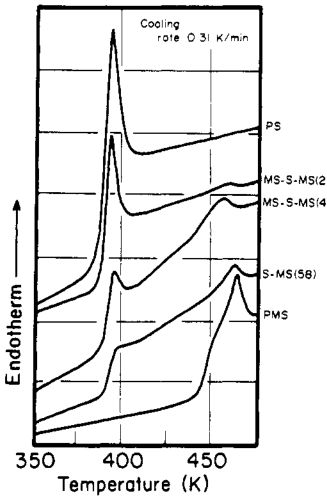

Figure 4. Comparison of the glass transition endothermic hysteresis peaks in block copolymers with PS and PMS homopolymers. All samples were cooled at 0.31 K/min and heated at 40 K/min.

The hysteresis curves of the three block copolymers cooled at 0.31 K min^{-1} are compared in Figure 4 with the hysteresis curves of the constituent homopolymers having the same thermal history. The areas under the endothermic peaks of the block copolymers are in general smaller than expected for the mole fraction of the homopolymers. This loss of hysteresis peak area is more apparent for the poly(α-methylstyrene) blocks than for the polystyrene blocks. Also, the poly(α-methylstyrene) block hysteresis peak appears broader and extends to lower temperature. Similar loss of hysteresis has been observed for styrene–isoprene diblock copolymers.[14] This strong reduction of the hysteresis behavior has also been observed by us recently for various other multiphase polymers, including mesophase macromolecules[32] and semicrystalline homopolymers.[33]

Quantitative information on the glass transition was obtained from heat capacity data. The measured heat capacities of the three block copolymers from 310 to 490

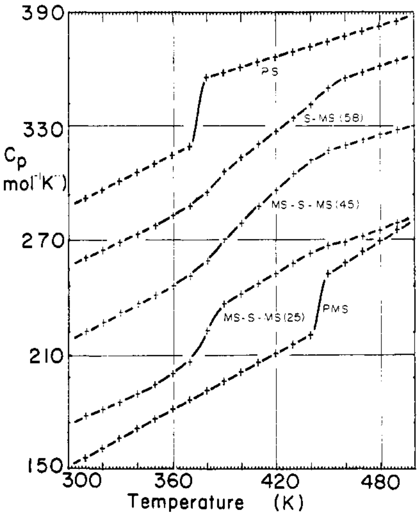

Figure 5. Heat capacities of polystyrene, poly(α-methylstyrene), and block copolymers. The heat capacity data on polystyrene are taken from ref 2. The y axis corresponds to data on poly(α-methylstyrene) only. Subsequent curves have been shifted successively by 40 J mol^{-1} K^{-1} each.

K are given in Figure 5. These are average data for each sample on three different measurements which agree with each other within ±1%. The heat capacities of the block copolymers can be compared with the heat capacities of both homopolymers (also shown in Figure 5). The data on polystyrene are taken from the heat capacity data bank and represent critically analyzed results on 29 samples.[2] Since no data were available for poly(α-methylstyrene) in the temperature region of interest, heat capacity measurements were also made for poly(α-methylstyrene) from 310 to 490 K. Three sets of measurements were made on the poly(α-methylstyrene) sample described in Table I. The data could be represented by the following equations:

$$C_p(\text{glassy}) = 29.42 + 0.4498T - 1.2798 \times 10^6 T^{-2}\ \text{J mol}^{-1}\ \text{K}^{-1}\ (300\text{–}441\ \text{K})$$

$$C_p(\text{melt}) = 0.5758T - 6.43\ \text{J mol}^{-1}\ \text{K}^{-1}\ (441\text{–}490\ \text{K})$$

The root-mean-square deviation was 0.3 and 0.6% for the heat capacity of glassy and molten poly(α-methylstyrene), respectively. The heat capacity at 300 K agrees within 0.6% with the data of Rabinovich and Lebedev,[34,35] who reported heat capacity data from 60 to 300 K only. All newly measured heat capacities and, for comparison, the data bank heat capacities of polystyrene are listed in Table III.

