Study of Phase Separation in Blends of Polystyrene and Poly(α-methylstyrene) in the Glass Transition Region Using Quantitative Thermal Analysis

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ABSTRACT: Differential scanning calorimetry of 11 solution blends of polystyrenes of molecular masses from 3×10^3 to 1×10^7 daltons with poly(α-methylstyrenes) of molecular masses from 1.9×10^4 to 5.1×10^5 daltons was carried out between 300 and 500 K. The various blends covered the ranges from miscibility to immiscibility. The glass transition temperatures, their ranges, and the change in heat capacity with composition in the transition ranges have been measured. Long before phase separation is macroscopically noticeable, it is possible to detect phase instability from a broadened glass transition region. This broadening is discussed in terms of concentration fluctuations.

Introduction

Compatibility in linear, flexible macromolecules is more difficult to study than in small molecules. Phase separation, as well as dissolution, may be quite slow and the thermodynamic driving force may be quite small.[1] In this paper we describe the analysis of blends of the system polystyrene–poly(α-methylstyrene) as a function of molecular mass of the two components. The molecular masses were chosen to cover the range from compatibility to incompatibility.

The main analysis tool was differential scanning calorimetry (DSC). The calorimeter can not only discover the glass transition but detect the beginning of phase separation long before it is macroscopically evident through turbidity, for example. In a study of block copolymers of the same two components, we could show earlier[2] the ability of DSC to detect microphase separation through asymmetric broadening of the glass transition. In this paper we will show that beginning phase separation is indicated by a symmetric broadening of the glass transition, which may be due to concentration fluctuations. In fact, we find that solutions of two macromolecules may frequently show a certain degree of glass transition broadening because of the inherent inability to mix along the chain direction.

The heat capacities of a series of these blends are reported and the glass transition temperatures are analyzed via some equations proposed in the literature. Hysteresis, which we analyzed earlier in detail for polystyrene,[3] was found to be a useful tool to pinpoint two-phase structures. In broadened glass transition regions it may be reduced, however, as was observed earlier by Fried et al.[4]

DSC is not capable of direct measurement of phase separation, but once the sample is quenched into the glassy state, the here presented analysis at the glass transition permits study of the phase structure of the sample as it existed at elevated temperature.

Experimental Section

Narrow molecular mass samples of atactic polystyrene (PS) and poly(α-methylstyrene) (PαMS) were purchased from Polysciences, Inc. The molecular masses and the characterization of the glass transition of the six homopolymers are given in Table I. The homopolymers are designated L, M, and H for each set for easy recognition of the molecular mass.

Eleven blends of the homopolymer were made by solution blending. Toluene was used as solvent for both homopolymers. The solutions were mixed to give the proper blend ratios. Films of the polymer blends were obtained by vacuum-drying at 320 K. The drying time was about 48 h. The blends were made in mass ratios 25:75, 50:50, and 75:25. In all designations of mass ratios, the polystyrene mass is listed first. Because of the similar repeating unit molecular masses (PS = 104.14 daltons and PαMS = 118.17 daltons), these mass ratios are not much different from the mole ratios, which are 27:73, 53:47, and 77:23, respectively. The 50:50 blends of H–H and H–M and sometimes also of M–H appeared optically cloudy, a sign of phase separation. The eight other blends, which all had one or both components of lower molecular mass than H–M or M–H, appeared always optically clear. The blends were chosen to cover one complete concentration range of compatibility (L–M), various combinations of concentrations and molecular masses close to the region of change to incompatibility (75:25 blends of L–H and M–L, 50:50 blends of L–H, M–M, and M–H, and 25:75 blend of H–L), and two incompatible blends (50:50 blends of H–M and H–H).

Thermal analysis was carried out on three levels. First, a series of six homopolymers and nine blends was analyzed with a DuPont 990 Thermal Analyzer and a standard 910 DSC cell. The samples were analyzed at a 20 K/min heating rate in a nitrogen atmosphere. Temperature calibration was done with five sharp melting standards, as described earlier.[5] Each recording was analyzed for the glass transition temperature(s), T_g. This temperature was taken at the point of half-unfreezing, as judged from the change in heat capacity. As long as the hysteresis peak is small (less than ΔC_p), this temperature is a close approximation to the glass transition temperature similarly measured on cooling, as well as the glass transition obtained by extrapolation of the glassy and liquid enthalpy or volume curves to the point of intersection. In addition, the beginning and end of the glass transition were taken from the DSC trace as judged from the first deviation from the glassy base line and the first attainment of the liquid base line, T_b and T_e, respectively. Furthermore, a tangent was drawn at the point of inflection of the heat capacity curve, which is close to the glass transition temperature. The intersections of this tangent with the extended glassy and liquid base lines were recorded as T_1 and T_2 and used to judge the sharpness of the transition. Table I contains all these temperatures for the homopolymers. Finally all DSC curves were normalized over the glass transition region to a standard ΔC_p to compare the detailed curve shapes.

