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Single-Chain Polystyrene Glasses

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ABSTRACT: The microemulsion free-radical polymerization of styrene generates particles containing one or at most a few high molecular weight polymer chains. Space-filling considerations preclude such chains from adopting their random-coil conformation; rather, they adopt a highly compact globular conformation and below T_g constitute essentially single-chain glasses. This paper reports apparent spectroscopic and thermal differences between single-chain and conventional multichain polystyrene glasses. FTIR measurements suggest that the conformational temperature of the single-chain glasses as prepared is higher than that for multichain glasses. DSC measurements on these same glasses displayed a first-order exotherm near to the conventional T_g of polystyrene but thereafter exhibited behavior similar to the multichain samples. The results were explained in terms of the existence of nematic cohesional entanglements in polystyrene glasses.

Introduction

It is possible by the free-radical polymerization of styrene in microemulsions to generate microlatex particles that contain only one or at most a few high molecular weight polymer chains.[1] Such chains at temperatures below their glass transition temperature (T_g) constitute essentially single-molecule glasses. In microparticles containing only one or just a few chains, the macromolecules are unable to adopt their random-coil conformation since a random coil, on average, occupies only a few percent of the total space accessible to it; random-coil conformations in bulk, as de Gennes[2] has pointed out, require the presence of order $N^{1/2}$ interpenetrating chains (where N = degree of polymerization) to fill the available space. For a high molecular weight polymer, $N^{1/2}$ is of order 100. In bulk single-chain systems, the requirement of adequate space filling necessarily implies that the polymer chains adopt a highly compact conformation that occupies only a few percent of the random-coil volume. An analogous phenomenon has long been known with certain naturally occurring biopolymers, such as globular proteins. The globular concept is equally applicable to microlatex particles containing just a few high molecular weight chains. The question then arises as to whether glasses composed of such globular single- or pauci-chain polystyrene (denoted here by SCPS) differ in any way from ordinary PS glasses that are composed of a large number of interpenetrating and entangled random coils. The purpose of this paper is to report some experimental differences in the spectroscopic and thermal properties of these two different types of glasses and to propose an explanation for these differences in terms of localized cohesional entanglements.

Experimental Section

The compositions (% w/v) of microemulsions polymerized in this study by γ-radiation from a ^{60}Co source were as follows: styrene, 1.90; n-hexanol, 0.95; cetyl trimethylammonium bromide, 1.90; water, 95.25. The microemulsion was prepared by titration at 60 °C and polymerized at this temperature to complete conversion at a dose rate of 4.4 mGy s^{-1}. Pure polymer was harvested by dilution of the latex with methanol (5% w/v), after which the system was allowed to stand for 30 min. The resultant polymer was filtered off using a Teflon membrane, washed three times with methanol, and air dried. The particle size distribution of the microlatex particles prior to harvesting was determined by transmission electron microscopy calibrated using a monodisperse polystyrene latex of 50.0-nm radius. The number- and weight-average diameters were determined to be 19 and 26 nm, respectively. These values were checked by ultracentrifugation, which gave a z-average diameter of 30 nm, somewhat larger than the corresponding electron microscope value of 28 nm; however, the modest agreement between the two methods suggests that the density of the polystyrene in microparticle form is not greatly different from the usual value (1.051 g cm^{-3} at 20 °C) adopted in the ultracentrifugation calculations, especially considering the uncertainty in the literature value of this quantity.[3] Polymer molecular weight was determined by gel permeation chromatography using polystyrene calibration standards. The sample of ordinary PS used was a commercial product. The infrared spectrum of SCPS was recorded on a Bruker IFS 113V FTIR spectrometer at 2-cm^{-1} resolution. The sample of purified SCPS microparticles was mixed with KBr and lightly pressed at 700 MPa to form the compact required to record the spectrum. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer Model DSC-2C system with a data station. Data processing was carried out with the software furnished by the instrument manufacturer. The rate of heating was 10 °C min^{-1} and a nitrogen gas purge was used. The instrument was calibrated with indium metal at the previously stated heating rate.

