DSC on Freeze-Dried Poly(methyl methacrylate)–Polystyrene Blends

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ABSTRACT: Homogeneous blends of the noncompatible polymers poly(methyl methacrylate) and polystyrene have been prepared by a rapid freezing of their co-solutions in naphthalene followed by room-temperature sublimation of the naphthalene. Differential scanning calorimetry (DSC) reveals single glass transition temperatures (T_g) for these blends intermediate between the glass transition temperatures of the component polymers. Specific heat vs. temperature curves exhibit maxima below T_g for the freeze-dried PMMA and PS/PMMA blends during 40 °C/min heating. The C_p maximum and subsequent minimum prior to T_g traverse are enhanced, narrowed, and shifted to higher temperatures by sub-T_g annealing. Such annealing can also produce a C_p maximum above T_g, thus yielding two C_p maxima during a heating scan. An assumption of a distribution of relaxation times for the freeze-dried glasses is necessary to rationalize these observations.

The freeze drying of co-solutions of thermodynamically incompatible polymer pairs is a method of capturing kinetically the unlike molecules in an intimate admixture. Molecular or "segmental" mixtures may be achieved thereby. Poly(methyl methacrylate)–poly(vinyl acetate) blends freeze-dried from co-solutions in benzene were reported homogeneous by dynamic mechanical and dilatometric observations of single glass transition temperatures intermediate between those of the pure polymers.[1] Further dilatometric and differential calorimetric data corroborated the findings of homogeneity in these blends.[2]

The freeze drying of incompatible polymer pairs was commenced in our laboratory in 1968. After initial work with benzene as the common solvent, naphthalene or *p*-dichlorobenzene was chosen as the solvent to permit sublimation at room temperature. Molecular mixing was inferred for poly(methyl methacrylate)–polystyrene blends freeze-dried as co-solutions in naphthalene.[3]

The present work reports extensive scanning differential calorimetric measurements on poly(methyl methacrylate), polystyrene, and poly(methyl methacrylate)–polystyrene blends freeze-dried in December 1969 (12-69) and June 1978 (6-78). From the specific heats, before and after annealing, of these samples observed during constant heating rate experiments the natures of segmental nonequilibrium "states" in freeze-dried polymers and polymer blends are deduced.

Experimental Section

Materials. The poly(methyl methacrylate), L1490, was obtained as a 187 mil thick sheet supplied by N. S. Steck (Rohm and Haas Co.) to J. P. Berry of this laboratory in 1959. GPC analysis gave $M_n = 2.74 \times 10^5$, $M_w = 1.20 \times 10^6$, and $M_z = 2.84 \times 10^6$ for this polymer. The polystyrene was anionically polymerized PS 2b ($M = 20\,400$; $M_w/M_n \leq 1.06$) obtained from Pressure Chemical Co., Inc.

Freeze Drying and Compaction. Five grams of polymer or polymer mixture were dissolved in 95 g of naphthalene at 100 °C with magnetic stirrer mixing under a nitrogen blanket. The hot solution was poured slowly into ice water undergoing high-speed stirring in a Waring blender to give rapid freezing of the naphthalene matrix. After filtration on a sintered-glass frit the naphthalene powder "solutions" were dried in an air stream through the powder on the frit for 24 h at room temperature. The (12-69) powders were then transferred to round-bottomed flasks, and the naphthalene was sublimed from the polymer blends at room temperature on a high-vacuum rack for 1 week. The naphthalene was sublimed from the (6-78) powders by continued passage of filtered room temperature air through the powder mass on the glass frit for 9 more days (a total of 10 days of sublimation) without resort to high-vacuum application. This procedure proved as efficient as the high-vacuum process since the slow step in the final removal of naphthalene from the polymers is the diffusion of the last traces of solvent to the surfaces of the glassy polymer platelets (of about 1 μm thickness).

Ten-milligram samples of the low bulk density freeze-dried powders were compacted at room temperature into disks approximately 0.48 cm in diameter and 0.066 cm thick by hammer impact on a steel plunger in a cylindrical steel mold. The polymer disks prepared in this manner are about 70–80% of the bulk polymer density. This provides a convenient geometry for DSC samples and a heat transfer rate not much less than that for bulk polymer samples.

