Novel Characteristics of Polystyrene Microspheres Prepared by Microemulsion Polymerization

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ABSTRACT: Two kinds of styrene microemulsion systems were polymerized to prepare polystyrene microspheres (micro-PS), one emulsified by sodium dodecyl sulfate (SDS) and coemulsified by 1-pentanol and the other emulsified by octylphenoxypoly(ethoxyethanol) (OP-10). Micro-PS possessed an essentially atactic configuration from ^{1}H-NMR measurement. Comparison of IR spectra showed some conformational differences between micro-PS and ordinary atactic PS (o-PS). Each polystyrene microsphere contains only about three macromolecular chains (so-called pauci-chain microspheres), which adopt a special conformation: individual chains are highly compact, while the whole structure of the microsphere is relatively loose in comparison with a random-coil chain in a multichain system. There were apparent differences in thermal behaviors between micro-PS and o-PS during the DSC scan. Micro-PS displayed two exotherms near 107 and 157 °C during the first scan. In the subsequent scan, both exotherms disappeared and only one glass transition similar to o-PS was shown. The first exotherm might be due to the sintering of polystyrene microspheres with small particle sizes. From wide-angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM) studies, the second exotherm could be ascribed to the relatively compact conformation of polystyrene chains and the consequently formed slightly ordered regions inside micro-PS during the heating process. The special conformation was the driving force leading to its novel thermal behaviors. This is perhaps the first report that polystyrene from direct free radical polymerization has the ability to form some kind of ordered structure.

Introduction

It is well-known that ordinary multichain polystyrene (o-PS) is composed of a large number of interpenetrating and entangled random-coil polystyrene chains. As for the microsphere containing single- or pauci-chain PS, up to now, however, there is only very little description of its conformation and corresponding thermal behaviors.

There are two main experimental methods to prepare single- or pauci-chain polystyrene, one by a physical route and the other by a chemical route, i.e. microemulsion polymerization.[1,2] Among physical methods, one is from a very dilute PS solution by atomizer spraying[3] or freeze-drying[4] and another one by accumulating single-chain PS from the water surface onto a substrate,[5] and so on.

Qian et al.[2] found that the single-chain polystyrene glass prepared by microemulsion polymerization had a higher conformational temperature than ordinary multichain PS from FTIR and displayed an exotherm near T_g during the first DSC scan, and the results were interpreted in terms of the existence of nematic localized cohesional entanglements in PS glass. As to the exotherm shown on DSC curves for atactic polystyrene microspheres, there are some different arguments in the literature.[6−8] Mahr[6] found that polystyrene microspheres prepared by conventional emulsion polymerization with a uniform particle size of 0.109 μm and M_w of 8.46×10^4 displayed an exotherm above its T_g, which was interpreted by the sintering of the polystyrene microsphere, i.e., the energy release due to the loss of surface area. Poly(vinylidene chloride) showed similar thermal behavior.[6] Guar and Wunderlich attributed this kind of exotherm of the polystyrene microsphere (85 nm diameter) to stress release.[7]

Pauci-chain polystyrene particles prepared from a physical route by Xue et al.[3,4] had a very low T_g, which is 45 deg lower than that of o-PS due to their high ratio of surface area to volume and showed some conformational differences from ordinary PS in the IR spectra. There were two exotherms both near the T_g of ordinary polystyrene in the first DSC scan for a PS particle prepared by the spraying method, but none for the quick cooling treatment.[3] Furthermore, Xue et al. reported there existed a certain amount of imperfect crystalline material in the PS particles obtained by the quick cooling treatment.[9]

De Gennes has pointed out that, in a single chain system, the requirement of adequate space filling implies that the polymer chains adopt a highly compact conformation, and the volume it occupies is only a few percent of its random-coil volume.[10] The density of pauci-chain polystyrene particles obtained from microemulsion polymerization was 0.95 g/cm^3 from porosimetry[11] or 0.92 g/cm^3 by laser light scattering[12] by Wu et al. The chain entanglement and interpenetrating style in micro-PS is different from that generated by freeze-drying or atomizer spraying. The conformation of micro-PS may be complicated than the latter, which will lead to different thermal behaviors between them.

The purpose of this paper is to report some experimental differences of micro-PS and o-PS during differential scanning calorimetry (DSC) and to purpose an explanation consistent with the results from wide-angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM) investigations of these materials.

