Chain Conformation Change upon Heating for Pauci-chain Polystyrene Microsphere Made by Microemulsion Polymerization

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SUMMARY: The conformation change of pauci-chain polystyrene microsphere (micro-PS) upon heating was investigated by in-situ FTIR. For the peaks at 1492 and 1452 cm^{-1} due to phenyl ring semicircle stretch, there are two discontinuities in the plots of peak height versus temperature. The first discontinuity at around 100 °C corresponds to the glass transition. The second discontinuity at about 155 °C is in good agreement with the second exotherm in the first DSC scan, which clearly suggests a non-negligible change of the chain conformation at this temperature. This finding may be of help in further illustrating the two exotherms of micro-PS in its first DSC scan.

Introduction

Microemulsion polymerization has been widely studied since the first studies by Stoffer^1,2), Atik^3), etc. in the early 1980's. Microemulsion polymerization is very capable of producing polymer particles in the diameter range of 10-50 nm^4,5). Considering its high molecular weight (10^6 or above), each microsphere generally contains only one or a few polymer chains. It can be thus called single- or pauci-chain polymer microsphere^6-9). Qian et al. found that the single-chain polystyrene glass prepared by microemulsion polymerization had a higher conformational temperature than ordinary multichain PS, and displayed an exotherm near Tg during the first differential scanning calorimetry (DSC) scan^6). The

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results were interpreted in terms of the existence of nematic localized cohesional entanglements in the PS “single chain glass”. The density of polystyrene particles prepared by microemulsion polymerization was 0.95 from porosimetry7) or 0.92 g/cm^3 by laser light scattering8) by Wu et al., much lower than that of ordinary PS, i.e., 1.05 g/cm^3, suggesting their free volume is significantly greater.

On the other hand, Mahr10) found that polystyrene microspheres (particle diameter of 109 nm and M_w of 8.46×10^4) made by conventional emulsion polymerization displayed an exotherm above its Tg in the first DSC scan. This exotherm was ascribed to the sintering of polystyrene microsphere, i.e., the energy release due to the loss of its surface area10). Poly(vinylidene chloride) particle showed a similar thermal behavior. Guar and Wunderlich attributed this kind of exotherm of polystyrene microsphere (85-nm diameter) to stress release11). However, in these cases10,11), the multi-chain systems, typically containing the number of chains in the order of 10^3 per particle, were investigated, which may be much different from the pauci-chain particles.

We reported previously the novel characteristics of pauci-chain polystyrene microspheres (micro-PS) made by microemulsion polymerization9). The configuration of micro-PS was essentially atactic, but its conformation was much different from ordinary PS. Individual chains are highly compact, while the whole structure of the microsphere is relatively loose in comparison with a random-coil chain in a multi-chain system. During the first DSC scan, micro-PS displayed an irregular exotherm above glass transition and an exotherm of about 6.4 J/g at around 157 °C. Both exotherms disappeared and only a normal glass transition was shown in the subsequent scan. The first exotherm might be due to the sintering of polystyrene microspheres with small particle size. Based on wide-angle X-ray diffraction (WAXD) results, the second exotherm could be related to the special conformation of individual polystyrene chains: upon heating during DSC scan, phenyl ring could stack to form some kind of ordered regions inside micro-PS. The special conformation of individual chains is the driving force leading to the novel thermal behaviors.

In this paper, the conformation change of micro-PS chain upon heating will be demonstrated by in-situ FTIR investigation. The chain conformation change is consistent with the glass transition and the second exotherm for micro-PS during the first DSC scan.

Experimental section

Materials. Styrene was distilled twice under reduced pressure before polymerization. Octylphenol polyethoxyethanol (OP-10) was used as received. Potassium persulfate (KPS) was purified by crystallization in water. Deionized water was used for all experiments.

Polymerization. The microemulsion was prepared by dropwise addition of styrene into OP-10/H_2O system at room temperature, and polymerized in a three-necked flask under a pure nitrogen atmosphere at 35 °C. The recipe was as follows (wt%): styrene 2.18, OP-10 14.53, and water 83.19. The concentration of KPS was 0.38 mM, based on the total reaction charge.

Purification of PS microparticles. Polystyrene latexes were precipitated in methanol and filtered with a Buchner filter with granular frit under reduced pressure. The crude micro-PS was washed extensively with water and methanol to remove emulsifier, then dried in a vacuum oven. The temperature was always kept below 50 °C during the purification to ensure that the conformation of micro-PS would not be changed.