Differential Scanning Calorimetry (DSC). All DSC measurements were made with a Perkin-Elmer DSC-2 instrument with an Autozero base line linearization attachment. The temperature calibration at the various heating rates was accomplished with indium, tin, and lead melting temperatures. A sapphire disk standard was used for specific heat calibration. Sealed aluminum cup containers were employed. Preliminary, nonquantitative DSC scans were made at the 20 °C/min heating rate to survey the glass transitions of various blend compositions. For quantitative specific heat a heating rate of 40 °C/min was most commonly used. This gave reasonable heat transfer without allowing excessive molecular diffusion in the glass transition region during a scan. Isothermal holds at the top temperature (e.g., 170 °C) of initial heating scans were generally maintained followed by "free cooling" of the samples to the initial low temperature and then heating a second time. "Free-cooling" rates were approximately −180 °C/min (200 °C), −135 °C/min (150 °C), −90 °C/min (100 °C), and −50 °C/min (50 °C). All isothermal annealings were conducted in the DSC apparatus.

Specific heat computations were facilitated by digital data logging of the DSC-2 10-V output with the use of a microcomputer (LAM, Laboratory Automation Module) constructed within this laboratory. The data were transferred from memory partitions to magnetic tape cassettes and subsequently processed by transmission to a Honeywell 605 computer. One thousand data points were recorded and computed per specific heat scan. At the 20 °C/min heating rate no corrections of machine readings are needed to give a C_p for sapphire (36 mg disk) in agreement with the National Bureau of Standards measured C_p.[4] At the 40 °C/min heating rate a correction factor of 0.983 ± 0.003 is required to adjust machine readings of C_p for sapphire to those reported.[4]

Results and Discussion

Morphology of Freeze-Dried Polymer Glasses. The rapid freeze technique employed in this study produced essentially spherical droplets of crystalline naphthalene/glassy polymer. The glass formation occurred well below the melting temperature of naphthalene (80.2 °C) but most likely above room temperature (20 °C). The temperature of naphthalene crystallization onset, its subsequent kinetics, and the thermal history are not defined. The heat of crystallization could cause some warming of the supercooled solution prior to the subsequent drop to 0 °C.

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Figure 1. Scanning electron microscopic picture of a freeze-dried 50/50 PS/PMMA particle surface. The original print magnification was 630×.

After room temperature sublimation of the naphthalene from the naphthalene/glassy polymer droplets, low bulk density spheres ($\rho \simeq 0.05$) of polymer remained. Figure 1 is a scanning electron microscopic picture (original print at 630×) of a 50/50 by weight PS/PMMA freeze-dried particle surface. The polymer platelets of approximately 1 μm thickness were the regions pushed aside by rapidly growing naphthalene crystals. The planar surfaces of the platelets replicated the faces of the naphthalene crystals in contact with the polymer + naphthalene regions when they became glassy. The thinness of the platelets facilitated diffusive loss during sublimation of the naphthalene remaining within them at the time of solidification. It is possible that the platelets are porous on a multi-nanometer scale. This remains to be determined by transmission electron microscopy.

Preliminary DSC Scans on (12-69) Samples. Previous indirect analyses by electron irradiation[3] indicated the homogeneity of 20/80 and 50/50 PS/PMMA blends freeze dried by the naphthalene technique. Preliminary DSC scans (+20 °C/min) in February 1978 on a series of PS/PMMA blends freeze dried from naphthalene in December 1969 revealed single glass transitions. These DSC scans on the (12-69) blends are shown in Figure 2. The third heat scans, after twice heating to 170 °C, are presented in Figure 3. Here the 60, 50, and 40 wt % PMMA blends reveal two distinct glass transitions. The upper transition is difficult to detect in the 20 and 10 wt % PMMA blends. Figure 4 displays the glass transition temperatures as marked in Figures 2 and 3. Although the data were not highly precise, the homogeneity of the freeze-dried blends down to a very local, segmental level and their rather rapid separation into two phases at elevated temperatures were demonstrated.

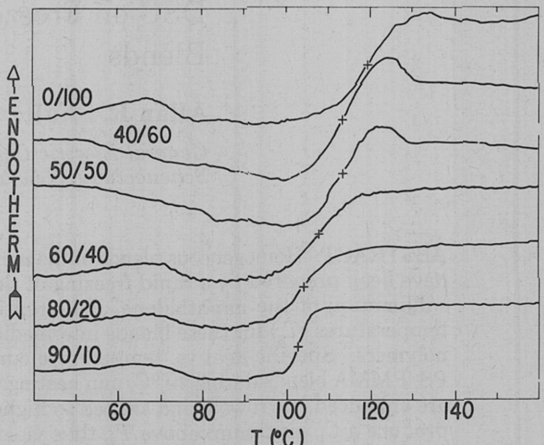

Figure 2. DSC scans of PS/PMMA (12-69) freeze-dried blends. The weight ratios of PS/PMMA are indicated; the heating rate was 20 °C/min.