The second level of thermal analysis was carried out on the six 50:50 blends of L–H, M–H, H–H, L–M, M–M, and H–M via a computer-interfaced Perkin-Elmer DSC-2.[6] The main goal in this series of experiments was the measurement of heat capacities in the glass transition region. The samples were heated at 10 K/min in a nitrogen atmosphere. Temperature calibration was done with sharp melting substances, as indicated above. The differential power amplitude was calibrated with sapphire (Al_2O_3) as secondary standard. The differential power amplitude was converted to digital form via a Data Precision 3600 digital voltmeter. The data were sampled every 0.2 s and stored on disk. Calculation of heat capacity from reference measurements (Al_2O_3), base-line runs, and the sample measurements was made with a Cromemco Z-2 minicomputer. Averaged data points are used for the discussion. The heat capacity program is based on our earlier heat capacity measurements and has been developed for us by

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Table I
Homopolymer Characterization

sample	M_w	M_w/M_n	T_g,[a] K	T_b,[b] K	T_e,[c] K	T_1,[d] K	T_2,[e] K	$T_2 - T_1$, K	$T_e - T_b$, K
PS-L	3.7×10^4	1.06	376	360	385	372	380	8	25
PS-M	1.0×10^5	1.06	377	363	389	374	380	6	27
PS-H	1.0×10^7	1.20	378	363	389	375	381	6	26
PαMS-L	1.9×10^4	1.20	443	425	455	440	447	7	30
PαMS-M	9.0×10^4	1.10	453	435	464	449	456	7	29
PαMS-H	5.1×10^5	1.05	453	433	460	451	456	5	27

[a] Temperature of half-unfreezing on heating at 20 K/min after cooling at the same rate from 490 K. [b] Temperature of first endothermic deviation from the base line before reaching the glass transition (beginning of glass transition interval). [c] Temperature of the final attainment of the base line after the glass transition (end of glass transition interval). [d] Temperature of the intersection of the tangent at T_g with the extrapolated base line of the glass. [e] Temperature of the intersection of the tangent at T_g with the extrapolated base line of the liquid.

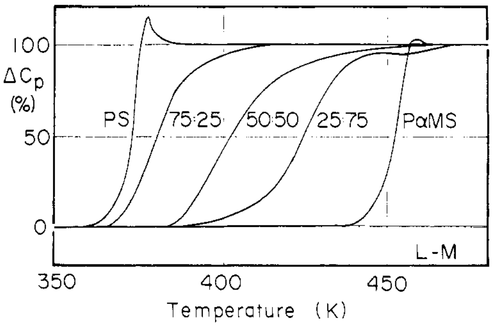

Figure 1. Change in heat capacity in the glass transition region for L–M polystyrene–poly(α-methylstyrene) blends (DuPont DSC; heating rate 20 K/min; recalculated into percentage change at the glass transition; for temperature data see Tables I and II; mass percentages as listed in the figure).

Laboratory MicroSystems, Inc.[7]

The third level of analysis involved the study of the hysteresis behavior. The samples of the first analysis series were cooled at 0.5 K/min and then reheated at 20 K/min as before. Since the glass transition on slow cooling occurs at a lower temperature than on heating, usually a strong endotherm is observed in such experiments, which can be used to identify glass transitions more clearly.[3]

In all three thermal analysis experiments the samples were cut from the dried films and placed into sealed aluminum pans. The total sample masses were 1–5 mg for the DuPont DSC (recording sensitivity 2 mJ/s) and 20–30 mg for the Perkin-Elmer DSC (recording sensitivity 20 mJ/s). The samples were heated several times to 490 or 500 K for a short period of time (3–15 min) and weighed after cooling at 20 K/min to room temperature. Constant mass and smooth preliminary DSC traces revealed complete absence of toluene. The third or fourth heating and all subsequent runs were reproducible.

