

Note

IR STUDY ON MONOMOLECULAR PARTICLE AGGLOMERATES OF
POLYSTYRENE OBTAINED BY FREEZE-DRYING OF ITS DILUTE SOLUTIONSong Wang^a, Qing-hua Wang^a and Rong-shi Cheng^{b*}^a Research Center of Materials, Beijing Institute of Technology, Beijing 100081, China^b Department of Chemistry, Nanjing University, Nanjing 210093, China

Abstract The monomolecular particle agglomerates of polystyrenes were obtained by freeze-drying of its very dilute solutions of 1.3×10^{-5} – 2.0×10^{-5} g/mL in benzene:cyclohexane (100:1) solvents, and they were annealed at room temperature for hundred days before use. According to ^{13}C -NMR measurement the polystyrenes should be practically atactic. The number average molecular weights of the samples are 2.80×10^3 , 2.00×10^4 , and 1.55×10^6 , respectively. The freeze-dried *a*PS with a molecular weight higher than 10^4 show two new IR absorption bands at 1098 and 1261 cm^{-1} , which are absent in the normal *a*PS and freeze-dried styrene oligomer. It was also found that the low molecular weight samples can only form powders, whereas the freeze-dried *a*PS with higher molecular weight form a mixture of powders and fibrils, of which the longer fibrils show a much stronger 1261 cm^{-1} band than the shorter fibrils and the powder. It seems that the 1261 cm^{-1} band corresponds to the stacking behavior of monomolecular particles.

Keywords Monomolecular particles, Atactic polystyrene, FTIR spectroscopy

INTRODUCTION

A monomolecular particle consists of a single polymer molecule. These particles have a very small diameter but a very large surface area. In addition, the molecule coils in the particles are exempt from the intermolecular entanglement that is unavoidable for ordinary polymers, so it may show specific conformation and be expected to have specific properties. Monomolecular particles can be obtained by freeze-drying of a very dilute solution, in which the concentration has to be much lower than the overlap concentration c^* and near or lower than the gelation threshold c_{gel} . ($\approx 10^{-5}$ g/mL)^[1]. We have studied the morphology of monomolecular particles of atactic polystyrenes (*a*PS) prepared by freeze-drying and their agglomerates or aggregates^[2]. It was found that some of these particles look like single-chain single crystals of isotactic polystyrenes. In this paper we investigated the IR spectra of agglomerates or aggregates of *a*PS monomolecular particles.

EXPERIMENTAL

Polystyrenes were prepared with *n*-butyllithium as the initiator in benzene by our laboratory. Their stereoregularity was determined by the ^{13}C -NMR method to be mm + mr:rr $\approx$ 62:38 and molecular weights determined by GPC are summarized in Table I. The samples were dissolved in the mixed solvents of benzene and cyclohexane (100:1) which were distilled before use. The polymer solutions of 0.0013%–0.0020% (*W/V*) concentrations were frozen in a round-bottom flask, by swirling the flask in liquid nitrogen. The frozen solutions were thawed at room temperature and then cooled in liquid nitrogen again. Finally, the twice frozen solvent was sublimed in vacuum. The resulting powder adhered to the wall of the flask and was kept there for hundred days at room temperature (5–38°C). The FTIR spectra were recorded on a Nicolet Impact 410 spectrometer by using the

* Corresponding author: Rong-shi Cheng (程镭时), E-mail: rscheng@nju.edu.cn

Received December 13, 2001; Revised December 21, 2001; Accepted December 22, 2001

KBr pellet method for the powdery samples and IR microscopic method for the fibril-like samples (as shown in Table 1).

Table 1. Relative IR absorbance at 1027 and 1261 cm^{-1} of the normal and the freeze-dried *a*PS samples*

Sample	M_n $\times 10^4$	c_0 $\times 10^5$ (g/mL)	c^* $\times 10^2$ (g/mL)	c_0/c^* $\times 10^3$	Sample morphology	Relative absorbance at		Preparation method
						1027 cm^{-1}	1261 cm^{-1}	
A_0	2.00	-	-	-	Powder	1.0	0.0	Not treated
A_{FD}	2.00	1.3	5.6	0.23	Powder	1.0	0.22	FD
$B1_{\text{FD}}$	155	1.3	0.24	5.4	Powder & shorter fibrils	1.0	0.19	FD
						1.0	0.13	FD
$B2_{\text{FD}}$	155	1.3	0.24	5.4	Longer fibrils	1.0	0.35	FD
						1.0	0.42	FD
C_{FD}	0.28	2	22	0.09	Powder	1.0	0.0	FD