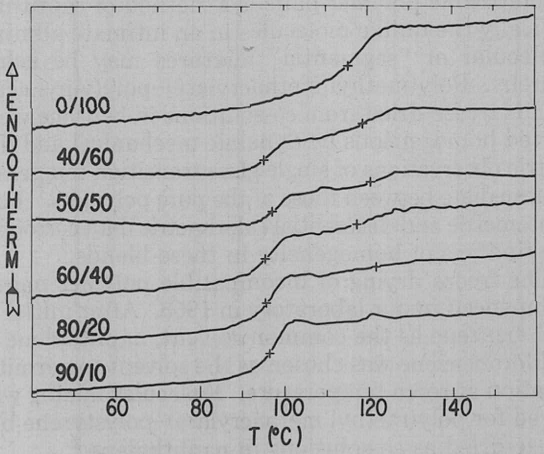

Figure 3. DSC scans of PS/PMMA (12-69) blends after two 20 °C/min scans from 0 to 170 °C and free cooling to 0 °C. The weight ratios of PS/PMMA are indicated; the heating rate was 20 °C/min.

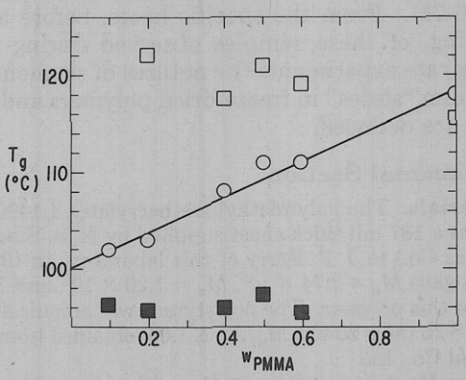

Figure 4. Glass transition temperatures vs. weight fraction PMMA in PS/PMMA freeze-dried blends (cf. Figures 2 and 3): circles, first heat; squares, third heat.

DSC scans at higher sensitivity and improved signal-to-noise ratio were performed on the 50/50 PS/PMMA (12-69) blend after three annealing regimens.

Figure 5 presents the DSC traces (+40 °C/min) obtained after 20 min of annealing of individual samples at 70, 80, 100, 110, 120, and 130 °C. Also shown is the trace for a sample annealed for 5 min at 170 °C after a 40 °C/min scan to that temperature. One notes in the 70, 80, and 100 °C annealed samples a specific heat maximum and minimum occurring prior to the glass transition C_p increase. The sample annealed at 110 °C displays a broad, continuous specific heat rise in its approach to the nonglass state. This broad, smooth transition is most likely the result of

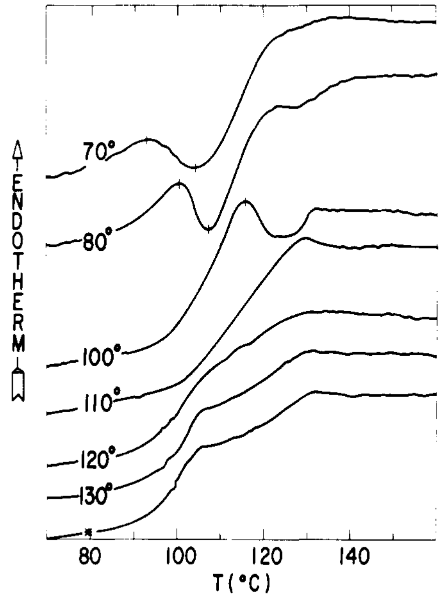

Figure 5. DSC scans on freeze-dried 50/50 PS/PMMA (12-69) blend annealed for 20 min at the indicated temperatures. The vertical placement is arbitrary. The bottom curve is for a sample previously heated from 0 to 170 °C at 40 °C/min, held at 170 °C for 5 min, and free cooled to 0 °C. The heating rate was 40 °C/min.

