Glass transition of expanded polystyrene coils

Gi Xue*, Yun Lu, Gaoquan Shi and Qinpin Dai†
Department of Chemistry, and † The Solid State Microstructure Laboratory, Nanjing University, Nanjing 210008, The People's Republic of China
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Monodisperse polystyrene (PS), with molecular weight of 1.8×10^6, was dissolved and refluxed in cyclohexane, keeping the polymer concentration below the critical value for chain shrinkage. After rapidly freezing the solution by injecting it directly into liquid nitrogen, the solvent was sublimed so that expanded chain coils with few entanglements could be obtained. The glass transition temperature, T_g, for this material was found to be 45°C lower than that of the ordinary PS, even after annealing up to 180°C. Comparison of the infra-red spectra showed some conformational differences between the rapidly frozen and the ordinary PS. Dilute polymer solution was rotated in a flask while it was immersed in a cold ethanol bath, so that the solution was frozen relatively slowly. After the solvent was sublimed, the resulting PS showed a lower T_g in its first d.s.c. scan, but exhibited the same T_g as ordinary PS after annealing.

(Keywords: glass transition; polystyrene; expanded coil)

Introduction

It has been reported that polystyrene (PS) microparticles were prepared by the free-radical polymerization of styrene in microemulsions[1]. It was expected that the glass transition temperature, T_g, of polymer microparticles, which contain only one or a few macromolecular chains, would be different from that of normal PS. However, annealing these particles at or above their T_g can cause the T_g to shift to a similar value to that of ordinary PS. De Gennes has pointed out that, in single-chain systems, the requirement of adequate space filling implies that the polymer chains adopt a highly compact conformation[2]. On the other hand, polymer chains can expand in a very dilute solution. We injected a dilute solution of PS directly into liquid nitrogen so that the solution was frozen in a fraction of a second. The expanded polymer coils were thus frozen before shrinkage and were expected to maintain their expanded shape in the solid state, since the speed of freezing was extremely fast. After subliming the solvent, PS powder with expanded coils would be obtained. The question then arises as to whether PS glass composed of such expanded coils differs in any way from ordinary PS glasses, which are composed of a large amount of interpenetrating and entangled random coils, and from the PS microparticles. The purpose of this communication is to report some experimental differences in thermal and spectroscopic properties of these different types of glass and to propose an explanation for these differences in terms of localized cohesional entanglements and topological entanglements.

Experimental

Monodisperse PS, with molecular weight of 1.8×10^6 and dispersity of 1.04, was dissolved in purified cyclohexane to make a 0.04% solution and refluxed for 6 h. After rapidly freezing the solution by injecting it directly into liquid nitrogen, the frozen solvent was then sublimed in vacuum. The resulting PS powder, designated as the rapidly frozen (or treated) PS, was examined by means of a Fourier transform infra-red spectrometer (Nicolet FT-TR 170 SX). Differential scanning calorimetry (d.s.c.) 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 heating rate was 10°C min^{-1}, while a nitrogen gas purge was used. An enclosed refrigeration unit (Perkin–Elmer Intracooler II) was attached to the d.s.c. cell for controlled cooling to subambient temperature.

Results and discussion

A dramatic difference between the rapidly frozen PS with expanded coils and the ordinary PS with random coils was obtained in the d.s.c. results, as shown in *Figure 1*. For the rapidly frozen PS, the d.s.c. measuring procedure was as follows: the sample was first scanned from 20 to 130°C (curve A), followed by air cooling to 20°C. A second scan from 20 to 180°C was then made (curve B). The sample was then cooled to 20°C to start the third scan (curve C). The ordinary PS was scanned at the same rate (curve D). All d.s.c. results are summarized in *Table 1*.

Figure 1 shows that the virgin expanded PS coils have a very low apparent T_g, which is 64°C lower than that of ordinary PS. Annealing the sample above the T_g can shift T_g to a higher temperature. The virgin material prepared by the present procedure is in a non-equilibrium state, therefore on heating it is expected that thermal

Table 1 Glass transition temperatures (T_g) of polystyrene

Sample	T_g (°C)
Rapidly frozen PS	
First scan	41
Second scan	60
Third scan	60
Ordinary PS	105