Experimental Section

Materials. Styrene from Shanghai Gaoqiao Chemical Co. was distilled twice under reduced pressure before polymerization. Sodium dodecyl sulfate (SDS), obtained from P. T. Palekao Co., was purified by recrystallization, and octylphenoxypoly(ethoxyethanol) (OP-10, from Rohm & Hass Co.) and

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Table 1. Molecular Weights and Particle Sizes of Synthesized Polystyrene Latexes

sample	M_w ($\times 10^5$)	d_M (M_w/M_n)	D_w (nm)	d_D (D_w/D_n)	N_p
micro-PS−SDS	9.8	1.2	21.6	1.6	3.0
PS−SDS-α	3.4	1.7	24.7	1.6	14.7
micro-PS−OP	6.4	1.2	18.2	1.4	2.7
conv-PS	14.0	2.0	53.8	1.2	36.8

1-pentanol were used as received. Potassium persulfate (KPS) from Shanghai First Reagent Plant was purified by crystallization in water. Monodisperse atactic polystyrene (o-PS) with a weight-average molecular weight of 45.52 × 10^4 and isotactic polystyrene (iso-PS) with an isotacticity of 90% were kindly provided by Jilin University and Scientific Polymer Products Inc., respectively. Deionized water was used for all experiments.

Polymerization. The microemulsion was prepared by dropwise addition of styrene into the SDS/1-pentanol/H_2O or OP-10/H_2O system at room temperature and polymerized in a three-necked flask under a pure nitrogen atmosphere to complete conversion at 70 °C for the former (micro-PS−SDS) and at 35 °C for the latter system (micro-PS−OP). The recipe was as follows (wt %): styrene 1.37, SDS 10.10, 1-pentanol 1.24, and water 87.29; or styrene 2.18, OP-10 14.53, and water 83.19. The concentration of KPS was 0.38 mM for both systems. In addition, for the system emulsified by SDS, a molecular weight adjusting agent, the dimer of α-methylstyrene (0.3% wt of monomer) was added, and the product was designated as PS−SDS-α. A conventional emulsion systems with styrene 7.84 wt %, SDS 1.96 wt %, water 90.20 wt %, and KPS 3.60 mM was also polymerized at 70 °C, and the product was designated as conv-PS.

Purification of PS Latexes. Polystyrene latexes were precipitated in methanol and filtered with a Buchner filter with granular fit. The crude micro-PS was washed extensively with water and methanol to remove emulsifier and 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 was not changed. Some of micro-PS was dissolved in toluene and reprecipitated in methanol. After filtration and drying, the final product (r-PS) was obtained. The same purification procedure was used for conv-PS.

Characterization. Differential scanning calorimetry (DSC) measurements were performed on a Setaram CS-92 instrument, with the heating rate of 10 °C/min, while a nitrogen gas purge was used. Data processing was carried out with the software furnished by the instrument manufacturer. Molecular weight and molecular weight distribution (MW & MWD) were measured on a Waters 510 gel permeation chromatographic instrument, with polystyrene standards used for calibration and THF as eluent. Particle size and particle size distribution (PS & PSD) were measured on a Malvern Autosizer IIC, and the results were checked by transmission electronic microscopy (TEM) using a Hitachi H-500H microscope. The infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer, and the samples were prepared by mixing with KBr and pressing into a compact pellet. ^{1}H-NMR spectra were obtained from a Bruker MSL-300 spectrometer using $CDCl_3$ as the solvent. The condensed-state properties were examined on a D/MAX-rB wide-angle X-ray diffractometer and a Leitz polarizing optical microscope, respectively.

Results and Discussion

Characterization of Synthesized PS Microlatexes. Molecular weights and particle sizes of polystyrene latexes are given in Table 1. Micro-PS−SDS prepared from the microemulsion emulsified by SDS had a weight-average particle size D_w = 21.6 nm, determined with the Malvern Autosizer IIC, which was consistent with the result from TEM (see Figure 1). Based on the data in Table 1, the macromolecular chain number per microsphere (N_p) can be estimated as follows:

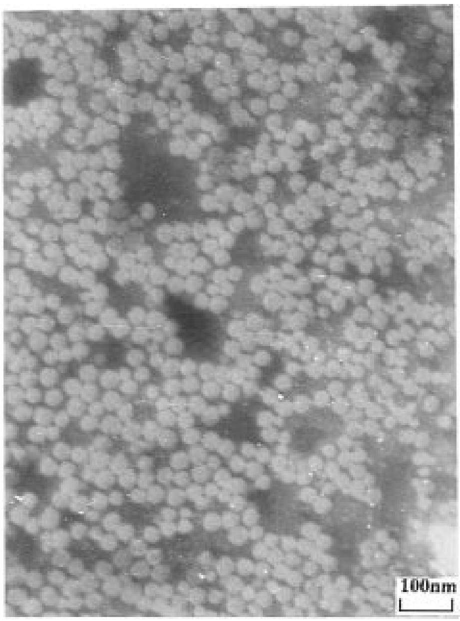

Figure 1. TEM photograph of micro-PS−SDS.