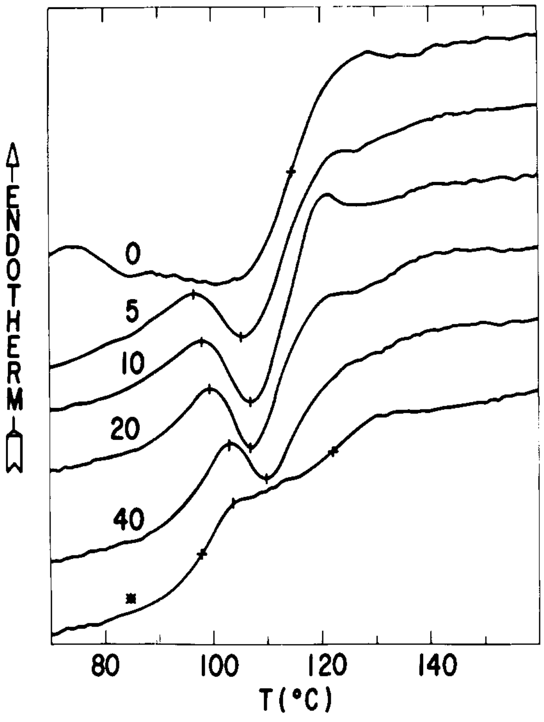

Figure 6. DSC scans at +40 °C/min on 50/50 PS/PMMA (12-69) annealed at 80 °C for the indicated number of minutes. The bottom curve is for a sample annealed at 170 °C and free cooled to 0 °C.

a near continum of local blend compositions produced by viscosity-limited phase separation during annealing between the T_g values of the pure components. The 120 and 130 °C annealed samples give evidence of the glass transitions of the separated PS and PMMA phases which are well delineated in the 170 °C annealed sample.

Further qualitative demonstration of the sub-T_g maxima and minima in C_p which could be sharpened and enhanced by annealing is provided by Figures 6 and 7. The 80 °C annealing for increasing lengths of time shifts the maxima and minima progressively to higher temperatures; the magnitudes of the extrema initially increase, but then decrease. Similar shifts in the extrema are produced by 70 °C annealings, but the enhancement continues to the longest period shown.

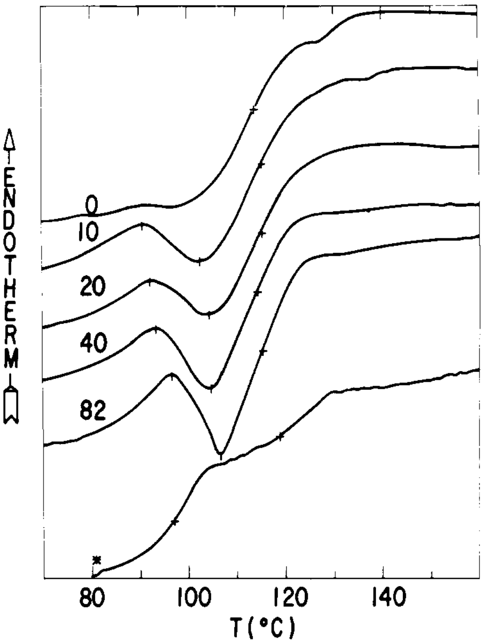

Figure 7. DSC scans at +40 °C/min on 50/50 PS/PMMA (12-69) annealed at 70 °C for the indicated number of minutes. The bottom curve is for a sample annealed at 170 °C and free cooled to 0 °C.

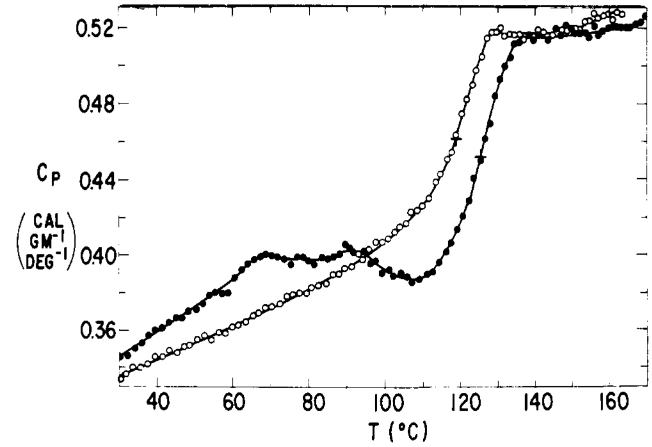

Figure 8. Specific heat measured at +40 °C/min on freeze-dried PMMA (12-69): filled circles, first heat from 0 to 170 °C; open circles, second heat after a 5 min hold at 170 °C and free cooling to 0 °C.

The development of pronounced maxima and minima within the glass transition region of 50/50 PS/PMMA (12-69) was initially unexpected. At first it was thought that these might be associated with local phase separation in the blend. However, the same phenomenon has been reported for rapidly-quenched poly(vinyl chloride) film.[5] This suggested that rapid quenching was achieved by the rapid-freeze process and that the observed C_p behavior arose from this rather than from the blend character of the material.