* To whom correspondence should be addressed

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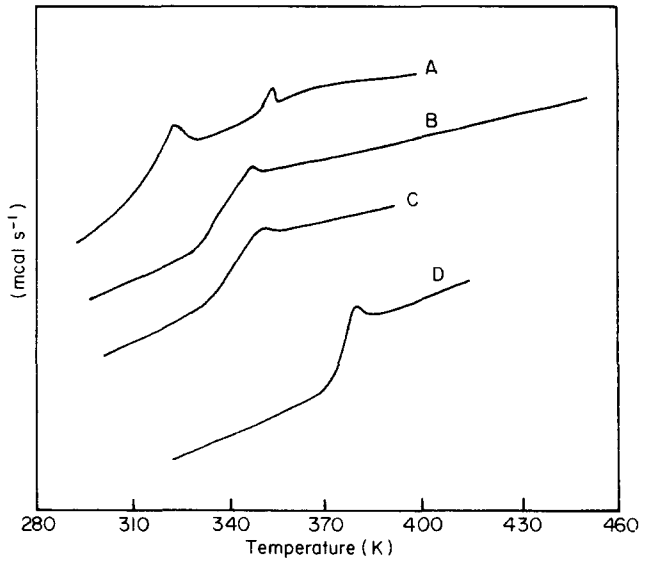

Figure 1 D.s.c. curves of PS samples. Rapidly frozen PS: A, first scan from 20 to 130°C; B, second scan from 20 to 180°C; C, third scan from 20 to 130°C. D, Ordinary PS

changes will be seen in the d.s.c. experiment as a sample goes to its equilibrium condition. The apparent T_g in *Figure 1A* is not a glass transition process in the usual sense. After two scans have been applied, the d.s.c. behaviour of the treated PS composed of expanded coils became nearly constant, indicating that the sample reached the equilibrium state. In the third scan, however, T_g is still 45°C lower than that of ordinary PS, even after heating the treated PS up to 180°C. This feature shows dramatic differences from previous work. It has been reported that the virgin single PS prepared by microemulsion polymerization shows a T_g about 10°C lower than that of ordinary PS, and that its ultimate T_g after annealing at 150°C becomes the same as the T_g of ordinary PS composed of random coils. It should be pointed out that there is one exothermic peak for the rapidly frozen PS in its first scan, but it vanishes in the second scan. This phenomenon has not been observed in either ordinary atactic PS or the PS microparticles. Further examination by electron microscopy found a certain amount of partially crystalline material in the rapidly frozen PS powder. We propose that the exothermic peak in *Figure 1A* is related to the melting process of the partially crystalline material, and we will discuss this in a separate paper[3].

Figure 2 shows the d.s.c. curves of PS glasses prepared by freezing the solution in a bottle immersed in an ethanol bath at −50°C, instead of injecting the solution directly into liquid nitrogen. Cooling in the bottle obviously takes place more slowly than in liquid nitrogen. After the frozen solvent was sublimed the virgin PS powder exhibited a T_g 40°C lower than that of ordinary PS. However, the d.s.c. behaviour of this sample became similar to the ordinary PS after two scans and had been applied, as shown in *Figure 2*. This result is similar to a previous report where the authors claimed that PS microparticles were prepared by a similar treatment process[4]. As described earlier, the apparent T_g of the virgin material is not by any means a T_g in the usual sense before it reaches the equilibrium state.

Single molecules of PS were isolated by the preparation conditions described by Richardson[5] and more recently by Kumaki[6] and Schulz[7]. Qian has recently put forward the concept of local nematic interactions between neighbouring chain segments in the condensed state as the kind of cohesional entanglement usually considered[8]. These cohesional and topological entanglements are important to the physical properties of polymers around T_g and in their glassy state. These entanglements lock into place the long-range cooperative conformational changes of the chain that are necessary for rubber elasticity; as these changes are prevented from occurring, the polymer exhibits glassy-state properties. During heating, the cohesional entanglements will gradually melt or disentangle, thus unlocking the long-range cooperative motions, and the polymer undergoes a transition to the rubbery state. This is the glass transition. It would be expected that the fewer the cohesional and topological entanglements that exist, the lower the T_g exhibited by the polymer. As PS dissolved in cyclohexane above the θ temperature (35°C), making a very dilute solution, the chains expanded.

Qian has put forward another concept of a concentration boundary of the solution from very dilute to semidilute[9]. At and beyond the critical concentration value, C_s, the effect of interchain interactions begins to be felt by the chains in solution. The C_s value of PS with M_w of 6×10^6 was about 0.044%, as measured by excimer fluorescence[9,10]. Based on this concept we propose that the coils of PS in a very dilute solution (concentration below C_s) are expanded with few entanglements. If this solution was frozen fast enough to maintain the expanded shape, PS composed of coils with few entanglements could be obtained in the solid state. These expanded coils are expected to exhibit a T_g much lower than that of ordinary PS. Since recovery of the number of chain entanglements is needed to melt the sample or to make a concentrated solution, simple annealing below the melting point would not increase T_g to the same level as in ordinary PS. This is why the d.s.c. curve C in *Figure 1* shows a T_g 45°C lower than that of ordinary PS, even after annealing at 180°C. However, if the speed of cooling of the dilute polymer solution is not rapid enough during the freezing treatment of the polymer, coils shrink before