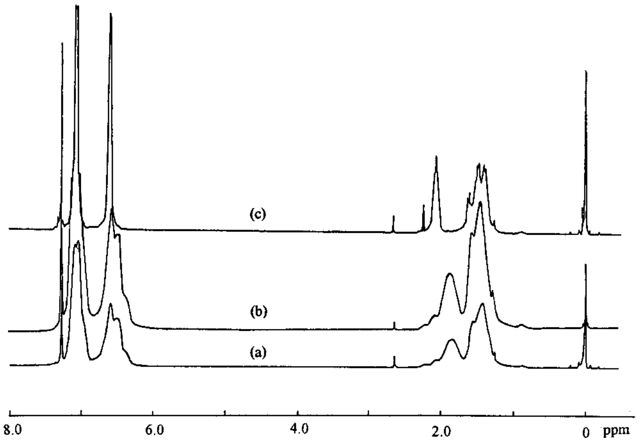

Figure 2. ^{1}H-NMR spectra of (a) atactic o-PS, (b) micro-PS−SDS, and (c) iso-PS.

$$N_p = (1/6)\pi D_w^{\,3} d_p/(M_w/N_A) \tag{1}$$

In above equation, d_p refers to the density of PS latexes, i.e., 0.92 g/cm^3 for micro-PS from Wu et al.[12] and 1.05 g/cm^3 for conv-PS and PS−SDS-α, respectively, and N_A is the Avogadro constant. For example, N_p of micro-PS−SDS is 3.0 from eq 1.

^{1}H-NMR spectra of micro-PS−SDS, ordinary atactic PS (o-PS), and iso-PS are shown in Figure 2. The iso-PS has very sharp peaks, and the methylene group (CH_2) absorption is split, while micro-PS and o-PS have similar broad absorptions, which suggests that micro-PS−SDS is essentially atactic. Moreover, no signal of monomer sytrene was demonstrated in the NMR spectrum (e.g., peaks at 5−6 ppm), indicating no existence of unreacted styrene in the purified PS microsphere. The IR spectra of micro-PS−SDS and o-PS are shown in Figure 3. There are some differences between micro-PS−SDS and o-PS with the absorption bands of 696, 905, 1202, and 1600 cm^{-1}; for example, the peak at 696.0 cm^{-1} shifted about 3 cm^{-1} in comparison with o-PS. On the other hand, no characteristic absorption of SDS

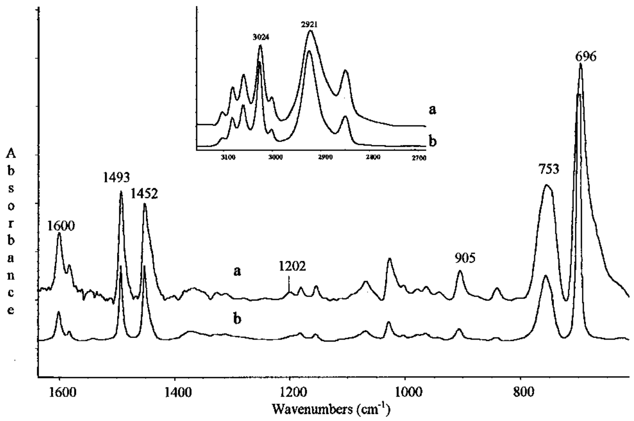

Figure 3. IR spectra of (a) micro-PS–SDS and (b) atactic o-PS.