Quantitative DSC Scans on PMMA (12-69) and PMMA (6-78). In order to achieve some rationalization of the preceding data, quantitative specific heat scans were made on freeze-dried PMMA (12-69) and PMMA (6-78).

In Figures 8 and 9 are plotted two specific heat scans on PMMA (12-69) and on PMMA (6-78), respectively. The principal features follow: (a) The initial freeze-dried glass

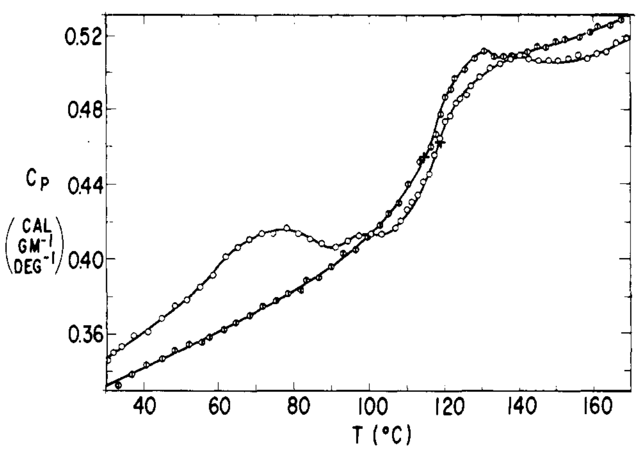

Figure 9. Specific heat measured at +40 °C/min on freeze-dried PMMA (6-78): open circles, first heat from 0 to 170 °C; slashed circles, second heat after 5 min hold at 170 °C and free cooling to 0 °C.

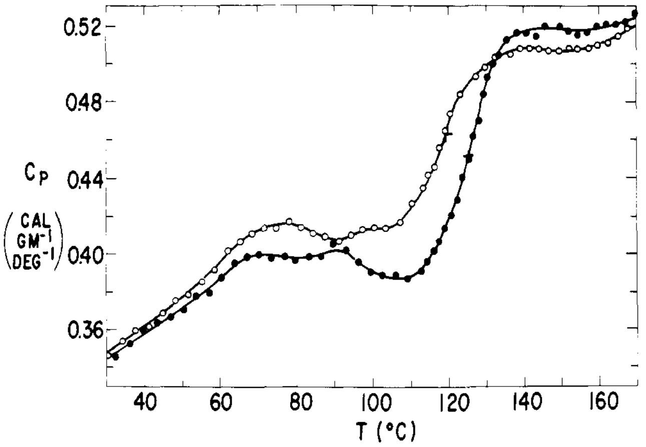

Figure 10. Specific heat measured at +40 °C/min on freeze-dried PMMA (6-78) (open circles) and freeze-dried PMMA (12-69) (filled circles).

exhibits a higher specific heat in the low-temperature region than does the 170 °C annealed and free-cooled glass. (b) The specific heat of the freeze-dried polymer glass passes through a maximum and then decreases prior to the glass transition. (c) The specific heat of the freeze-dried polymer is lower than that of the free-cooled polymer in the final approach to the glass transition, and T_g appears to be higher in the former. The observed differences between the polymer glasses are due to their different "states". These differences will also be noted in the PMMA/PS blends and should be recognized as sample history effects.

The specific heat of PMMA (12-69), which had annealed for 8.5 years at room temperature, is seen to be lower and its T_g higher than those of PMMA (6-78) which had not aged 1 month (Figure 10). This indicates continuing relaxation even at temperatures 90–100 °C below the center of the glass transition.

Remarkably close agreement was found (Figure 11) between the specific heats of the PMMA (12-69) and PMMA (6-78) preparations after subjecting them to identical 40 °C/min scans to 170 °C, 5-min holds at 170 °C, and free cooling to 0 °C. The free cooling rate at T_g was about −100 °C/min, i.e., about two and one-half times the heating rate of the scan.

Quantitative DSC Scans on PMMA (6-78), PS (6-78), and 50/50 PS/PMMA (6-78). Figure 12 presents the specific heats of PMMA (6-78), PS (6-78), and 50/50 PS/PMMA (6-78) *after* annealing at, and free-cooling from, 170 °C. The specific heat vs. temperature curve of the 50/50 blend exhibits the expected two glass transition regions and lies approximately midway between the curves of the individual component polymers. The specific heats of the PS glass (in the 30–70 °C region) are about 2% lower than those recently published by Gilmour and Hay[6] and those obtained by Dainton, Evans, Hoare, and Melia[7] (isotactic PS). This near agreement on C_p for the different PS glasses is very good. On the other hand, the PMMA C_p and dC_p/dT values shown here (Figure 12) are distinctly higher than those indicated by the treatment[8] of the data of Sochava and Trapeznikova.[9] The source of this disagreement is not known. The present data extrapolate well (linearly) to the smoothed C_p values at 200, 210, and 220 K of the previous work.