In-situ FTIR investigation. In order to keep track of the conformation change of PS chains in micro-PS during heating-up process, micro-PS was heated from ambient temperature to 180 °C while IR spectra were simultaneously collected. Heating was controlled by an Omega CS-4001KC hot stage at an accuracy of ±1 °C to allow the simultaneous spectral collection. Samples were prepared by mixing with KBr and pressing into a compact pellet. All spectra were recorded at 4 cm^{-1} resolution with a Nicolet Magna 550 FTIR spectrometer, with 32 scans per spectrum. An ordinary PS (o-PS, $M_n = 4\times10^4$, courtesy of Prof. M. Jiang at Fudan University) prepared by anionic polymerization was also investigated by a similar procedure.

Results and Discussion

The produced micro-PS has a weight-average molecular weight (M_w) of 6.4×10^5 and a weight-average particle diameter (D_w) of 18.2 nm, thus the number of polystyrene chain

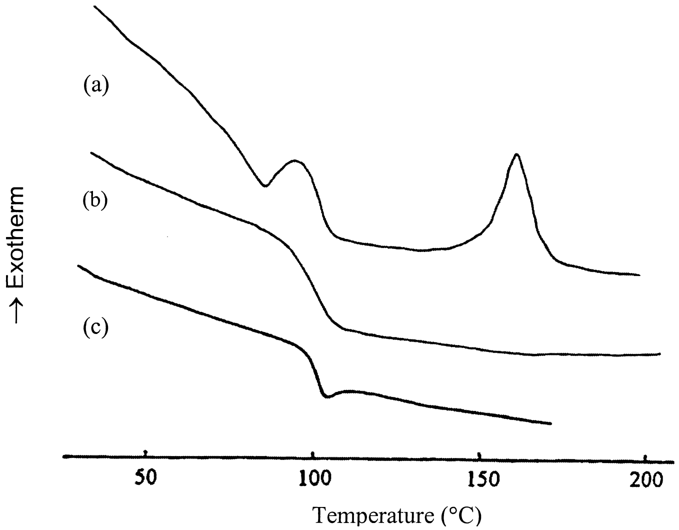

Figure 1. DSC curves of (a) first scan of micro-PS, (b) second scan of micro-PS, and (c) o-PS, on a Setaram CS-92 instrument at a heating rate of 10 °C/min.

per particle is approximately 2.7 (pauci-chain particle). The DSC curves for micro-PS and o-PS are shown in Figure 1. Ordinary PS (o-PS) demonstrated a glass temperature at about 100 °C, while micro-PS displayed two exotherms in its first scan. The first irregular exotherm overlapped with the glass transition, and the second one appeared at about 157 °C (Figure 1a). Both exotherms disappeared and only a glass transition was shown in the subsequent scan (Figure 1b). The first exotherm might be due to the sintering of polystyrene microspheres, and the second one corresponded to some ordered region formed at around 157 °C9). It was also shown previously that the exotherms were not due to the stereoregularity of micro-PS chain9). The formation of the ordered structure may be related to the conformation change of micro-PS chain, especially the conformation change of phenyl ring, which will be studied by in-situ FTIR as follows.