Results

The characterizations of the various homopolymers are listed in Table I. The glass transition interval of the compatible blend series L–M, including the homopolymers, as obtained by the DuPont DSC is shown in Figure 1. The characteristic temperatures of all blends so analyzed are listed in Table II.

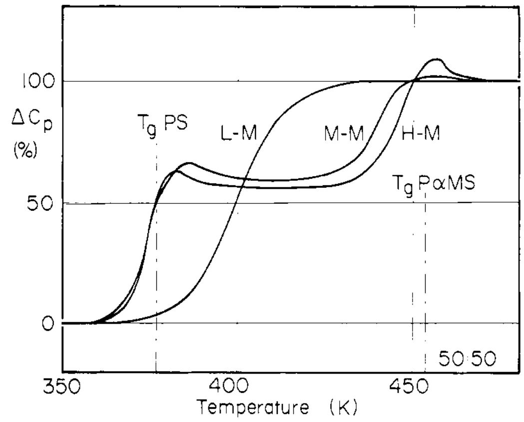

Figure 2. Change in heat capacity in the glass transition region for 50:50 mass percentage of blends of polystyrene with poly(α-methylstyrene)-M (Perkin-Elmer DSC; heating rate 10 K/min; recalculated into percentage changes at the glass transition; for ΔC_p data see Table IV; for heat capacities see Table III; molecular masses of PS as listed in the figure).

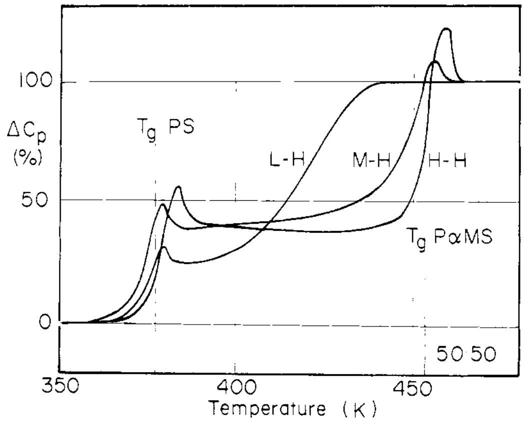

Figure 3. Change in heat capacity in the glass transition region for 50:50 mass percentage of blends of polystyrene with poly(α-methylstyrene)-H (Perkin-Elmer DSC; heating rate 10 K/min; recalculated into percentage changes at the glass transition; for ΔC_p data see Table IV; for heat capacities see Table III; molecular masses of PS as listed in the figure).

The heat capacities of the homopolymers and the 50:50 blends are listed in Table III. The data points represent averaged values for the given temperature intervals (±5 K) of two determinations. For the complete temperature range these two separate data sets have a standard deviation of ±1.2%. Below the glass transition range (365 K) the 12 data points of the different molecular mass blends agree within ±1.0%. The appropriate average of the data bank data on the homopolymers agrees with the blend data within 0.3%. Above the glass transition range (455 K) the 12 data points of the different molecular mass blends agree within ±0.6%. The appropriate average of the data bank data[8] on the homopolymers agrees with the blend data within 1.9%.

Normalized plots of heat capacity in the glass transition region for medium (M) and high (H) molecular mass of poly(α-methylstyrene) are given in Figures 2 and 3, respectively. The values of the increase in heat capacity at the glass transition temperatures, ΔC_p, are given in Table IV.

A selected number of normalized DSC traces taken under conditions that should show considerable hysteresis

Table II
Blend Characterization

sample[a]	T_g,[b] K	T_b,[b] K	T_e,[b] K	T_1,[b] K	T_2,[b] K	$T_2 - T_1$, K	$T_e - T_b$, K
L-M							
25:75	425	388	465	410	439	29	77
50:50	404	377	454	387	420	33	75
75:25	382	363	415	371	392	21	52
L-H							
75:25	375	361	379	370	379	9	18
	(415)	379	435				56
M-L							
75:25	386	365	(400)	374	(389)	15	35
	(420)	(400)	448				48
M-M							
50:50	375	367	384	372	381	9	17
	444	386	454	428	454	2	68
M-H							
50:50	374	363	383	372	379	7	20
	445	384	457	444	457	31	73
H-L							
25:75	(385)						
	419	381	447	385	446	61	66
H-H							
50:50	379	365	389	376	382	6	24
	454	447	466	450	458	8	19

[a] The designation of the sample is polystyrene to poly(α-methylstyrene); the molecular masses L, M, and H are given in Table I; the blend ratios are given as mass ratios. [b] For description of the various temperatures see the corresponding footnotes in Table I.