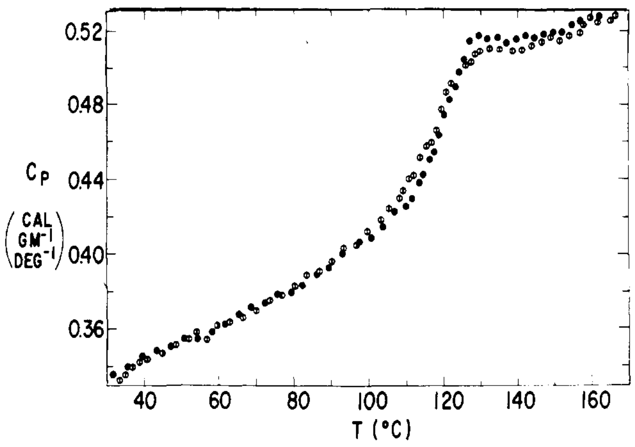

Figure 11. Comparison of specific heats of PMMA (12-69) (solid circles) and PMMA (6-78) (slashed circles) after 5 min at 170 °C and free cooling to 0 °C. The heating rate was 40 °C/min.

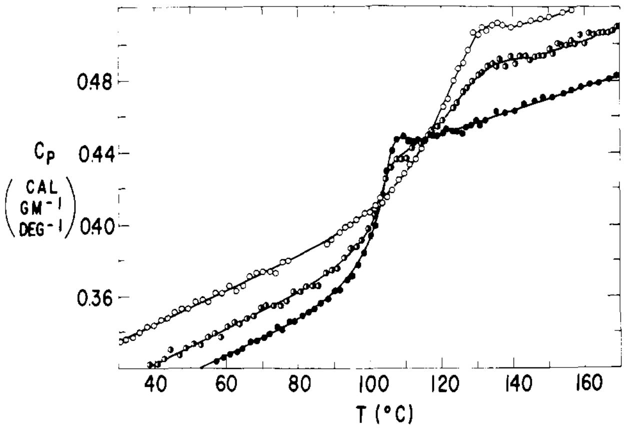

Figure 12. Specific heats measured at +40 °C/min on PS (6-78) (filled circles), 50/50 PS/PMMA (6-78) (half-filled circles), and PMMA (6-78) (open circles). Prior to the measurement, each freeze-dried sample was annealed at 170 °C for 5 min and free cooled to 0 °C.

The specific heat vs. temperature characteristics of 50/50 PS/PMMA (6-78) are exemplified by Figure 13 for three different thermal histories. The original freeze-dried blend (solid circles) exhibits a higher specific heat at low temperatures than do the 70 °C annealed or 170 °C annealed samples. Its specific heat rises to a maximum at 76 °C, decreases to a broad minimum at about 103 °C, and then rises smoothly through a glass transition (115 °C) to the nonglass state (≥124 °C). An annealing of the freeze-dried blend for 32 h at 70 °C led to the dynamic C_p vs. T curve represented by the half-filled circles. The gradual rise in C_p to a maximum in the nonannealed blend

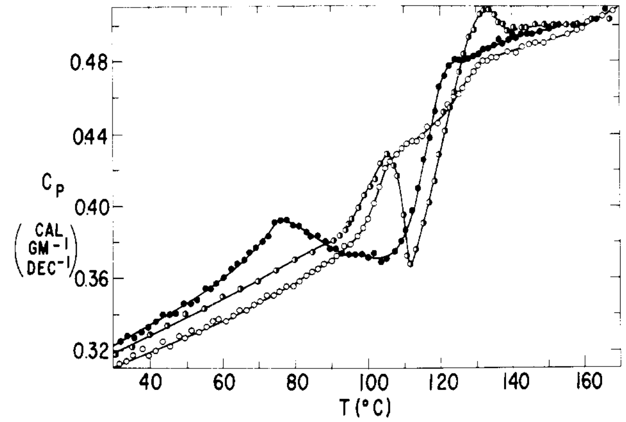

Figure 13. Specific heats of 50/50 PS/PMMA (6-78) at a 40 °C/min heating rate: filled circles, original freeze-dried blend; half-filled circles, freeze-dried blend annealed for 32 h at 70 °C; open circles, freeze-dried blend after a 0–170 °C scan plus 5 min at 170 °C and free cooling to 0 °C. The heating rate was 40 °C/min.