The difference in heat capacity between glassy and molten poly(α-methylstyrene) at the glass transition is 26.3 J mol^{-1} K^{-1}. This corresponds to 13.2 J (mol bead)$^{-1}$ K^{-1}, where one mole refers to a bead defined as the smallest section of the molecule that can move independently as a unit in internal chain rotation. This is somewhat higher than our rule of constant heat capacity change at the glass transition would predict [ΔC_p = 11.3 J (mol bead)$^{-1}$ K^{-1}].[6] However, it compares favorably with polystyrene, which has a ΔC_p at T_g of 30.7 J mol^{-1} K^{-1}. Similar deviations of molecules with phenyl-group beads have been observed for aromatic polyoxides[2,36,38] and ladder-type polymers.[37]

To further analyze the heat capacity on block copolymers we checked to see if the measured heat capacities can be related to the block compositions. This was done by plotting the heat capacity of block copolymers and homopolymers as a function of composition. The data at 330 K, for the glassy state of both blocks, and at 470 K, for the molten state of both blocks, are shown in Figure 6. In both cases the heat capacity was found to vary linearly with the composition. The data were additive within ±1.7%. Note that there seems to be a systematic error of slightly larger magnitude for sample S-MS(58), which will also show up in all subsequent analyses.

Table III
Heat Capacities (J mol^{-1} K^{-1}) of Styrene–α-Methylstyrene Block Copolymers, Polystyrene, and Poly(α-methylstyrene)[a]

T, K	PMS	MS–S–MS(25)	MS–S–MS(45)	S–MS(58)	PS
310	155.5	137.9	142.2	141.1	132.2
320	160.8	141.4	147.2	145.1	137.0
330	166.1	145.2	152.4	149.1	141.9
340	171.3	149.7	157.0	153.4	146.8
350	176.4	154.6	161.5	158.0	151.8
360	181.5	160.4	166.3	163.3	156.8
370	186.5	166.6	171.6	168.4	161.8
380	191.5	183.1	179.5	175.7	195.9
390	196.4	197.2	190.8	186.8	198.6
400	201.3	202.2	199.0	194.3	201.2
410	206.2	207.6	208.0	201.2	203.9
420	211.1	212.9	216.6	207.9	206.5
430	215.9	218.3	225.3	214.9	209.2
440	220.7	223.4	232.7	221.9	211.9
450	252.7	227.5	237.6	230.5	214.5
460	258.4	229.1	240.3	235.7	217.2
470	264.2	232.2	243.2	238.7	219.8
480	269.9	235.6	246.0	242.0	222.5
490	275.7	239.3	248.4	244.8	225.1

[a] Molecular weights of the repeat unit for the block copolymers were calculated by adding the appropriate mole fraction of the blocks.

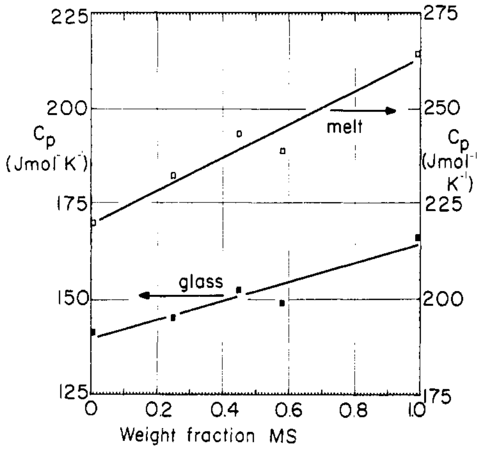

Figure 6. Additivity of the heat capacity of α-methylstyrene and styrene blocks in the glassy phase (330 K, below T_g of the soft segments) and the molten phase (470 K, above T_g of the hard segments).