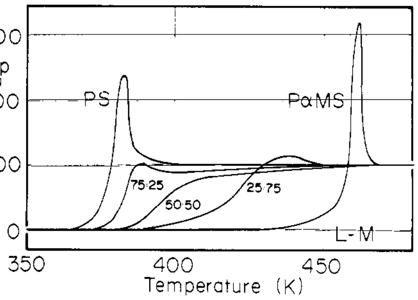

Figure 4. Hysteresis in the glass transition region for L-M polystyrene-poly(α-methylstyrene) blends and the corresponding homopolymers (DuPont DSC; recalculated into percentage change at the glass transition; cooling rate 0.5 K/min; heating rate 20 K/min; compare with Figure 1).

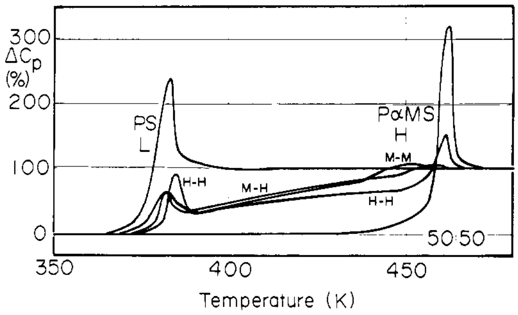

Figure 5. Hysteresis in the glass transition for various 50:50 blends of polystyrene-poly(α-methylstyrene) blends and the homopolymers PS-L and PαMS-H (DuPont DSC; recalculated into percentage change at the glass transition; cooling rate 0.5 K/min; heating rate 20 K/min; compare with Figures 2 and 3).

due to 40 times faster heating than cooling are shown in Figures 4 and 5.

Discussion

The glass transition data in the investigation cover a wide range of homopolymers and blends. For the homopolymers one notices from Table I that both polymers have a narrow glass transition range of about 7 K when expressed by $T_2 - T_1$, and about 30 K when expressed by $T_e - T_b$. The beginning and end of the transition (T_b and T_e) are not far from equal distances from T_g. The heat capacity change extrapolated to T_g, listed in Table IV, corresponds to the simple, empirical rule of 11.3 J K^{-1} mol^{-1} of beads when one takes into consideration a correction for large side or main-chain groups as discussed earlier.[9]

Turning to the series of compatible blends L-M, one notices from Figure 1 and Table II that despite solubility, the glass transition range has doubled to tripled. This broadening of the glass transition is still close to symmetric to T_g, and the corresponding values for T_b and T_e recede only little from the values for the homopolymers. We suggest that this broadening results from concentration inhomogeneities on the scale of the number of mobile units involved in the motion at the glass transition, i.e., perhaps 3-10. A comparison of the breadth of low molecular weight solution glasses with the here presented polymers shows no such broadening.[10] Similarly, random copolymers usually display sharp glass transitions.[11] On the other hand, the observation of somewhat broadened glass transitions in blends seems widespread.[12] It is reasonable to assume that the connectedness in one dimension along the chain provides the main reason for an inhomogeneity in concentration sufficient to cause a glass transition broadening. The type of broadening is different from the broadening observed in block copolymers where an asymmetric broadening was caused by microphase separation.[2] Similarly, the broadening of the less compatible high molecular weight samples of this research shows a more systematic broadening whenever one may suspect phase separation. In the present case this broadening is in some cases coupled with the effect of partial solubility (see below).

The change in heat capacity at T_g of the polymer solution is additive, as can be derived by comparison of the heat capacity above and below the transition region for sample A in Table III with the data bank data on the homopolymers. In the transition region of 370-450 K, the deviations are larger because of the glass transition broadening. The process of least error adopted for the data bank handling of heat capacities is to extrapolate the glass and liquid heat capacities to T_g and replace the transition

Table III
Heat Capacity (J mol^{-1} K^{-1})