has now become a sharp rise to a maximum at 105 °C, a rapid drop to a minimum at 112 °C, followed by passage through a glass transition (120 °C) to a nonglass state at about 135 °C. The glass transition temperature, here and in the non-annealed blend, is defined as the temperature at which one-half the specific heat step in the final rise has occurred. In the 70 °C annealed blend the C_p observed at this T_g is coincidentally matched by the C_p of the 105 °C maximum. The small endotherm peak at the end of the annealed blend's transition is believed to be the "excess enthalpy endotherm" of an annealed glass.[10] The C_p vs. T curve (open circles, Figure 13) of the two-phase blend after 170 °C annealing and free cooling was presented previously in Figure 12. The establishment of calorimetrically distinct phases from the freeze-dried blend at temperatures well above the glass transition is reasonably rapid.

There have been many discussions and kinetic/thermodynamic treatments of the properties of nonequilibrium glasses as functions of their thermal and mechanical histories. We shall refer to only a few of these to allow qualitative interpretation of the present data.

The existing hole theory of liquids as applied to glass transition phenomena was given a more quantitative, kinetic formulation by Wunderlich and co-workers.[11,12] This theory predicts a specific heat minimum prior to the glass transition when the heating rate is slower than the cooling rate which produced the glass. The more rapid the glass-forming quench the deeper is this predicted dynamic C_p minimum. The theory predicts a C_p maximum after heating through T_g when the heating rate is faster than the cooling rate which produced the glass. This maximum can be augmented by annealing at temperatures somewhat below T_g. Kinetic analysis of the glass relaxation as reflected in dynamic C_p behavior within the hole theory approach has been useful.[11-13] The hole theory, however, does not predict a C_p maximum below T_g during a heating scan. It is, therefore, not adequate for a complete description of the dynamic C_p behavior of polymer glasses prepared by the present freeze-drying process or by very rapid thermal quench methods.

A 50 °C "transition" in polystyrene was reported on the basis of a very small ΔT peak observed in differential thermal analysis (DTA) heating traces at 5.5 °C/min on large (0.5 g) PS glasses prepared by −5.2 °C/min cooling.[14] We observed no such peak in DSC scans at +40 °C/min on 10-mg PS glasses prepared by free cooling in the DSC samples annealed at 170 °C. The C_p vs. T curve (not shown) for the initial freeze-dried PS (6-78) does not exhibit the sub-T_g maximum exhibited by PMMA (6-78) and 50/50 PS/PMMA (6-78). Rather, it exhibits a minimum which could be treated within the framework of the hole theory for rapidly-quenched glasses.

Quite promising theoretical treatments of the relaxation phenomena in polymer glasses have recently appeared. Earlier mechanistic[14-16] and phenomenological[17] treatments involving a single characteristic relaxation time have been extended[18-20] to encompass distributions of relaxation times which depend on, or are modulated by, a distribution of local environments. This leads to the possibility of explaining theoretically[20] the existence of a "misplaced" C_p peak in a rapidly-quenched poly(vinyl acetate) sample,[21] a sub-T_g C_p peak in rapidly-quenched poly(vinyl chloride) film,[5] two expansion coefficient peaks in sub-T_g annealed polystyrene,[17] and, in the present study, a sub-T_g C_p peak in freeze-dried PMMA and PS/PMMA blends and two C_p peaks in the freeze-dried blends after sub-T_g annealing. The magnitude of the specific heat enhancement and of the sub-T_g peak in the present glasses prepared by rapid-freeze plus matrix sublimation suggests a very "open" glass structure with a broad distribution of relaxation times. The ease of sharpening the sub-T_g peak and shifting it to a higher temperature by annealing also suggests a broad relaxation spectrum. The peak sharpness is accentuated by the subsequent minimum which, in the hole theory terminology, results from diminishing the population of holes entrapped by the rapid quench (and possibly holes left by the naphthalene during its low-temperature sublimation from the glass). The development of an excess endotherm peak following T_g in the sub-T_g annealed blend is further evidence for its local environment heterogeneity. Unfortunately, the undefined conditions of the glass formation in the rapid-freeze plus freeze-drying technique make quantitative theoretical evaluation of its structure impossible at present.