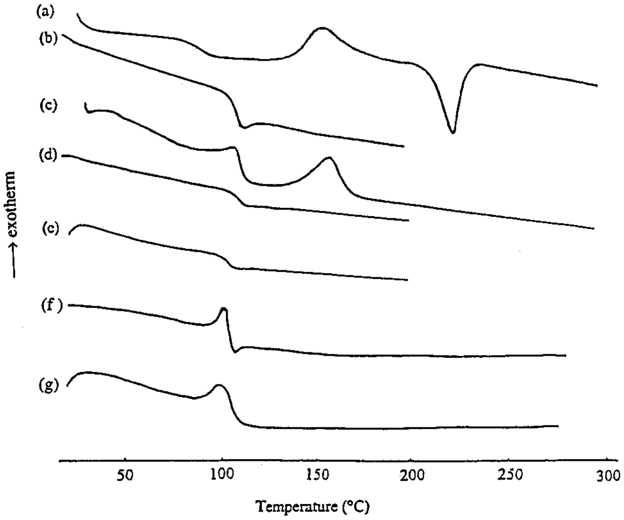

Figure 4. DSC curves of (a) iso-PS, (b) atactic o-PS, (c) first scan of micro-PS–SDS, (d) second scan of micro-PS–SDS, (e) r-PS, (f) PS–SDS-α, and (g) conv-PS.

(such as 1220 and 985 cm^{-1}) was detected in the spectrum of micro-PS–SDS, which means that SDS was almost completely removed from micro-PS–SDS during purification. NMR and IR spectra of micro-PS–OP and micro-PS–SDS are similar.

Novel Thermal Behavior of Micro-PS. The dramatic thermal behavior of micro-PS–SDS shown in Figure 4c was examined in the DSC scan. In Figure 4 are also shown the DSC curves of o-PS, r-PS, iso-PS, conv-PS, and PS–SDS-α. All samples were scanned to 300 °C for the first scan. o-PS and r-PS demonstrated only their glass transitions at about 105 °C, while micro-PS–SDS displayed two exotherms, one at 107 °C, just around the T_g of ordinary PS, the other at 157 °C. The peak at 107 °C is seemingly the superposition of one exothermic transition and one glass transition. A subsequent scan after cooling to ambient temperature showed only one T_g, and both exotherms disappeared. Surprisingly, the second exotherm (157 °C) had a position similar to that of iso-PS and syn-PS.[13] It is more surprising, however, that no endotherm was observed even when micro-PS was heated to 300 °C after the occurrence of the second exotherm. The exothermic enthalpy of the second peak of micro-PS–SDS is 6.4 J/g, about one-third of that of iso-PS, which was 19.5 J/g from Figure 4, or two-thirds of that of syn-PS whose enthalpy was 9.2 J/g.[13]

As to conv-PS, an exotherm above T_g was observed, similar to the reported results by Mahr.[6] Since its diameter is only 53.8 nm (D_w), the loss of surface area results in the energy release, i.e., the observed exotherm. For PS–SDS-α, only an exotherm above its glass transition could be examined, too. There were about 15 macromolecular chains inside each sphere, so it could not be classed as a pauci-chain microsphere any more. Because of its very small particle size (24.7 nm, in Table 1), the sintering phenomenon was also observed, much like conv-PS. The chain conformation inside PS–SDS-α should be more similar with conv-PS than micro-PS–SDS. Similarly, the first exotherm in the DSC scan of micro-PS–SDS might be due to the sintering of polystyrene microspheres.

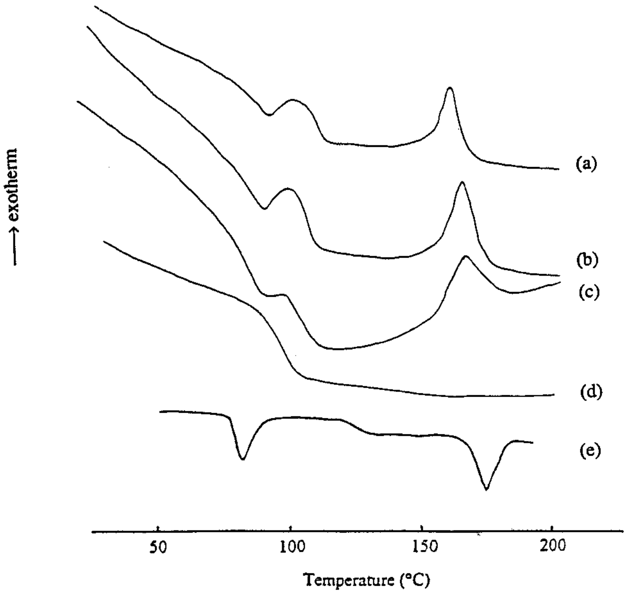

Figure 5. DSC curves: micro-PS–OP with heating rates of (a) 5 °C/min, (b) 10 °C/min, and (c) 20 °C/min; (d) Second san of micro-PS–OP at a heating rate of 10 °C/min; (e) Pure SDS.