T, K	PS[a]	A[b]	B[b]	C[b]	D[b]	E[b]	F[b]	PαMS[a]
310	132.2	143.4	142.8	143.8	141.1	143.4	143.6	155.7
		145.7	144.1	145.5	143.4	145.8	146.1	
320	137.0	147.7	147.2	148.0	146.0	148.1	148.5	160.7
		150.2	149.3	150.3	148.3	150.5	151.0	
330	141.9	152.6	151.6	152.7	150.9	152.9	153.5	165.8
		155.2	153.8	155.1	153.5	155.0	156.0	
340	146.8	157.4	156.3	157.7	156.3	157.5	158.5	170.8
		159.8	158.5	160.0	158.7	159.7	160.8	
350	151.8	162.4	160.9	162.5	161.6	162.3	163.6	175.9
		164.8	163.3	165.1	164.2	164.9	166.4	
360	156.8	167.2	166.0	167.9	167.4	167.9	169.2	181.0
		170.0	169.3	171.1	170.2	171.3	171.8	
370	161.8	172.6	174.7	176.2	174.0	176.1	175.3	186.1
		175.2	183.2	185.8	180.6	186.5	180.5	
380	195.9	178.3	189.5	194.6	187.6	195.2	193.9	191.1
		182.5	194.1	197.2	188.5	194.5	199.4	
390	198.6	188.4	195.8	198.4	191.7	197.0	199.3	196.2
		195.8	197.8	200.3	194.6	199.1	200.9	
400	201.2	203.6	199.6	202.7	197.7	201.2	202.7	201.3
		211.5	201.6	204.6	201.5	203.3	204.3	
410	203.9	217.9	203.8	207.1	206.0	205.8	206.7	206.4
		222.7	206.1	209.4	211.1	207.9	208.4	
420	206.5	226.1	208.5	210.6	217.5	210.5	210.8	211.5
		228.9	211.0	213.9	222.8	213.1	212.6	
430	209.2	231.0	214.3	216.8	228.8	216.3	215.3	216.6
		232.4	218.2	219.5	231.6	218.8	217.0	
440	211.9	234.6	223.9	223.3	234.4	222.7	219.9	221.7
		236.3	229.1	228.4	237.2	226.8	222.4	
450	214.5	237.9	233.0	235.3	238.0	234.1	227.8	252.7
		239.3	235.6	239.2	240.2	242.6	238.9	
460	217.2	240.9	237.4	240.7	241.3	241.9	244.7	258.4
		242.9	239.7	241.8	243.3	243.5	243.2	
470	219.8	245.1	242.0	243.9	246.0	245.2	244.8	264.2
		246.7	244.1	245.5	247.5	246.3	246.3	
480	222.5	248.8	246.6	247.9	250.2	248.0	247.9	270.0
		250.3	249.5	250.2	251.5	249.7	249.9	
490	225.1	251.4	251.6	252.4	252.7	250.8	251.1	275.7
		253.4	253.5	254.2	253.8	252.8	252.5	

[a] Heat capacity value from the ATHAS Data Bank.[8] [b] Measured data for 50:50 w/w blends of polystyrene and poly(α-methylstyrene) of various molecular masses: A, L-M; B, M-M; C, H-M; D, L-H; E, M-H; F, H-H. For actual molecular masses see Table I.

range by a step of size ΔC_p. The change in glass transition temperature with concentration has been discussed frequently in the literature. Figure 6 shows the change of glass transition with concentration. Also shown are the predictions of the equation derived by Couchman[13]

$$\ln T_g = \frac{m_1 \Delta C_{p_1} \ln T_{g_1} + m_2 \Delta C_{p_2} \ln T_{g_2}}{m_1 \Delta C_{p_1} + m_2 \Delta C_{p_2}} \qquad (1)$$

the equation suggested by Fox[14]

$$1/T_g = m_1/T_{g_1} + m_2/T_{g_2} \qquad (2)$$

the equation proposed by Pochan et al.[15]

$$\ln T_g = m_1 \ln T_{g_1} + m_2 \ln T_{g_2} \qquad (3)$$

and, finally, the simple equation

$$T_g = m_1 T_{g_1} + m_2 T_{g_2} \qquad (4)$$

It is clear that none of these equations fit the data particularly well; Wood's[16] equation, which has an adjustable parameter k,

$$T_g = [T_{g_1} + (kT_{g_2} - T_{g_1})m_2]/[1 - (1 - k)m_2] \qquad (5)$$

can be made to fit the data better with an average value for k of 0.14. The maximum deviation remains, however, 6 K in the middle of the concentration region. It is thus quite clear that more complicated interaction and molecular geometry dependent terms have to be introduced into the description of the glass transition dependence of blends on composition.