In conclusion, the specific heat data on the freeze-dried PS/PMMA blends indicate that segmental mixing of the incompatible polymers was achieved. The data on the freeze-dried blends and also on the individual freeze-dried polymers suggest glass structures equivalent to those one would achieve by very rapid thermal quenches of the bulk polymer liquids. The presence of maxima and minima in specific heat at temperatures below T_g during constant heating requires postulation of a broad relaxation spectrum for these glasses. This requirement is made even more evident in the development of two C_p peaks with sub-T_g annealing.

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Photon Correlation Spectroscopy of Polystyrene Solutions

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ABSTRACT: The mutual diffusion coefficient in polystyrene solutions is examined both theoretically and experimentally. The measurements are shown to be incapable of testing the scaling law predictions for the osmotic modulus and friction coefficient. Measured values of D_c in carbon tetrachloride and ethyl acetate yield no hint of a crossover region between dilute and semidilute solutions. The mutual diffusion coefficient eventually reaches a maximum with concentration.

Concentration fluctuations in fluid mixtures lead to light scattering which can be analyzed by using photon correlation spectroscopy. The physical quantity that is determined is the mutual diffusion coefficient D_c. At infinite dilution the mutual diffusion coefficient is equal to the self-diffusion coefficient of the solute. Photon correlation spectroscopy has become a standard technique for determining the self-diffusion coefficient for polymers in solution.[1]

There has been a great deal of current interest[2-5] in the behavior of the mutual diffusion coefficient as a function of concentration. This has been stimulated by the theoretical predictions of deGennes.[6] Certain asymptotic results are obtained in the semidilute region of concentration for the osmotic pressure and for the friction per unit volume, using scaling law arguments. In the present paper we examine the validity of this approach in the description of concentration fluctuations in polymer solutions. Measurements of the mutual diffusion coefficient for 600 000 molecular weight atactic polystyrene in carbon tetrachloride and in ethyl acetate were carried out as a function of concentration.

Theory

Photon correlation spectroscopy measures the quantity

$$C(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2 \qquad (1)$$

where $I(t)$ is the intensity of light scattered by the sample at time t. For pure thermal density and concentration fluctuations the correlation function is given by

$$C(t) = 1 + \phi^2(t) \qquad (2)$$

where $\phi(t)$ is the relaxation function for the fluctuations which give rise to the light scattering. For all the samples studied in this work, the density fluctuations are too fast to be observed by photon correlation spectroscopy. The concentration fluctuations can be described by a relaxation function

$$\phi_c(t) = \exp(-D_c q^2 t) \qquad (3)$$

where $q = 4\pi n/\lambda \sin \theta/2$ is the magnitude of the scattering vector for light of vacuum wavelength λ in a medium of refractive index n scattered at an angle θ in the scattering plane. Because not all the scattered intensity is due to concentration fluctuations, the value of $C(t)$ at the shortest measured times will be less than 2. The exact value can be calculated from a knowledge of the fraction of scattered light associated with the concentration fluctuations. Care was taken to assure that this theoretical value was realized in practice.

The value of the mutual diffusion coefficient is determined by the restoring force for the concentration fluctuations divided by the frictional resistance

$$D_c = E_c/\Phi \qquad (4)$$

where $E_c = c\, \partial\pi/\partial c$ is the osmotic modulus and π is the osmotic pressure, and Φ is the friction per unit volume. At infinite dilution the diffusion coefficient is given by

$$D_0 = kT/6\pi\eta R_h \qquad (5)$$

where k is Boltzmann's constant, η is the solvent viscosity, and R_h is the effective hydrodynamic radius. As the concentration of polymer is increased in a good solvent, the osmotic modulus increases substantially and so does the friction per unit volume. The observed behavior of the mutual diffusion coefficient is a balance between these two effects. If we ignore the small term related to the partial specific volume of the polymer in solution, the behavior of D_c in dilute solution depends on the difference $2A_2M - k_f$, where A_2 is the osmotic second virial coefficient, M is the molecular weight of the polymer, and k_f is the second virial coefficient for the friction coefficient. For a Θ solvent, the mutual diffusion coefficient falls as the concentration is increased. In a very good solvent, D_c can increase substantially, even in dilute solution.

In order to discuss the semidilute concentration region, it is necessary to specify what is meant by semidilute. A concentration c^* is taken as the boundary between dilute and semidilute regions. It has been proposed by deGennes[6] that c^* is proportional to the polymerization index N di-

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