The heat capacities were, however, not additive in the temperature range between the two glass transitions. Measured heat capacities of the block copolymers are compared with the heat capacity obtained by adding the appropriate contributions from glassy or molten polystyrene and poly(α-methylstyrene) in Figures 7–9. One can see that in each case the glass transitions are broadened but not changed in expected magnitude. One can further see that only the upper part of the polystyrene glass transition is broadened (to higher temperatures) and only the lower part of the poly(α-methylstyrene) glass transition is broadened (to lower temperatures). Since just above the glass transition temperature of polystyrene the heat capacity of the block copolymers is higher than the calculated heat capacity, assuming both blocks to be glassy, it can be concluded that the glass transition temperature has not

Table IV
Apparent Heat Capacity Change at the Glass Transition

sample		T_g,[a] K	$\Delta C_p(T_g)$, J mol^{-1} K^{-1}	$\Delta C_p/\Delta C_p$(homopolymer)[b]	ΔT_g,[c] K
S-MS(58)	PS	375	13.9	0.45	27
	PMS	443	15.0	0.57	26
MS-S-MS(45)	PS	374	5.6	0.18	31
	PMS	441	1.3	0.05	37
MS-S-MS(25)	PS	374	28.8	0.94	19
	PMS	445	0.5	0.02	43
PS-latex-085	1st heat	371	21.9	0.71	43
	2nd heat	371	31.1	1.01	
	3rd heat		30.6	1.00	
PS-latex-222	1st heat	372	29.5	0.96	33
	2nd heat	373	32.4	1.06	
PS-latex-868	1st heat	371	31.4	1.02	
	2nd heat	372	31.6	1.03	

[a] The temperature of half-freezing (half-unfreezing) determined by extrapolation of enthalpy above and below the glass transition (error ±2 K). [b] This ratio contains ΔC_p as it is derived by extrapolating heat capacities above and below T_g, without regard to the actual glassy and melt heat capacities, divided by the ΔC_p expected from composition and homopolymer ΔC_p's. [c] ΔT_g is the difference in temperature of the beginning or end of the glass transition from T_g.

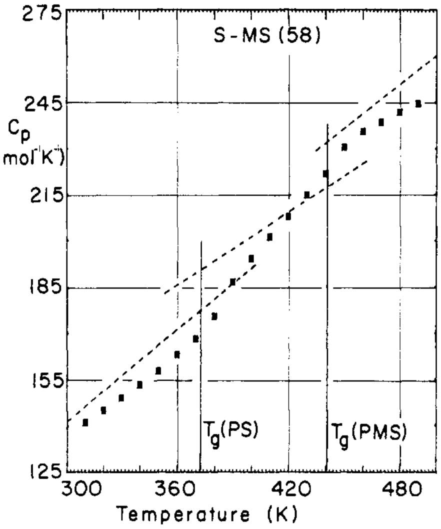

Figure 7. Heat capacity of S-MS(58) diblock copolymer. The dashed lines represent the expected heat capacity from additivity.

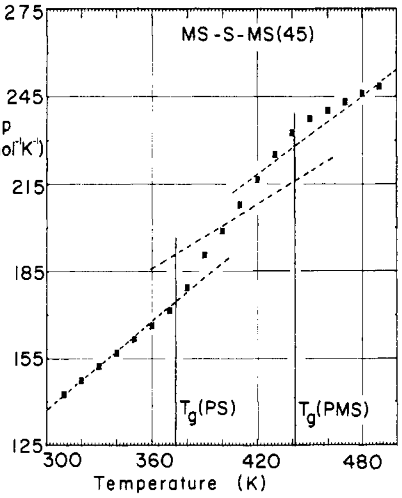

Figure 8. Heat capacity of MS-S-MS(45) triblock copolymer. The dashed lines represent the expected heat capacity from additivity.

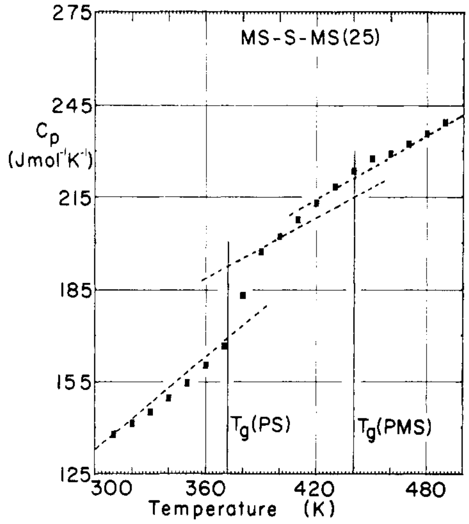

Figure 9. Heat capacity of MS-S-MS(25) triblock copolymer. The dashed lines represent the expected heat capacity from additivity.