Table IV
Heat Capacity Increase at the Glass Transition

sample[a]	T_g, K	ΔC_p, J K^{-1} mol^{-1}
PS	337[b]	30.7[c]
PαMS	453[b]	25.3[c]
L-H 50:50	373, 422	7.94, 17.18
M-H 50:50	373, 448	15.82, 14.98
H-H 50:50	378, 452	15.67, 15.27
L-M 50:50	400	34.0
M-M 50:50	373, 439	16.47, 11.14
H-M 50:50	374, 444	16.29, 9.99

[a] The designations of the samples are PS for polystyrene and PαMS for poly(α-methylstyrene). Blend molecular masses and mass ratios are listed as PS to PαMS. Molecular masses L, M, and H are listed in Table I. [b] Average values for PS L, M, and H and for PαMS H and M from Table I. [c] Data bank data.

An effort to adjust eq 1 for the temperature dependence of ΔC_p, which is not included in eq 1, improves the fit of the data; in fact, it made the agreement between calculated and measured data come close to the error limit. The temperature-independent ΔC_p was introduced by Couchman[13] to reach a somewhat simpler equation. Our data show that sometimes this simplification is not valid.

The 50:50 blends with high molecular mass PαMS show all two glass transitions (see Figure 3), although only blends H-H and M-H appeared optically cloudy. Sample H-H has two glass transitions of similar sharpness and hysteresis behavior as the homopolymers. Within the limits of ability

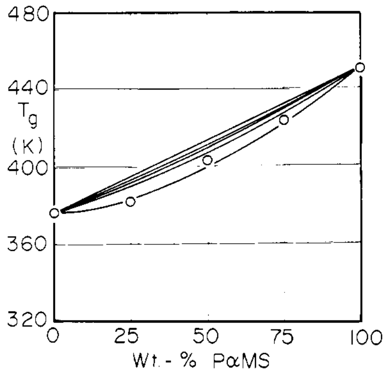

Figure 6. Plot of the glass transition temperatures of the L–M polystyrene–poly(α-methylstyrene) blends as a function of concentration. The upper four curves correspond to plots of eq 4, 3, 2, and 1 from the top down, respectively. The bottom curve represents the experimental points.

to separate the base lines, the two ΔC_p steps correspond to the two pure homopolymers (Tables II and IV). Sample M–H shows already a 5–8 K decrease in T_g (Tables II and IV) and a considerable broadening of the upper glass transition (Table II). Within the accuracy of separation of the base-line between the two transitions, it is not possible to detect much of a shift in the ΔC_p's (see Table IV). Blend L–H, in contrast, shows now a 21 K lowering in the upper T_g and a clear decrease in the lower ΔC_p (Table IV). The lower T_g is not shifted, so that one must assume that the blend separated into pure PS and a solution of PS in PαMS. From T_g and Figure 4 one can estimate that the PαMS phase contains about 0.25 mass fraction PS. This translates into a ΔC_p of about 7.7 J K^{-1} mol^{-1}, which is in good agreement with the data of Table IV. An increase in PS concentration in the 75:25 L–H sample broadened the upper glass transition even more, so that the PαMS transition practically reaches the PS transition (see Table II). From the estimate of the upper T_g one can see that PαMS phase has not taken up much more PS, but it broadened its transition further.

The 50:50 blends with medium molecular mass PαMS reach to compatibility as shown in Figures 1 and 2. The high and medium molecular mass PS blends H–M and M–M show still two glass transitions. The uptake of the PαMS phase of PS is more when judged from the data of Table IV. The residual PS again appears as pure polystyrene. Blend L–M indicates no leftover pure polystyrene but has a broadened T_g as discussed before.

The data on blends with low molecular mass PαMS are shown in Table II. The 75:25 blend of M–L shows some signs of an increase in T_g of the PS phase and a very much broadened and lowered PαMS T_g, which is difficult to discern from the DSC trace. The 25:75 blend of H–L has a very broad transition region with a very small indication of a step at perhaps 385 K as a small residual amount of PαMS dissolved in PS. From Figure 6 one estimates that a T_g of 385 K could indeed correspond to a concentration of about 25 wt % PαMS in PS.

The hysteresis behavior shown in Figures 4 and 5 supports the above discussion in the following way: the homopolymers always show strong hysteresis peaks of a magnitude larger than ΔC_p. None of the L–M series show significant hysteresis. The 50:50 blend shows no discernible hysteresis. The 75:25 and 25:75 blends have one broad hysteresis peak each. It is likely that the hysteresis is lost or diminished in these cases due to the breadth of the glass transition as suggested earlier by Fried et al.[4] A sum of many small hysteresis peaks would disappear in the overall recording. Figure 5 illustrates that for the 50:50 blends with two-step glass transitions (samples M–H, M–M, and H–H) there are clearly two hysteresis peaks. Furthermore, the greater the solubility of PS in PαMS, the broader the PαMS hysteresis peak. Note that the hysteresis experiments were done in a more qualitative heat measurement (but more quantitative temperature measurement). The shallow slope between the two glass transitions was shown in Figures 2 and 3 to be caused by poor base-line separation and should practically be horizontal.