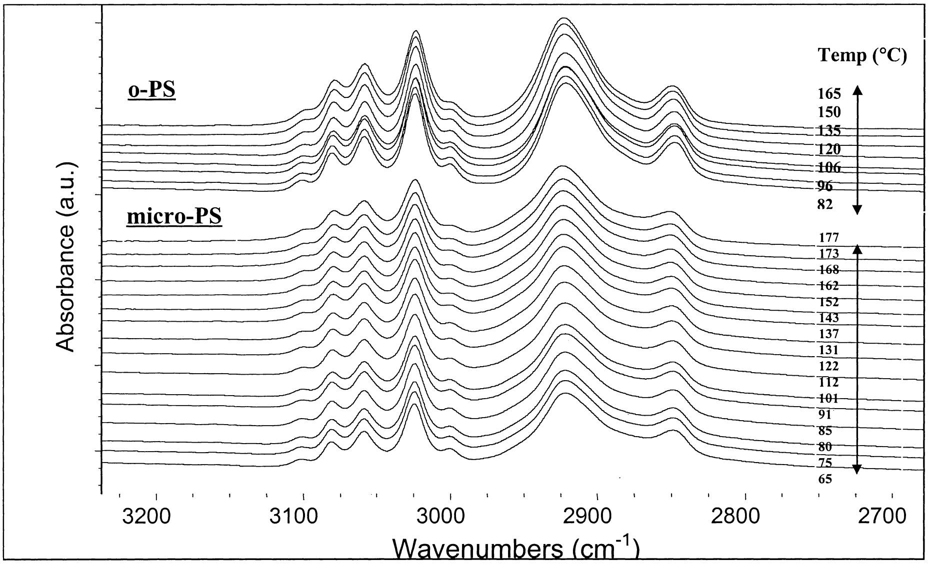

Figure 2. FTIR spectra of micro-PS (bottom part) and o-PS (upper part) of frequency-expanded scale between 3200 and 2700 cm^{-1}.

It was found that noise in the FTIR spectra increased with the increasing temperature, especially at the region from 1300 to 2000 cm^{-1}. Despite the noise, it was possible to observe the effect of temperature change on the characteristic peaks of PS. Attention was focused on the changes of the characteristic peaks[12,13)] at 3000-3100 cm^{-1} (aromatic CH stretch), 2924 cm^{-1} (CH_2 asymmetric stretch), 1492 and 1452 cm^{-1} (ring semicircle stretch), 758 cm^{-1} (mono-substituted ring in-phase H wag), 697 cm^{-1} (mono-substituted ring out-of-plane bend), and so on. Infrared spectra of frequency-expanded scale between 3200 and 2700 cm^{-1} (Figure 2), and between 1200 and 600 cm^{-1}, clearly show that no obvious peak change for both micro-PS and o-PS could be detected. It implies that temperature change from ambient temperature to about 170 °C does not have major influence on CH_2 stretch, phenyl ring out-of-plane bend, and phenyl ring in-phase H-wag.

On the other hand, peaks at 1492.6 and 1452 cm^{-1} red-shifted to 1490.7 and 1450 cm^{-1}, respectively, as shown in Figure 3. Both peaks correspond to ring semicircle stretch. Because the resolution was 4 cm^{-1}, these two peaks are zigzag in shape, but this does not

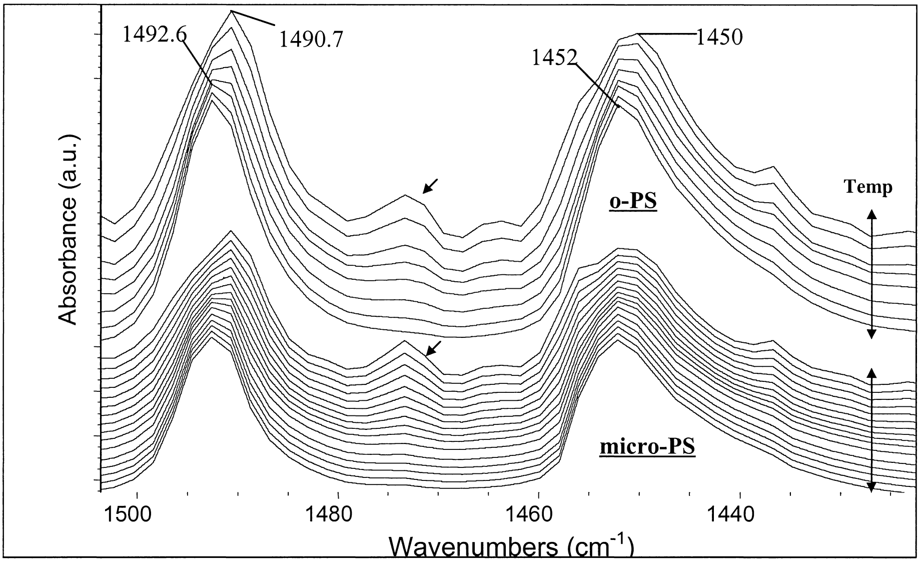

Figure 3. FTIR spectra of micro-PS (bottom part) and o-PS (upper part) of frequency-expanded scale between 1505 and 1420 cm^{-1}. Temperature scale is the same with Figure 1. Small peaks indicated by an arrow are believed to result from noise enlargement with the increasing temperature.