been shifted to higher temperature to any significant extent. [For S-MS(58) the systematic error in the experimental heat capacity data is to be taken into account to observe the increase in C_p.] The upper end of the glass transition is, however, strongly shifted. This broadening of the upper end of the polystyrene glass transition region to higher temperature extends from 19 K in MS-S-MS(25) to 31 K in MS-S-MS(45). Similarly, for poly(α-methylstyrene) the beginning of the glass transition is shifted to lower temperature. The observed shifts range from 26 K in S-MS(58) to 43 K in MS-S-MS(25). These shifts in the glass transition limits for the three block copolymers are listed in Table IV (ΔT_g). Probable error limits in calculating the glass transition shifts are about ±5 K.

The changes in the glass transition were also judged by comparing the apparent ΔC_p of the block copolymers at the homopolymer glass transition temperatures, as obtained by extrapolation of the measured heat capacities from above and below the T_g with the concentration-corrected ΔC_p (at T_g) of the homopolymers. These data are also listed in Table IV. For a block copolymer without any changes in the glass transition this ratio would be expected to be 1.0 at both the homopolymer T_g's. For a block copolymer with changed heat capacity-temperature slopes between the glass transitions the ratio should decrease.

The glass transition temperatures determined by extrapolation of enthalpies above and below T_g are also listed in Table IV (cooling rates 20 K min^{-1}). The glass transition temperatures of polystyrene and poly(α-methylstyrene) blocks are in agreement with the usually reported homo-

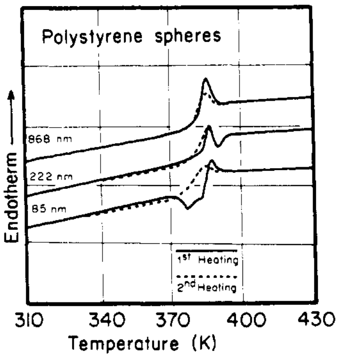

Figure 10. DSC curves of polystyrene beads of various sizes. The solid lines are for the first heating and the dashed lines represent the second heating of the sample after cooling at 20 K/min. Heating rate 20 K/min.

polymer glass transition temperatures.

A final set of measurements involved heat capacity measurements on small polystyrene spheres. Figure 10 shows the DSC curves of polystyrene spheres of various sizes (diameters of 85, 222, and 868 nm). Heat capacity measurements were made on first heating from 300 to 490 K, and then, after cooling the sample at 20 K min^{-1}, the heat capacity was remeasured over the same temperature range. On first heating, exotherms were observed which are most likely related to stress release. In the case of the smallest spheres (85 mm) the exotherm is just below the glass transition temperature and in the case of 222-nm spheres, the exotherm is just above the glass transition temperature. For the largest spheres (868 nm) only a very slight exotherm above the glass transition was observed. Since all the spheres have the same thermal history, this seems to indicate that the amount of exothermic stress release is largest in the smallest spheres and occurs at lower temperature. Also, on comparing the first and second heating DSC curves, it is clear that for the smallest spheres the onset of the glass transition is considerably lowered. The shift in the beginning of the glass transition becomes less as the size of the spheres increases. Shifting of the beginning of the glass transition to a lower temperature lowers the apparent heat capacity change at the normal glass transition of polystyrene (373 K), as shown in Table IV. On second heating, all the spheres showed normal heat capacities (agreement with the data bank values of Table III: ±1%). On subsequent third and fourth heatings no further changes in heat capacities were observed. The glass transition temperatures taken from enthalpy extrapolations are listed also in Table IV. These are in good agreement with normal polystyrene T_g.

Discussion

The heat capacities of Figure 5 and Table III show the expected additivity outside of the glass transition region (Figure 6). Similar additivity was illustrated earlier for random copolymers. Both the solid and the liquid phases show additivity within experimental error. As a consequence, the overall increase in heat capacity at the glass transition, ΔC_p, is also additive. Thus ΔC_p's at polystyrene and poly(α-methylstyrene) glass transitions should correspond to the mole fractions of both the blocks. The reported difficulties in detecting the glass transition of the MS block is thus not to be ascribed to a diminished heat capacity effect.