Conclusions

The present experiments reveal that double glass transitions and excessive broadening of the glass transition occur before phase separation is apparent by observation of cloudiness.

A comparison of data on random and block copolymers with blends reveals that only random copolymers seem to have a sharp glass transition. Even compatible blends have a broadened glass transition, which may be due to an intrinsic concentration fluctuation caused by the one-dimensional connection along the homopolymer chains. The asymmetric broadening in block copolymers, which was linked to microphase separation, can also be found in blends in the region of partial solubility.

The additivity of C_p above and below the glass transition region allows a quantitative assessment of the concentrations in partially compatible blends. In the present case polystyrene shows solubility in poly(α-methylstyrene) to much higher molecular mass than poly(α-methylstyrene) in polystyrene.

The composition dependence of the glass transition temperature is not well represented by various equations in the literature, which were largely derived for copolymers, as long as they contain no adjustable parameters. The Couchman equation corrected for the temperature dependence of ΔC_p is an exception.

The hystersis allows better identification of two phase structures but is reduced as the glass transition region is broadened.

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References and Notes

(1) See, for example: Paul, D. R.; Newman, S., Eds. "Polymer Blends"; Academic Press: New York, 1978.
(2) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 1618.
(3) Wunderlich, B.; Bodily, D. M.; Kaplan, M. H. *J. Appl. Phys.* **1964**, *35*, 95.
(4) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1978, 11, 150.
(5) Wunderlich, B.; Bopp, R. C. *J. Thermal Anal.* **1974**, *6*, 335.
(6) Gaur, U.; Mehta, A.; Wunderlich, B. *J. Thermal Anal.* **1978**, *13*, 71.
(7) Laboratory MicroSystems, Inc., Troy, N.Y.
(8) Gaur, U.; Wunderlich, B. *J. Phys. Chem. Ref. Data*, submitted for publication.
(9) Wunderlich, B.; Gaur, U. *Pure Appl. Chem.* **1980**, *52*, 445.
(10) $H_2SO_4\cdot 3H_2O$: Kunzler, W. E.; Giauque, W. F. *J. Am. Chem. Soc.* **1952**, *74*, 797. $Ni(3\text{-}CH_3O\text{-}SAL\cdot i\text{-}C_3H_7)_2$: Arai, N.; Sorai, M.; Seki, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2398. $CaNO_3\cdot xH_2O$ and $Mg(OAc)_2\cdot xH_2O$: Angell, C. A.; Tuker, J. C. *J. Phys. Chem.* **1980**, *84*, 268. Supercooled mixtures of alkoxy–azoxybenzene mesophases: Grebowicz, J.; Wunderlich, B. *Mol. Cryst. Liq. Cryst.* **1981**, *76*, 287.
(11) See, for example, the following. Styrene–butadiene copolymers: Wood, L. A.; Bekkedahl, N. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, 5, 169 and other references given there. Brominated poly(2,6-dimethyl-1,4-phenylene oxide): Bopp, R. C.; Gaur, U.; Kambour, R. P.; Wunderlich, B. *J. Thermal Anal.*, submitted for publication.
(12) See, for example, the following. Poly(vinyl chloride) blends: Anderson, E. W.; Bair, H. E.; Johnson, G. E.; Kwei, T. K.;

Padden, F. J., Jr.; Williams, D. *Adv. Chem. Ser.* **1979**, *No. 176*, 413. Aubia, M.; Abdia, M.; Prud'homme, R. E. *Macromolecules* **1980**, *13*, 365. Polystyrene blends: Shultz, A. R.; Young, A. L. *Ibid.* **1980**, *13*, 663. Stoelting, J.; Karasz, F. E.; MacKnight, W. J. *Polym. Eng. Sci.* **1970**, *10*, 247. Shultz, A. R.; Gendron, B. M. *J. Appl. Polym. Sci.* **1972**, *16*, 461. Similarly a common effect of a plasticizer is a broadening of the glass transition in dissolution of a small molecule (in addition to the glass transition lowering). See, for example: Bair, H. E. In Turi, E. A., Ed. "Thermal Characterization of Polymeric Materials"; Academic Press: New York, 1981.