At the beginning, it was considered that the second exotherm was due to stereoregulatiry of the polystyrene chain in micro-PS–SDS, since its position in the DSC curve was just similar to that of iso-PS and syn-PS. But, ^{1}H-NMR results ruled out this possibility. Further evidence against it is provided by the second DSC scan of micro-PS–SDS; there was no exotherm. If micro-PS had stereoregularity, the second peak would not disappear. In addition, the thermal behavior of r-PS was greatly different from the virgin micro-PS–SDS, but the same as o-PS. The procedure of dissolving could only change the conformation of micro-PS but would have no effect on its configuration.

It was also doubted that the second exotherm was, perhaps, related to the impurity of micro-PS–SDS sample, for example, the existence of very little SDS resulting in the above phenomenon. Although IR and NMR did not detect the existence of SDS, for the sake of insurance, another styrene microemulsion system, styrene/OP-10/water, was polymerized, and pure SDS was scanned on DSC. The produced micro-PS–OP had a molecular weight and particle size similar to those of micro-PS–SDS (see Table 1). As can be seen in Figure 5, micro-PS–OP has the same thermal behaviors as micro-PS–SDS. At room temperature, OP-10 is in the liquid state, so it is impossible for OP-10 to have any exothermic peak during the DSC scan at 157 °C. At the same time, there was no exotherm in the whole DSC scan for pure SDS. On the basis of these observations, it is confirmed that the novel exotherm cannot be

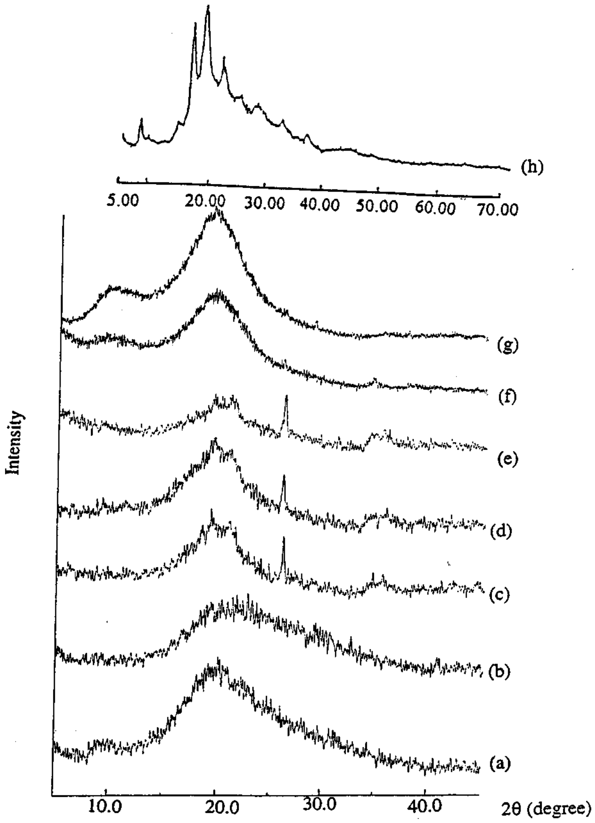

Figure 6. WAXD patterns of micro-PS−OP: (a) original sample, (b) quenched at 115 °C, (c) quenched at 180 °C, (d) quenched at 220 °C, (e) quenched at 250 °C, and (f) quenched after annealing at 250 °C for 10 min; (g) conv-PS quenched at 180 °C; (h) crystallized iso-PS.

attributed either to impurity or to the stereoregularity of micro-PS chains. The driving force for the formation of exotherms may be ascribed to the special conformation of the polystyrene chain inside the micro-PS microspheres.

The effects of heating rate on enthalpy of the exotherms of micro-PS−OP are also shown in Figure 5. The first exotherm was influenced dramatically by the heating rate, while the enthalpy of the second exotherm changed only a little. It means to some extent that the first exotherm is more susceptible to environmental influences than the second, and it originates from a special structure formed during the polymerization, i.e., very small sphere with a large surface energy. According to the literature, it is reasonable to ascribe it to the effects of sintering and/or stress release.