The study of the hysteresis endotherms on fast heating after slow cooling in Figures 1–4 leads to the surprising fact that the hysteresis is reduced in block copolymers. Despite this reduction, hysteresis enhances the recognition of the glass transitions of the two block components. The hysteresis peaks of the blocks occur close to the temperatures of the homopolymer hysteresis peaks. The reasons for the decrease in peak area and height are unclear at present. Even larger reductions in hysteresis peaks have been observed for mesophase glasses and semicrystalline homopolymers, suggesting that these are perhaps a general phenomenon of multiphase structures. A more detailed study of this phenomenon is presently under way.

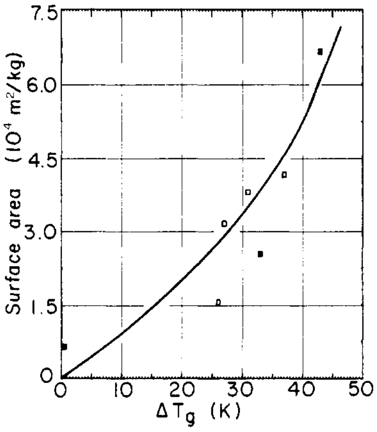

Figure 11. Microphase surface areas vs. change of the temperature of the beginning or end of the glass transition. Open squares represent lamellar microphases in block copolymers and filled squares represent polystyrene spheres.

The quantitative study of the glass transition regions of the block copolymers as given in Figures 7–9 and in Table IV reveals a considerable amount of detail. First, the glass transition (as measured by enthalpy extrapolation), which corresponds in homopolymers closely to the temperature of half-freezing, is unchanged within ±2 K. This must be interpreted that there is no significant solubility of the blocks in each other in the samples investigated. Dissolution of significant amounts (few percent) of one block into the other would lead to changes in the glass transition temperature. Clear evidence is shown, however, that the end of the glass transition region of the S blocks and the beginning of the glass transition temperature of the MS blocks, as measured by ΔT_g (see Table IV), is moved to higher and lower temperatures, respectively. In the homopolymers PS and PMS, ΔT_g, the separation of the beginning or end of the glass transition temperature from the temperature of half-freezing, T_g, is typically 4 and 5 K for the beginning and 8 and 9 K for the end (at the chosen heating and cooling rate of 20 K/min). The data on small spheres of PS in Figure 10 and Table IV, which show a decrease in the beginning of the glass transition of magnitude similar to that of the MS blocks, indicate that these shifts are phase-size dependent. Electron microscopy shown in Figure 13 proved that the dried spheres had not fused in the preparation (see also ref 39). The decrease in the temperature of the beginning of the glass transition is thus clearly linked with the large surface area, which is in the PS case a glass–air interface and in the MS-block case a glass–melt interface. It is a reasonable extension of this result to suggest that the increase in the temperature of the end of the glass transition of the S blocks is caused by the rigid nature of the glass–glass interface. There is no need to involve the presence of an interfacial, mixed phase to account for the broadening of the glass transition. Thermodynamic considerations also indicate that interfaces between microphases should be sharp.[20] Figure 11 shows a plot of the interfacial area calculated from the morphology of the microphases given in Table II vs. all observed ΔT_g's, irrespective of interface nature. All points fit approximately on one curve.

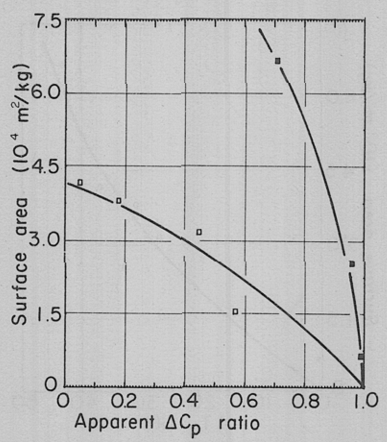

Figure 12. Surface area vs. the fraction of the apparent heat capacity change observed at the glass transition on extrapolation of measured heat capacities. Open squares represent lamellar microphases in block copolymers and filled squares represent polystyrene spheres.

