

Glass transition temperature of polystyrene microparticles

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Polystyrene (PS) microparticles were prepared by freeze-drying a very dilute cyclohexane solution and by spraying a dilute benzene solution into methanol. D.s.c. studies showed that the microparticles have a transition at a temperature lower than the T_g of bulk PS. This low temperature transition was regarded as the glass transition of the PS microparticles, and it was suggested that the decrease in T_g of the particles was due to their high surface area to volume ratio.

(Keywords: polystyrene; microparticles; d.s.c.; glass transition temperature)

Introduction

The state of polymer microparticles containing only one or a few high molecular weight polymer chains is expected to be different from that of the bulk polymer, and some unusual behaviour of the microparticles could be expected. In a microparticle, it was proposed that the intramolecular interaction causes the macromolecule to be greatly compressed and the chains are unable to adopt the random coil conformation, as adopted by a macromolecule in the amorphous phase¹. Several researchers^{2,3} have suggested that the density of microparticles is similar to or slightly less than that of the bulk.

On the other hand, the particle has a very small diameter and a high surface area to volume ratio. Kumaki³ has reported that the particles can only pack loosely, and the packing of the particles contains about 20–30 vol% voids. This means that more voids or a higher surface area exist in the packing than in the bulk. Furthermore, the molecules in particles are free of the intermolecular entanglement that is characteristic of the bulk. This behaviour is expected to cause easier movement of the molecules in particles than in bulk. Our recent dynamic mechanical analysis for crazed samples of polystyrene (PS) shows that the glass transition temperature of PS in craze fibrils is about 45°C lower than that of the bulk⁴, due to their very high surface area to volume ratio. The purpose of this communication is to report the similar characteristics of the glass transition of PS microparticles.

Experimental

A narrow molecular weight disperse PS ($M_n = 2.67 \times 10^5$, $M_w/M_n = 1.07$) obtained from Nanjing University was used. The sample is referred to as the ordinary sample (OPS). Two samples of microparticles were prepared by freeze-drying a dilute solution and by spraying dilute solution into methanol as follows. Freeze-dried sample (FPS): 150 cm³ cyclohexane solution with a concentration 0.07% in a round-bottom flask was rotated while it was

immersed in liquid nitrogen, so that it froze within about 1 min. The frozen solution was maintained between –10 and –5°C, and was dried in vacuum at about 13.3 Pa for 18 h. After the solvent had been extracted, the sample was maintained in vacuum for an additional 3 days at 10°C to remove any residual solvent. Sprayed sample (SPS): 10 cm³ benzene solution with a concentration 0.5% was sprayed into 200 cm³ methanol with vigorous agitation. The emulsion-like mixture formed was centrifuged to obtain a white powder. SPS was obtained by drying the powder in vacuum at 10°C for 3 days.

The thermal behaviour of all samples was measured by using a differential scanning calorimeter (Perkin–Elmer Model DSC-2C) with a heating rate of 10°C min⁻¹. A refrigeration unit was attached to the d.s.c. block for controlled cooling to subambient temperatures. The size of the microparticles was observed by transmission electron microscopy (TEM) as follows: a little particle powder was dissociated in 50 ml methanol by vigorously agitating the mixture for 3 h and the mixture was cast onto a microscope grid. After the methanol had evaporated, the sample was stained with OsO₄ and investigated by TEM.

Results and discussion

In dilute solution, polymers can exist as isolated molecules. When the solution is freeze-dried at low temperature, the isolated polymer chains are expected to have a structure of non-interpenetrating spheroids. If they were in their random coil conformation, the root-mean square end-to-end distance of such polymer chains would be about 11 nm. If they were in a more compressed conformation with density similar to that in the bulk, the diameter of the spheroids would be about 9.5 nm.

A microphotograph of the FPS microparticles is shown in *Figure 1a*. It shows that the diameter of the particles is larger than that of single-chain particles, as discussed above, ranging from 20 to 60 nm. This implies that each particle contains two to five chains by supposing that the particle is a compact spheroid. Because the θ

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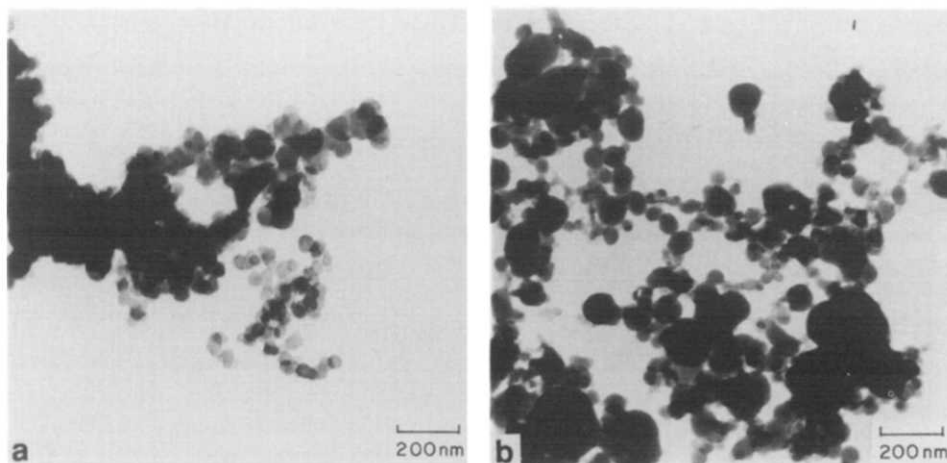


Figure 1 TEM pictures of the microparticles: (a) FPS; (b) SPS

temperature of the cyclohexane is about 35°C, it is difficult to avoid phase separation of the solution during cooling and the concentrated microphase of solution may be formed before the solution is frozen, therefore each concentrated microphase may contain a few polymer chains. It is possible that the chains in the concentrated microphase partially interpenetrate. The microparticles of the sample are expected to correspond to the microphase in solution. Figure 1a also shows that the microparticles tend to pack loosely. It is expected that the collection of particles has a lower density than the bulk.