Results and Discussions

The polystyrene in the microlatex particles had a weight-average molecular weight of $M_w = 4 \times 10^6$. The root-mean-square end-to-end distance of such polymer chains would be about 95 nm if they were in their random-coil conformation. Instead, the chains were generated in microlatex particles of weight-average diameter 26 nm. In this form, the intramolecular expansion factor of each chain is about 0.3 and the volume it occupies is only a few percent of its random-coil volume. From these data, it can be calculated that each microlatex particle contained, on average, only about 1.3 high molecular weight chains. Use of the corresponding number-average values instead of the weight-average values increased the calculated number of chains per particle to 2.2; however, the number-average molecular weight (1×10^6) is unduly sensitive to lower molecular weight species. The relatively broad molecular weight distribution of the polystyrene generated in the

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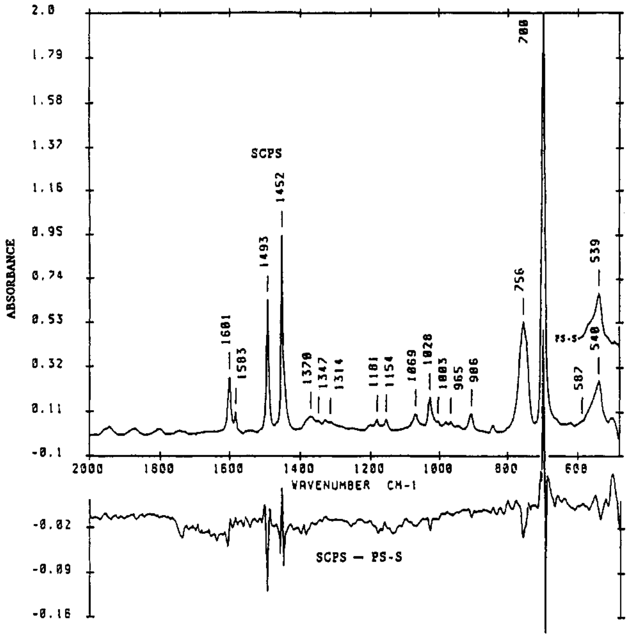

Figure 1. IR spectrum of SCPS and the difference spectrum (SCPS – PS–S).

Table I. Differences in the IR Absorption Bands (in cm^{-1}) of SCPS and PS–S

PS–S	PS–S to SCPS	SCPS
539		540
699	broadened	700
1452	sharpened and the peak absorbance increased	1452
1493	broadened and the peak absorbance decreased	1493
1602	peak moved to lower frequency	1601

microlatex particles is a characteristic feature of microemulsion polymerizations carried out at high dose rates. This broadening appears to be associated with the occurrence of significant mutual annihilation of propagating radicals in particles subjected to high radical flux; as a result, the chain length is controlled not just by chain transfer to monomer, as happens at lower dose rates, but also by bimolecular termination. Harvesting the polymer with methanol could in principle allow some interaction of the chains to occur. However, since care was taken during purification to ensure that the polymer was always maintained some 80 °C below T_g, it seems reasonable to assume that harvesting did not markedly affect the conformational properties of the glasses.