There is, however, no apparent reason that the data from PS spheres involving the glass–air interface and the block copolymers involving glass–glass and glass–melt interfaces should fall on the same curve. Taking this curve as a measure of microphase effect, one can conclude that down to 10^4 m^2 kg^{-1} surface area, which corresponds to about a 0.5-μm microphase dimension, changes in the width of the glass transition region are noticeable. Since this broadening of the glass transition region is a measure of interaction between the different microphases, one can use the glass transition as a measure to distinguish between microphase and macroscopic phase separation. In macroscopic phase separation one expects only negligible changes of the thermodynamic parameters due to the presence of an interface. This limit seems to be reached with micrometer phase dimensions.

After clarification of the quantitative aspects of the glass transition region of the block copolymers, it remains to point out that thermal analysis using only base-line analysis must lead to erroneous results. The shallower increase in heat capacity above T_g of the S blocks and the steeper increase in heat capacity below T_g of the MS blocks tend to merge the two transitions. Trying to find temperatures of half-unfreezing is unreliable. In Figure 12 and Table IV we have listed the apparent increase in heat capacity at the respective glass transition temperatures which one would obtain using the base-line extrapolation method. The apparent increases in heat capacity at the glass transition temperature are very much reduced with increasing surface area of the microphases and reach practically zero for the MS blocks in MS–S–MS(45) and MS–S–MS(25) and for the S blocks in MS–S–MS(45). As both blocks reach close to zero apparent ΔC_p, the glass transition may easily be misinterpreted as a broad, single transition at some intermediate temperature, indicative of a homogenous phase structure. Electron microscopy and quantitative thermal analysis have shown this not to be the case for MS–S–MS(45). For a truly homogeneous phase structure the glass transition region must be narrow, comparable to that of homopolymers.

Through this first detailed analysis of the glass transition region of a block copolymer we hope to have shown that quantitative thermal analysis involving measurement of C_p(glass), C_p(liquid), T_g, ΔC_p, and the beginning and end of the glass transition is a tool which can give valuable information on microphase separation of block copolymers. The method is presently applied in our laboratory to polymer blends and other multiple-phase structures. It became also clear that the less accurate base-line method not only yields less information but also is subject to wrong interpretation.