But, what causes the second exotherm? It cannot simply be regarded as the effect of sintering; otherwise, PS−SDS-α should also demonstrate this exotherm since the only difference between micro-PS−SDS and PS−SDS-α is the number of macromolecular chains per microsphere. At the same time, because unlike syn-PS and iso-PS, there was no melting peak (endotherm) in the DSC curve of micro-PS, it is not suitable to assume it as a crystallization peak. We would prefer to attribute this exotherm to the formation of some kind of ordered structure of several (ca. three) polystyrene chains inside the space-confined microspheres during the heating process, as discussed below.

Condensed-State Properties of Micro-PS. During the DSC measurements of micro-PS−OP, sample cells were removed at some designated temperatures and quenched quickly into liquid nitrogen. The samples were examined on a wide-angle X-ray diffractometer and polarizing optical microscope. (Here only the results from micro-PS−OP are given, for micro-PS−SDS shows properties similar to those of the former.)

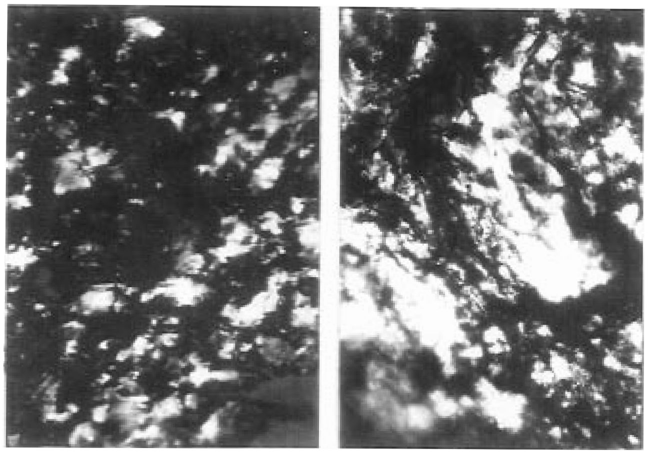
(a) (b)

Figure 7. Polarizing optical microscopy photographs of (a) micro-PS−OP quenched at 180 °C and (b) crystallized iso-PS.

Wide-angle X-ray diffraction patterns are shown in Figure 6. The original sample (a) and the one quenched at 115 °C (b) demonstrated ordinarily broad noncrystalline peaks, much like conv-PS (g) by conventional emulsion polymerization. However, when micro-PS−OP was heated to 180 °C, i.e., after the occurrence of the second exotherm, and then quenched into liquid nitrogen, a peak at 2θ of 26.2° (c) was shown in the WAXD diagram. Meanwhile, the broad peak around 20° was not so smooth as (a) and (b), with a small peak at 19.3° coming forth. When quenched at 220 °C (d) and 250 °C (e), respectively, WAXD patterns of each sample did not change much from (c). When the sample was annealed at 250 °C for 10 min and then quenched into liquid nitrogen, the peak at 26.2° almost disappeared (f), and at the same time, the broad peak around 20° recovered the shape of sample (a). Compared with iso-PS (h), micro-PS−OP had a less ordered structure and the ordered regions were imperfect.

The quenched micro-PS−OP samples were also observed on a polarizing optical microscope (POM). For the sample quenched at 180 °C, a "light area" can be obviously seen in the photograph (Figure 7). But for the original sample and the one quenched at 115 °C, no obvious "light area" was shown. The light area represents some kind of ordered regions. In Figure 7 is also given a POM photograph of crystallized iso-PS, which had a much larger "light area" and, in other words, more ordered regions than micro-PS−OP. POM photographs of those samples quenched at higher temperatures have not been obtained successfully because of the difficulty of sample preparation.

From WAXD and POM results, it can be concluded that the first exotherm of micro-PS during the DSC scan may not be caused by the conformation change (to some kind of ordered structure) of polystyrene chains; otherwise, the WAXD pattern of the sample quenched at 115 °C would not still be a smooth broad peak. The ordered structure corresponding to the second exotherm can be produced by the heating process. We may call it a heat-induced orientation of macromolecular chains. In some aspects, the orientation is similar to the concept of nematic localized cohensional entanglement proposed by Qian et al.[2] But the difference is that according to Qian's argument, the ordered entanglement (nematic)