interfere seriously with the analysis of temperature effects. To illustrate the temperature effect, the peak 1452 cm^{-1} will be divided into two parts: 1452 and 1450 cm^{-1}; and so for peak 1492.6 cm^{-1}: 1492.6 and 1490.7 cm^{-1}. Plots of height and height ratio of 1450 and 1452 cm^{-1} versus temperature are shown in Figures 4 and 5, respectively. For micro-PS, peak heights at 1452 and 1450 cm^{-1} both decrease with the increasing temperature (Figure 4), but two obvious turning points (discontinuity) at around 100 and 155 °C are shown. These two turning points are also illustrated clearly in a plot of peak height ratio A1450/A1452 versus temperature in Figure 5. A1450/A1452 ratio increases as temperature increases, indicating the peak frequency red-shifts upon heating. However, for o-PS, as shown in Figures 6 and 7, only one turning point at about 100 °C can be seen. This is consistent with an early result reported by Joss et al.,[14] in which a discontinuity near 100 °C for atactic PS was shown in a plot of peak frequency at 1452 cm^{-1} versus temperature.

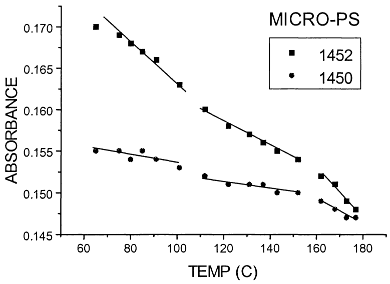

Figure 4. Peak height of 1452 and 1450 cm^{-1} as a function of temperature for micro-PS.

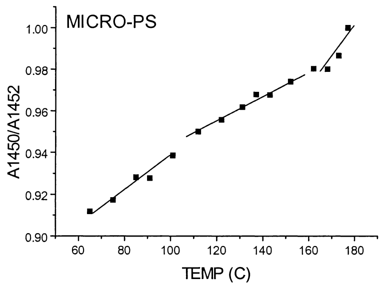

Figure 5. Peak height ratio of A1450/A1452 as a function of temperature for micro-PS.

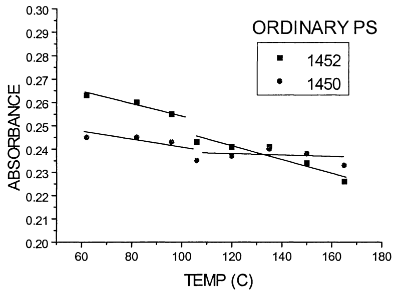

Figure 6. Peak height of 1452 and 1450 cm^{-1} as a function of temperature for o-PS.

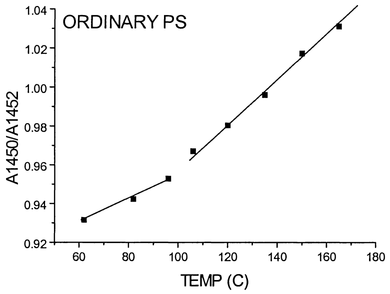

Figure 7. Peak height ratio of A1450/A1452 as a function of temperature for o-PS.

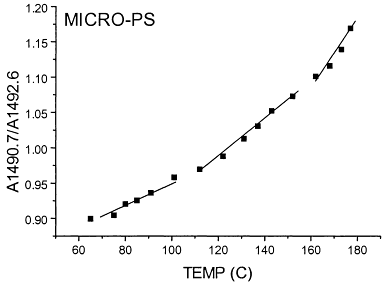

Figure 8. Peak height ratio of A1490.7/ A1492.6 as a function of temperature for micro-PS.

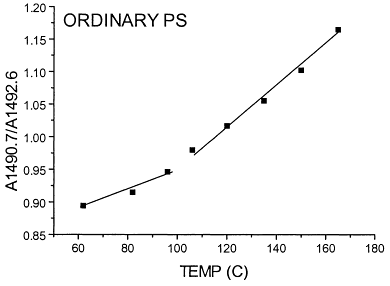

Figure 9. Peak height ratio of A1490.7/ A1492.6 as a function of temperature for o-PS.

As seen in Figures 8 and 9, peak height ratio of A1490.7/A1492.6 as a function of temperature for micro-PS and o-PS gives the similar trends.

For o-PS, the discontinuity at 100 °C corresponds to its glass transition. For micro-PS, the two above-shown turning points are in good agreement with the glass transition and the second exotherm, respectively, in the first DSC scan. The second discontinuity in the plot of peak height ratio versus temperature clearly suggests a non-negligible change of the chain conformation. The change of chain conformation might be brought about by the change of phenyl ring stretch mode, which may be due to the formation of phenyl ring stacking. This result further ascertains our understandings of the two exotherms of micro-PS in its first DSC scan9).

Acknowledgments

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