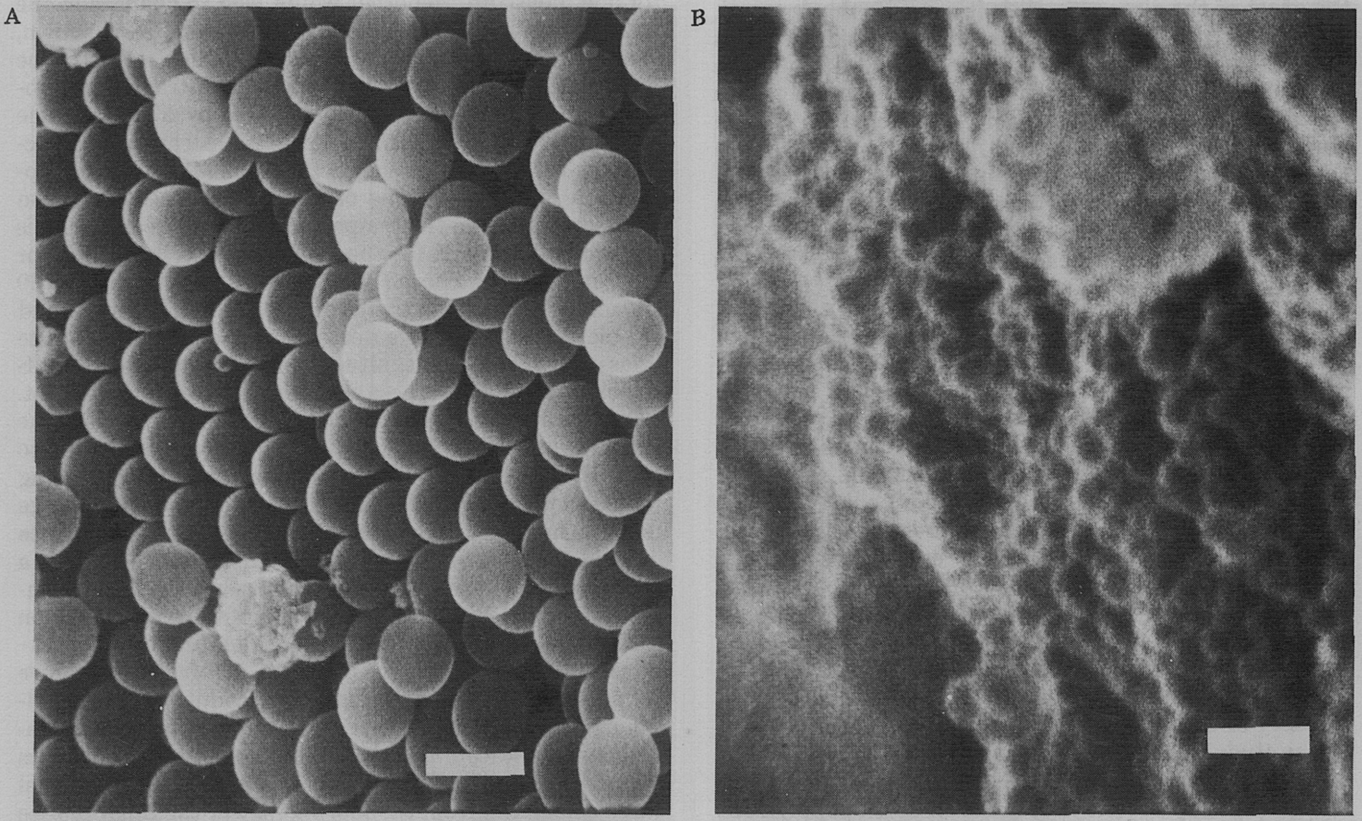

Figure 13. Scanning electron micrographs of dried polystyrene latex spheres (A, diameter 868 nm; B, diameter 85 nm) prepared by vacuum drying a dispersion of polystyrene latex spheres in water. Scale bar: (A) 1 μm; (B) 0.2 μm.

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Electron Spin Resonance Study of Chain Motion of Spin-Labeled Poly(ethylene oxide) in Dilute Solution

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ABSTRACT: The rotational correlation times τ_c of end-labeled poly(ethylene oxide) ($M_w = 9000$) were measured in a variety of solvents as a function of temperature. An expression of the correlation time has been found to be the same as that predicted by Kramers' theory in its dependence on solvent viscosity and temperature. The energy barrier for the rotation was found to be 1.45 kcal/mol. Assuming the transition to be that of the crankshaft and employing Kramers' expression, it appears that about one monomer unit may be considered as involved in the ESR relaxation process.

Introduction

The dynamic properties of macromolecules in dilute solutions constitute a problem of considerable interest. In recent years, many investigations have been carried out by techniques well adapted to the study of fast movements, e.g., dielectric relaxation,[1-3] fluorescence polarization,[4] ^{13}C and ^{1}H nuclear magnetic relaxation,[5-13] and line-shape analysis of the paramagnetic resonance of spin labels,[5,14-17] to find a description of the molecular motions under a variety of conditions.

In our previous paper[5] special attention has been paid to the information which can be derived from differences between the rotational correlation times τ_c determined for poly(ethylene oxide) (PEO) from ^{13}C NMR, ^{1}H NMR, and ESR measurements and from the dependence of these correlation times on the viscosity and nature of the solvent. The isotropic rotational model was found to be a satisfactory approximation for describing both ESR and ^{1}H and ^{13}C NMR relaxation measurements of PEO in dilute solution. When aromatic solvents or CCl_4, CH_2I_2, CH_2Br_2, $(CH_2Cl)_2$, and $(CH_2Br)_2$ were used in preparing PEO solutions, the viscosity dependence of the resulting PEO τ_c values was significantly different from that observed in CH_2Cl_2, $CHCl_3$, $CHBr_3$, $(CHCl_2)_2$ and $(CHBr_2)_2$ solutions. The τ_c values obtained in the first family of solvents were found the least viscosity sensitive.

In the present investigation, line-shape analysis of the paramagnetic resonance of spin-labeled PEO is carried out

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