* Each sample of $B1_{\text{FD}}$ and $B2_{\text{FD}}$ has two groups of data obtained from replicate IR determinations, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of the freeze-dried samples A_{FD} , $B1_{\text{FD}}$ together with the normal sample A_0 that has not been treated by freeze-drying. Spectra of A_{FD} and $B1_{\text{FD}}$ exhibit absorption bands at 1261 and 1098 cm^{-1} which are absent in the spectrum of A_0 . This means that the chain conformation of the freeze-dried samples is different from the normal conformation of polystyrenes. It is also noted that three absorption bands (1047, 1098, 1262 cm^{-1}) appear for the freeze-dried *a*PS from the higher c_0 (the concentration of the prepared solutions) in the same solvents^[3]. The c_0 reported in Ref. [3] was about 0.1% which is nearly equal to the c^* and about 100 times higher than that used in this paper. According to the polymer solution theory, polymer chains exist as single molecules in a very dilute solution, the concentration of which is about 0.001% or lower and is much lower than c^* . Therefore, we suggest that the two absorption peaks at 1098, 1261 cm^{-1} in the IR spectra of A_{FD} and $B1_{\text{FD}}$ in Fig. 1 correspond to the structure of monomolecular agglomerates or aggregates, but the third peak at 1047 cm^{-1} probably corresponds to some structure related to chain overlapping.

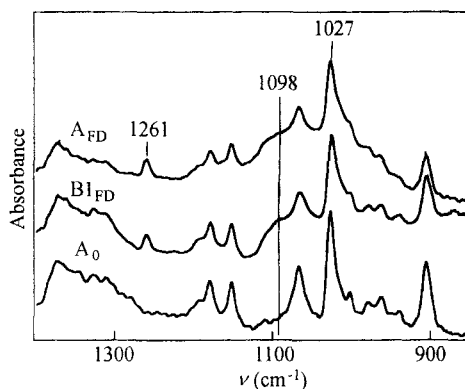


Fig. 1 IR spectra of the freeze-dried *a*PS samples (A_{FD} : $M_n = 20000$; $B1_{\text{FD}}$: $M_n = 1550000$) and the normal *a*PS sample (A_0 : $M_n = 20000$). The freeze-dried samples were prepared from 0.001% benzene/cyclohexane (100/1) solution.

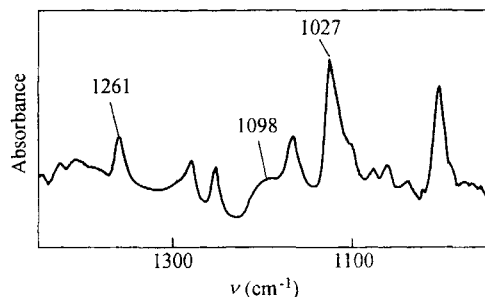


Fig. 2 IR spectra of the freeze-dried *a*PS sample $B2_{\text{FD}}$ ($M_n = 1550000$) prepared from 0.001% benzene/cyclohexane (100/1) solution

Figure 2 shows the FT-IR spectrum of freeze-dried sample $B2_{\text{FD}}$. Samples $B2_{\text{FD}}$ and $B1_{\text{FD}}$ were derived from the same sample but with different shape and dimensions as shown in Table 1. We can estimate the relative absorption intensity of 1261 cm^{-1} peak in both spectra ($B2_{\text{FD}}$ and $B1_{\text{FD}}$) by taking the peak height of 1027 cm^{-1} as

reference. Our result shows that the sample with longer fibril ($B2_{FD}$) has a higher 1261cm^{-1} peak than that with shorter fibril and powders ($B1_{FD}$). It seems that the 1098 and 1261cm^{-1} bands may be related to the stacking behavior of monomolecular particles. We have studied the morphology of monomolecular particles of atactic polystyrenes (*a*PS) prepared by freeze-drying and their agglomerates or aggregates^[2]. It was found that some of the single-chain particles look like single-chain single crystals of isotactic polystyrenes, and some of them were just spherical. Their agglomerates or aggregates also exhibit various shapes and some of them look polygonal or quasi-polygonal while others show complex irregular outlines. Is it possible that the spherical and some crystal-like single chain particles aggregate together to form the powdery or shorter fibril-like particles and only crystal-like single chain particles aggregate to form the longer fibrils sample? Further work on the stacking behavior of monomolecular particles will be published shortly.

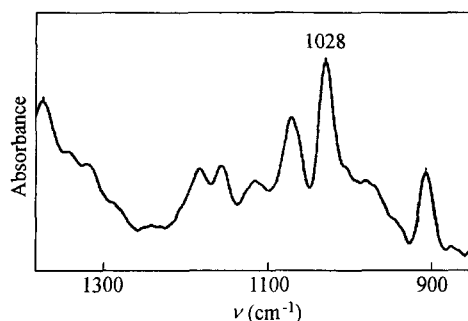


Fig. 3 IR spectra of the freeze-dried *a*PS sample C_{FD} ($M_n = 2800$) prepared from 0.001% benzene/cyclohexane (100/1) solution

Figure 3 is the FT-IR spectrum of the freeze-dried sample C_{FD} . The absorption bands at 1098 , 1261cm^{-1} do not appear in this sample and this spectrum is different from the spectra of other freeze-dried samples. One possible explanation is that the specific structure of the freeze-dried sample was destroyed during the long annealing time, because the molecular weight of C_{FD} is much lower than the other samples, so its T_g (about 36°C or lower as measured by DSC^[2]) may be even lower than the ambient temperature ($\leq 38^\circ\text{C}$).

ACKNOWLEDGEMENT We are grateful to Prof. He-sun Zhu for his support.

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