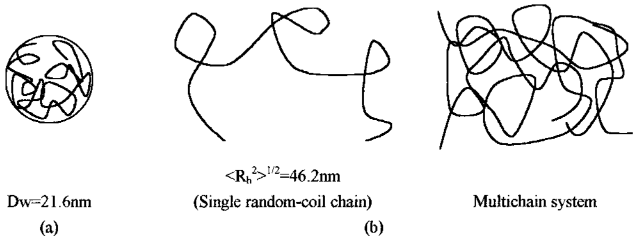

Figure 8. Schemes of conformations of (a) micro-PS and (b) o-PS with M_w 1 × 10^6.

was produced during microemulsion polymerization and contributed to the exotherm above the glass transition of polystyrene microspheres; meanwhile, the ordered structure of micro-PS in our research is formed at the temperatures above the T_g. Up to the present, we may say the driving force of the second exotherm is the special conformation of several (ca. three) polystyrene chains inside the microspheres with very small diameters.

The number of PS chains in each microsphere is about three from the calculation. Microemulsion polymerization is performed in particles with space limitation (D_n = 10−20 nm), so the PS chain cannot propagate randomly. For example, for the PS with weight average molecular weight $M_w = 1.0 \times 10^6$, the unperturbed root-mean-square end-to-end distance ($\langle R_h^2\rangle^{1/2}$) of such polymer chains would be about 46.3 nm if they were in their random-coil conformation. Therefore, when they are confined in a spatially limited sphere with a weight-average diameter of 21.6 nm, the conformation of polystyrene chains must be highly compact. Figure 8 is a scheme of conformations of micro-PS and o-PS. As for the micro-PS, the main interpenetrating and entanglement of segments are intramacromolecular, and a substantial fraction of the nearest-neighbor segments in the space of micro-PS are necessarily segments of the same chain, but in the case of o-PS, there exists mainly interchain interpenetrating and entanglement. It is evidently much more difficult for a polystyrene chain to adopt intramacromolecular entanglement than intermacromolecular entanglement. So micro-PS has a loose structure and lower density in contrast to o-PS, although for an individual chain inside micro-PS, it is more compact than in the random-coil state because of spatial limitation. Wu has determined that the density of micro-PS is 0.92 g/cm^3 by laser light scattering,[12] which is much smaller than 1.05 g/cm^3 of o-PS. Due to the spatial limitation, polystyrene chains of micro-PS are forced to stack more compactly than they are in the case of random coils. This special conformation results in special physical properties, as discussed above.

Although after the microemulsion polymerization, the individual polystyrene chain lies in a highly compact state because of spatial limitation in comparison with the random-coil state, the chain alignment is still mainly disordered. When micro-PS is heated to 115 °C (above the glass transition temperature), the motion of the polystyrene chain becomes a little easier, and during the glass transition the sphere shape of micro-PS is destroyed, resulting in the release of surface area energy. However, the chain still has not enough mobility to align in orderly conformation, although it is in a loose environment (ca. microsphere). As reflected from the X-ray diffraction, no obvious peak can be examined till 115 °C. On the other hand, the loose structure has the potential to make the chain motion easier in micro-PS than in o-PS, and the adjustment of conformation of micro-PS to some kind of ordered state is possible through the intrachain cooperative adjustments in an individual chain, without hindrance from other chains as in o-PS. At about 157 °C, the motion of segments is much easier and can make great adjustments of its conformation into a more ordered state, resulting in the second exotherm in the DSC curve and sharp peaks in WAXD patterns. After the first DSC scan of micro-PS to 300 °C, polystyrene chains from different microspheres permeate into each other, and they are not single chain in character any more, but rather like o-PS. The conformation of this kind of sample is changed by heating while that of r-PS is changed by dissolving. So both of them displayed different DSC curves from virgin micro-PS. It is the special chain conformation in virgin micro-PS that causes the formation of ordered regions of micro-PS during the first DSC scan.

Owing to the imperfection and small size of the ordered regions of micro-PS, there is no endotherm when it is heated after the second exotherm. The ordered structure may be relaxed gradually by absorbing energy from the environment during a relatively long period when heated to 300 °C. Of course, direct experimental evidence is needed. It was also considered, to some extent, that the phenyl ring effect[14] is the key to the formation of localized ordered regions inside micro-PS microspheres, which makes micro-PS exhibit the second exotherm. Further investigation shows the second exotherm has a strong dependence on polymerization conditions, such as styrene concentration and polymerization temperature, and the resulting different numbers of macromolecular chains per microsphere. These features will be discussed in a forthcoming paper.

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