The IR spectrum of SCPS is shown in Figure 1. It is compared with the spectrum of a sample (denoted by PS–S) of the same material that had been dissolved in chloroform and then the solvent removed by evaporation at 60 °C. The dried polymer was then mixed with KBr and pressed into a disk. The difference spectrum (SCPS – PS–S) is shown in the same figure. Table I records some of the differences in the positions and shapes of the absorption bands of the two samples, most of the other bands being virtually identical. The identification of the listed absorption bands is as follows. The 540-cm^{-1} band results from the phenyl ring out of the plane deformation mode of long trans sequences; this is known to be sensitive to heating through the glass transition temperature.[4] The 1452-, 1493-, and 1601-cm^{-1} bands all arise from the phenyl ring stretching modes and are known to be sensitive to hydrostatic pressure.[5,6] All of the aforementioned bands are sensitive to interchain interactions. The 700-cm^{-1} band is the out-of-plane bending mode of the phenyl C–H. Due to the complexity of the effect of the solution evaporation process and the slow diffusion resulting from the high molar mass, the chain conformation of PS–S might not have reached the equilibrium state of fully interpenetrating chains. It is difficult to interpret unequivocally the difference spectrum in terms of the differences in the local environment of the chain segments. Nonetheless, comparison of the band shapes in the 500–600-cm^{-1} region suggests that the polystyrene in SCPS had a higher conformational temperature than that in PS–S. This is inferred from the more pronounced absorption shoulder (see Figure 1) at 568 cm^{-1} for PS–S than for SCPS (the resolved peak actually being located at 557–553 cm^{-1}, depending upon the temperature[4]), which leads to the appearance of a negative peak at 567 cm^{-1} in the difference spectrum (SCPS – PS–S) that is also presented in Figure 1. The slight frequency shift of the 540-cm^{-1} bands of SCPS and PS–S, as detailed in Table I, results in the difference spectrum in this region displaying both positive and negative peaks, the overall shape of which bears a qualitative resemblance to the temperature difference spectrum observed previously[4] on heating multichain polystyrene.

In the case of single-chain particle SCPS, the nearest-neighbor segments in space are necessarily segments of the same chain; these may be located remotely along the contour of the chain but are placed in close proximity by coiling. It seems reasonable to postulate that, for PS–S, the nearest-neighbor segments after dissolution and evaporation are more likely to be those from other interpenetrating chains, similar to an ordinary multichain random-coil PS sample. The conclusion that the compact globular form of polystyrene in SCPS at room temperature appears to have a higher conformational temperature than that in the more random-coil-like PS–S sample is reinforced by the changes in the 1452- and 1601-cm^{-1} bands. It has been reported[5,6] that hydrostatic pressure shifts both of these bands to higher frequencies and causes each of them to broaden. The opposite behavior was observed for these two peaks in going from PS–S to SCPS (Table I), implying that the polystyrene in the SCPS microparticles exists in a more dilated state than that in PS–S. Notice, however, that the 1493-cm^{-1} peak behaves in an apparently contrary fashion, which is difficult to explain. Kumaki[7] has generated single-chain particles of PS (M_w = 3.8 × 10^6) by accumulation on a substrate spread on water. He showed that these particles had a lower refractive index (1.45) compared with that of ordinary PS (1.60). This implied that single-chain PS particles prepared by interfacial spreading had a significantly lower density than multichain PS. It seems unlikely from what was reported in the Experimental Section that the density of the SCPS particles prepared by microemulsion polymerization differs as much from that of ordinary PS as might be inferred from Kumaki's experiments.

A more dramatic difference between single-chain and multichain samples was observed in the DSC results. For both SCPS and an ordinary PS sample, the measuring procedure was as follows: The samples as received were first scanned from 30 to 150 °C (DSC curve i), followed by rapid air quenching to room temperature, and the second scan from 30 to 150 °C made (ii). The sample was held at 130 °C for 3 min and then cooled at 1.25 °C/min to room temperature to start the third scan (iii). The procedure was repeated with a cooling rate of 0.31 °C/min before the fourth scan (iv). A DSC scan was also made on the virgin SCPS sample after being annealed at 90 °C for 45 min (v). The results are summarized in Figure 2 from which curve iii has been omitted because it is similar to curve iv but displays a smaller endothermic peak. The

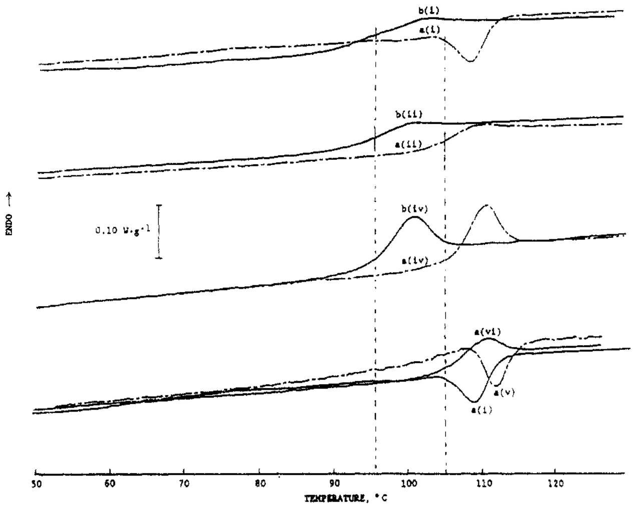

Figure 2. DSC curves for SCPS (a) and ordinary PS (b) for various scan procedures explained in the text. All curves were normalized to the same weight of sample.