(13) Couchman, P. R. *Macromolecules* **1978**, *11*, 117, 1156.

(14) Fox, T. G *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(15) Pochan, J. M.; Beatty, C. L.; Pochan, D. F. *Polymer* **1979**, *20*, 879.

(16) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.

Theory of Phase Equilibria in Mixtures of Copolymers and Homopolymers. 2. Interfaces near the Consolute Point

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ABSTRACT: A simple mean field formalism is developed to study the interfacial properties of nearly compatible mixtures of two homopolymers A and B and a copolymer A–B. The interfacial composition profile and interfacial tension are calculated analytically, and the interfacial activity of copolymer additives is discussed. The mechanism involved is quite different from that evoked for highly immiscible species: the dominant effect is the presence of copolymer chains in both A-monomer-rich and B-monomer-rich phases. The effect of preferential location of copolymer chains at the interface plays only a role for high copolymer contents. The reduction of interfacial tension is shown to be stronger in the case of diblock rather than multiblock copolymer chains.

I. Introduction

Copolymer molecules may show an important interfacial activity when added into a multiphase system. For example, in the case of two immiscible low-molecular-weight liquids, copolymer chains act in a way analogous to that of classical nonionic or soap surfactants and may even lead to a microemulsion formation.[1–5] Another particular case of practical importance is a blend containing highly incompatible homopolymers.[6–13] It has been recognized that copolymer additives lower the interfacial tension[9,13] and, therefore, may facilitate phase dispersion and improve mechanical properties of blends.[14,15] The interfacial activity of copolymers has been attributed to their preferential location at the interface.[16] This interpretation has been confirmed recently by Noolandi and Hong, who have developed a detailed theory of interaces in a quaternary system, a solution in a good solvent of two highly incompatible homopolymers, and a diblock copolymer.[17] Actually, the calculation of interfacial density profiles has shown that the block copolymers locate at the interface and exclude the homopolymers from the interphase region.[17] However, the important question remained (cf. ref 10 and 18) whether the same effect will occur for a system in which the two homopolymers are relatively compatible. The present theory indicates that for nearly miscible species the copolymer chains still play an important emulsifying role although the mechanism involved is very different.

We will deal with a ternary amorphous blend containing two homopolymers A and B and a copolymer A–B. In a previous paper[19] the phase diagram of such a system has been discussed for different degrees of incompatibility of the chains. In particular, it has been concluded that in the case of nearly miscible species, on which we focus in the present paper, copolymer additives play an interesting compatibilizing role. First, the addition of copolymers displaces the critical point of demixing and may even cause a two-phase blend to become one phase. Second, the copolymer chains are present in both phases of the two-phase blend and favor a closer mixing of the chemical species A and B. Our aim here is to calculate both the interfacial concentration profile and the interfacial tension in order to extend the analysis of emulsifying properties of copolymer additives. We will compare the effectiveness of diblock and multiblock copolymers.

The essential problem encountered by microscopic theories of interfacial properties is to find the free energy of the nonhomogeneous system, i.e., to include the spatial density fluctuations. For a macromolecular system two equivalent mean field approaches have been hitherto applied. The first one uses the functional integral representation of the partition function, as introduced by Edwards.[25] When copolymers are present in the system, this method is not particularly convenient as it leads to a complex set of integrodifferential equations which requires complicated numerical methods to be solved.[17,23,24,26] The second method expresses the free energy in terms of monomer concentration correlation functions. The correlation functions are calculated in a self-consistent way within the random phase approximation introduced by de Gennes.[27,28] This method particularly adapted to study concentration profiles of diffuse interfaces[29,30] will be used in this work.

In section II we study monomer concentration fluctuations and find the free energy density of a nonhomogeneous system. Then in section III we calculate the composition profile and interfacial tension, focusing on the systems close to the critical point of demixing. Physical mechanisms underlying the emulsifying activity of copolymer chains are discussed in section IV.

II. Correlation Functions and Free Energy of a Nonuniform System

We study a liquid mixture composed of two flexible homopolymers A and B and a copolymer A–B. For the sake of simplicity we will deal with the symmetric case, assuming that all chains have the same polymerization index N and that each copolymer chain contains $N/2$ monomers A (B). Various types of copolymer structures (diblock, multiblock) will be considered but it will be supposed that the copolymer molecule is symmetric with

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