For the SPS microparticles, the size of the particles was dependent on the concentration of the solution and the size of particles of the spray. Figure 1b shows that the size distribution of the sprayed particles is slightly larger than the freeze-dried particles.

A dramatic difference between microparticles of PS and OPS samples was observed in the d.s.c. results (Figure 2). The measuring procedure for FPS was as follows: the sample was first scanned from -30 to 140°C (curve 1), then followed by air cooling to room temperature. The procedure was repeated with the same cooling routine for the second scan from -30 to 170°C (curve 2), for the third scan from -30 to 180°C (curve 3), and for the last scan (curve 4). Two scans were applied for the SPS sample (Figure 3). The first scan was from -30 to 140°C, then the sample was air cooled to room temperature and the second scan was applied from -30 to 140°C. All d.s.c. results are summarized in Table 1. Figure 2 shows that the virgin FPS sample has a very low glass transition temperature (T_g), 40°C lower than that of the OPS sample. Annealing the sample above T_g can shift T_g to higher temperature, and after three scans have been applied the d.s.c. behaviour of the sample becomes similar to the OPS sample. The d.s.c. results of SPS (Figure 3) show a similar transition behaviour to FPS. The virgin SPS sample also has a low T_g at 67.1°C, which is 38°C lower than that of OPS. But the intensity of this transition is weaker than FPS. The microphotographs in Figure 1 show that the amount of small microparticles with a diameter similar to FPS, which is expected to have a low T_g , is low in the SPS sample. Another interesting observation is the appearance of two exothermic peaks around the T_g of OPS in the first scan of the SPS sample; these peaks vanished in the second scan. This

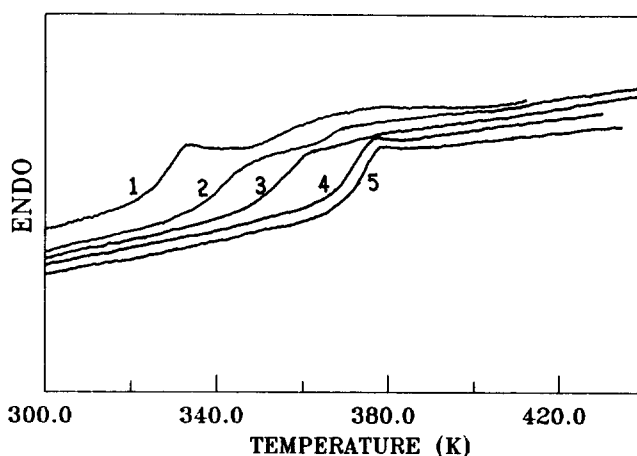


Figure 2 D.s.c. curves for FPS: 1, first scan; 2, second scan; 3, third scan; 4, fourth scan; 5, first scan for OPS. All curves were normalized to the same weight of sample

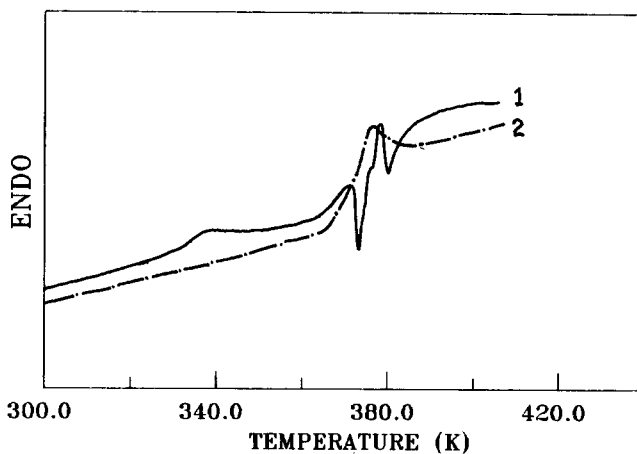


Figure 3 D.s.c. curves for SPS: 1, first scan; 2, second scan

Table 1 T_g (°C) of the samples measured by d.s.c.

Scan	FPS	SPS	OPS
1	65.0	67.1	105.1
2	76.1	103.4	
3	88.7		
4	99.3		

phenomenon has not been observed in the FPS sample, in which the particle size is smaller than in SPS. Gaur and Wunderlich⁵ reported a similar exothermic peak for small PS latex particles with diameters of 85 and 222 nm. So, the exothermic peaks in curve 1 of *Figure 3* are thought to be due to the larger particles, the diameter of which was measured from microscopy (*Figure 1b*) to be in the range of 60–200 nm.

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