most interesting observation is the appearance in curve i of an exothermic peak near T_g for the virgin SCPS sample. This exothermic peak is reminiscent of that reported by Gaur and Wunderlich[8] for small (85-nm diameter) polystyrene latex particles, occurring as it does just below T_g. The exothermic peak disappeared on the second scan (ii). Sub-T_g annealing did not remove the exothermic peak but moved it to a 2.8 °C higher temperature (curve v). Annealing at 100 °C removed the exothermic peak altogether (curve vi). After the first DSC scan to 130 °C, subsequent scans for SCPS are normal, similar in behavior to an ordinary PS sample except that the T_g of SCPS is seemingly higher than that for ordinary PS. The appearance of an endothermic peak around T_g is similar for both samples. The fact that T_g of the ordinary PS, 96 °C, as obtained by the temperature corresponding to half of the endothermic step, is 9 °C lower than that of SCPS on the second scan, 105 °C, is of no particular significance. The values of T_g determined under the same conditions for various commercial PS samples varied widely: Styron 666D (Dow), 94 °C; Styron 685D (Dow), 104 °C; Polystyrol 143E (BASF), 84 °C; Polystyrol 168N (BASF), 104 °C. These commercial PS pellets may contain various amounts of plasticizer and processing additives.

DSC measurements were also made of a PS–S film cast from a solution (1 g L^{-1}) of SCPS in chloroform and vacuum dried at 50 °C for 7 days. The results are summarized in Figure 3. The film as prepared was heated to 130 °C at a rate of 10 °C/min to give curve 1. The film was held at 130 °C for 3 min and then rapidly cooled to room temperature. Curve 2 shows the second DSC run when the film was subsequently heated to 150 °C. The film was next held at 150 °C for 3 min and then rapidly cooled. Curves 3–6 were all obtained similarly by successive heating to 150, 170, 190, and 220 °C, respectively. The lower T_g value observed for the solution-cast film and its gradual increase with increasing temperature is likely to be a consequence of residual solvent being retained in the solution-cast film and is subsequent removal on heating. The T_g value for the solvent-cast film heat treated above 200 °C approached the value observed for heat-treated SCPS, which was constant and independent of the temperature of heat treatment above 130 °C.

Very recently Qian[9] has put forward the concept of local nematic interactions between neighboring chain segments in the condensed state. These nematic interactions constitute a type of chain entanglement that is not topological in character but supplements the more usual topological entanglements. Such cohesional entanglements are important to the physical properties of polymers near T_g and in their glassy state. Below T_g, the average cohesional entanglement spacing along the chain is much smaller than that of the topological entanglements. When these cohesional entanglements lock into place the long-range cooperative conformational changes of the chain that are necessary for rubber elasticity and so prevent their occurrence, the polymer exhibits glassy state properties. During heating, the cohesional entanglements will gradually melt or disentangle, thus unlocking the long-range cooperative motions. As soon as a temperature is reached where the cohesional entanglement spacing along the chain is sufficiently large to permit cooperative changes of conformation involving a hundred or so successive backbone bonds, the polymer transforms into its rubbery state. This is the glass transition. At temperatures higher than T_g, the cohesional entanglement spacing is necessarily greater than the critical length needed for rubber elasticity. Rapid quenching of this rubbery state to temperatures below T_g does not allow sufficient time for the formation of new cohesional entanglements so that the quenched sample on heating displays a simple step endothermic curve (i.e., a conventional second-order-like glass transition). Slow cooling from the rubbery state or sub-T_g annealing of the quenched sample should both result in the formation of new cohesional entanglements along the chain. Consequently, on being heated, an endothermic peak will appear around T_g. The variation in the cohesional entanglement spacing is postulated to be the origin of the thermal history effects that have been long recognized in DSC measurements and which have been described elsewhere.[10-12]