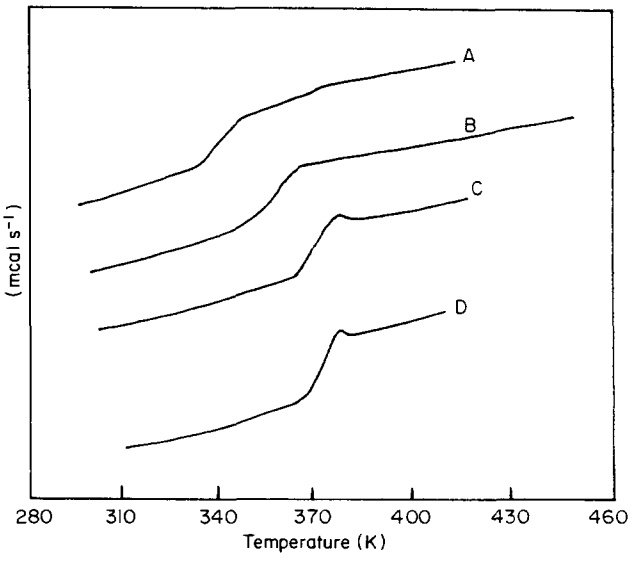

Figure 2 D.s.c. curves of PS samples. A–C, first, second and third scans of PS powder frozen more slowly than the samples in *Figure 1*. D, Ordinary PS

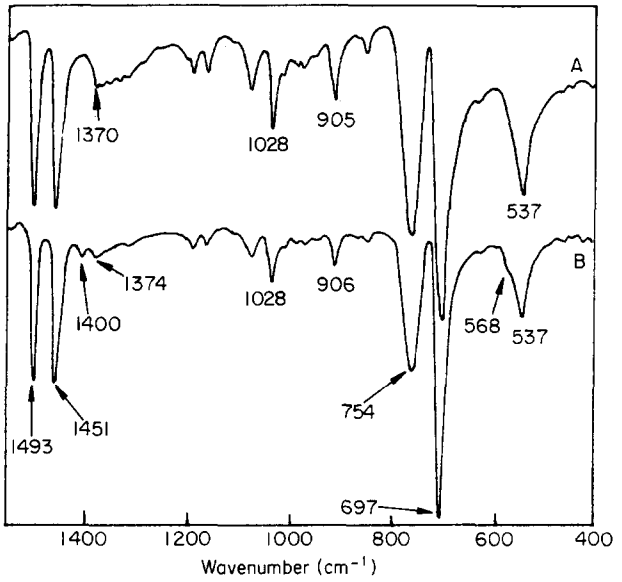

Figure 3 I.r. spectra of PS. A, Ordinary atactic PS; B, rapidly frozen PS

freezing, resulting in a considerable number of chain entanglements. Then the polymer might show a lower T_g in its initial d.s.c. curve due to the effect of the thermal history, but the ultimate T_g after annealing would be about the same as that of ordinary PS. This is the case for the glass transition of so-called microparticles reported previously[4].

Shultz and Young prepared PS/poly(methyl methacrylate) (PMMA) homogeneous blends by freezing the co-solution (5%) in ice/water followed by sublimation of the solvent. D.s.c. revealed a single T_g for the blends, intermediate between the T_gs of the component polymers[11]. Since the concentration used in that experiment was much greater than C_s and the rate of cooling provided by ice/water was not so fast as that by liquid nitrogen, expanded coils of polymer chains were not expected to form in the solid blends of PS/PMMA. As a result, the material exhibited a much higher T_g than the expanded coils of PS prepared by the present procedure.

The i.r. spectra of the rapidly frozen PS and ordinary PS are shown in *Figure 3*. Several differences are observed in the i.r. data, related to the different chain conformations of the two samples, especially in the regions of 537, 697, 754 and 1400 cm^{-1}. Atactic PS exhibits a broad band at 537 cm^{-1}, which results from the phenyl ring in the out-of-plane deformation mode of the long *trans* sequence; this is known to be sensitive to heating through the glass transition[11]. Comparison of the band shapes in this region suggests that the rapidly frozen PS had a lower conformational temperature than the ordinary PS. This is inferred from the more pronounced absorption shoulder (*Figure 3B*) at 568 cm^{-1}. The 698 cm^{-1} band is the phenyl ring bending mode and the 754 cm^{-1} band is due to the five adjacent H wag modes of the monosubstituted benzene. The relative intensities of these two bands are different in spectra *Figure 3A* and *B*. In the 1100–1400 cm^{-1} region, a number of conformation-sensitive skeletal vibrations exist. It is also quite likely that these bands are sensitive to chain packing. Several differences can be observed between the two i.r. spectra, such as the intensity changes and the appearance of a new band at 1400 cm^{-1} for the rapidly frozen PS. Due to the complexity of the effect of the freezing process, the chain conformation of the treated PS might not have reached the equilibrium state. It is difficult to interpret unequivocally the spectral differences in terms of the differences in the local environment of the chain segments.

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