It might be expected that the polystyrene prepared in single-molecule form would have fewer cohesional entanglement regions because the conformations of the polymer chains in the compact globules prepared by direct polymerization are probably kinetically controlled rather than thermodynamically controlled. The appearance of an exotherm in curve i of Figure 2 is really a manifestation of the formation of cohesional entanglements as minimization of the free energy of the polymer becomes possible just below the T_g. It is significant that the magnitude of the total energy involved in the exothermic peak, ca. 1 J g^{-1}, is comparable to that involved in the endothermic peak of slowly cooled or sub-T_g annealed samples. Hence, the interpretation presented here is internally consistent: the exotherm arises from the formation of the localized

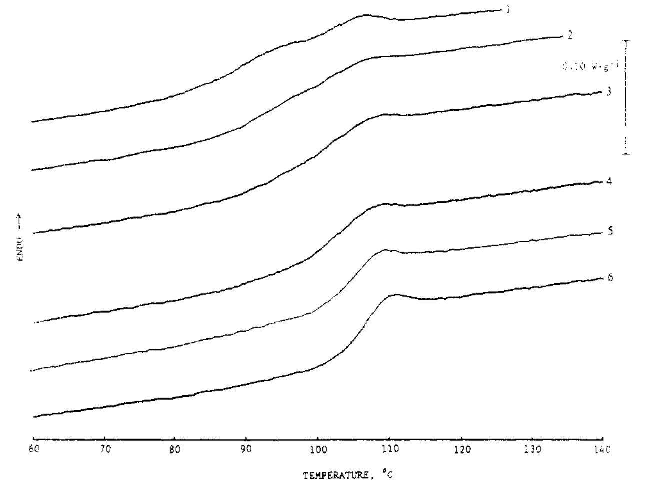

Figure 3. DSC curves for PS–S for various scan procedures elaborated on in the text.

nematic cohesional entanglements, whereas the endotherm results from their destruction (or melting). Gaur and Wunderlich[8] attributed the exotherm on first heating to "stress release", the molecular origin of this so-called stress not being specified. Furthermore, no connection was made between the endothermic and exothermic peaks. The explanation given here provides a physical basis for the stress and makes the important connection between the two types of DSC peaks. The effects that the large surface area of these small particles exert on their thermal properties merit further investigation. Note, in addition, that other explanations have been advanced for the origin of exothermic peaks observed with multichain glasses subjected to mechanical stress, especially where these occur well below T_g.[11,12]

Two further questions merit consideration: First, why does ordinary PS not show an exotherm on first heating through T_g? Second, why does a quenched ordinary PS sample not show an exothermic peak on heating through T_g while on sub-T_g annealing cohesional entanglements are seen to be formed? Herein probably resides the essential differences between single-chain particles and multichain samples. The answer to the first question may reside in the formation of the multichain sample by, e.g., bulk polymerization where the conformations of the chains are thermodynamically rather than kinetically controlled, in contrast to the likely kinetic control in microparticles. Under these circumstances, it would be expected in ordinary polymers that the local cohesional entanglements would be formed during the polymerization process, as the free energy should be easier to minimize in a multichain system. As to the second question, it might be presumed that, even though the cohesional entanglement spacings are large in a multichain sample quenched rapidly from temperatures above T_g, the longer range chain motions are still somewhat hindered kinetically so that the rate of cohesional entanglement formation is very slow on the time scale of the DSC measurements. No exothermic peak is therefore observed. Sub-T_g annealing usually takes a long time to induce an observable effect. In a single-chain particle, no neighboring chains are involved so that it is reasonable to expect that the longer range chain motions will remain more or less free and the kinetics of cohesional entanglement formation will be much faster. If this explanation is correct, it requires some coalescence and interpenetration of the single-molecule coils above T_g in order to explain a similar absence of an exothermic peak for the SCPS sample after rapid quenching.

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