Front. Chem. China (2006) 4: 465–468
DOI 10.1007/s11458-006-0044-7

RESEARCH ARTICLE

Xin Yan, Yu Ying, Zhang Yu, Fan Zhongyong

Crystallization behavior of single or pauci chain aggregates of isotactic polystyrene

Abstract Single and pauci chain aggregates of isotactic polystyrene (*i*-PS) were prepared by the freeze-drying process from dilute solutions with the concentration from 1×10^{-3} to 2×10^{-5} g/mL. It was found by DSC measurements that the melting point of samples gradually shifted to lower temperatures with the decrease of the solution concentration used for sample preparation. As a result, the lamella thickness of bulk samples and the samples prepared by the freeze-drying process from a solution of 2×10^{-5} g/mL was 19.3 and 12.6 nm, respectively. At 468.3 K the half crystallization time ($t_{1/2}$) of samples freeze-dried from a solution of 1×10^{-4} g/mL was about 36 s, which was merely one tenth of that of the bulk sample. In addition, the growth rate of spherulite (*dr/dt*) of samples prepared from a solution of 2×10^{-5} g/mL was faster than that of the bulk sample annealed at 478.3 K. All these results should be attributed to the fewer entanglements in samples prepared by freeze-drying process from dilute solutions, and presented clear evidence for the influence of chain entanglements on the crystallization behavior of polymers.

Keywords isotactic polystyrene, single chain aggregates, pauci chain aggregates, crystallization

1 Introduction

Hoffman and Miller proposed the nucleation theory of polymer crystallization in 1960, which successfully described the crystal growth rate in melt crystallization of polymers and the variation of lamellae thickness with annealing temperature and time and so on. In 1997, Hoffman and Miller [1] published a revised nucleation theory of polymer crystallization, introducing the reptation concept of de Gennes [2] into the surface nucleation process. It was estimated that the time needed to reel in a macromolecule from the melt onto the growing crystal surface might be about three orders of magnitude less than the one predicted by Flory and Yoon [3]. Thus, Hoffman concluded that the "reptation" rate of macromolecules in forced steady state was sufficiently rapid for them to escape from their entanglements with other chains in the melt crystallization. However, Flory and Yoon argued that the rate of disentanglement of chains in the melt was much slower than the move rate of the crystallization front in the crystal growth process. Polymer chains do not have enough time to make adjustments of their chain conformation to enter into the crystallographic site without disentanglement during the crystallization process. Just parts of segments are adjusted to form crystals and the interchain entanglements are excluded on the surface of the crystals to form the non-crystalline regions. As a result the "switch board model" of semicrystalline polymers was proposed.

Although the opinions of these theories are opposite, they all consider that the interchain entanglements have no effect on the behavior of melt crystallization of polymers in fact. However, in earlier research work, we found that the cold crystallization temperature (T_c) of single chain particles was much lower than that of bulk samples, indicating that the crystallization of the single chain particles with few interchain entanglements was quite easier than that of bulk samples. Experiments proved that chain entanglements had distinct effects on crystallization behavior of polymers. These results indicate that the existing theories for polymer crystallization cannot explain clearly the effects of interchain entanglements [4, 5]. Further investigation is still needed for understanding the real features of the mechanism of polymer crystallization.

In this paper, single and pauci chain aggregates of isotactic polystyrene (*i*-PS) were prepared by the freeze-drying

Translated from *Chemical Journal of Chinese Universities*, 2005, 26(10) (in Chinese)

Xin Yan, Yu Ying, Zhang Yu, Fan Zhongyong(✉)
Department of Materials Science, Fudan University,
Shanghai 200433, China
E-mail: zyfan@fudan.edu.cn

process from solutions with concentrations from 1×10^{-3} to 2×10^{-5} g/mL. Differential scanning calorimetry (DSC) was applied to investigate the crystallization behavior of the single and pauci chain aggregates. The growth rate of spherulites in single and pauci chain aggregates was studied by polarizing optical microscopy (POM) and the influence of interchain entanglements on the melt crystallization of polymer was discussed.

2 Experimental

Isotactic polystyrene (*i*-PS) was purchased from American Scientific Polymer Products, Inc. with isotacticity above 90%, $\overline{M}_n$=580 000, $\overline{M}_w/\overline{M}_n$=1.07. The *i*-PS sample was melted at 519 K for 5 min under a nitrogen atmosphere, quenched subsequently by liquid nitrogen, and the amorphous *i*-PS sample was gained. The amorphous *i*-PS was circumfluent dissolved in twice-distilled benzene at 353.3 K for 24 h, and the resulting solution was diluted to various concentrations for preparing the single and pauci chain samples by the freeze-drying process. The solution was put in a rapidly rotated round-bottom flask, which was large enough for the charged solution to form a thin layer on the wall of the flask. Then liquid nitrogen was poured into the flask, and the solution froze immediately. The frozen solvent was sublimed at 258 K in an ice–salt bath under vacuum of 1.33×10^{-1}–1.33×10^{-2} Pa. The white fluffy-like *i*-PS samples that remained in the flask were collected. Moreover, in order to get rid of the trace of benzene that may remain in samples, the *i*-PS prepared by freeze-drying process was kept again under vacuum of 1.33×10^{-2}–1.33×10^{-3} Pa for 5 h. After total sublimation of the solvent, the dried samples of single and pauci chain amorphous aggregates were collected at the bottom of the flask and stored at low temperature for use.

Differential scanning calorimetry (DSC) measurements were carried out with a DuPont 910 DSC apparatus in a nitrogen atmosphere. To avoid the influence of sample weight and heating rate on the analysis of results, the sample weight was 1.5 ± 0.1 mg and the heating rate was 10 K/min in all cases. The temperature corresponding to the maxima of the exothermal and endothermic peaks was taken as the crystallization temperature (T_c) and melt temperature (T_m) of samples.

Morphological observations were made by polarizing optical microscopy (POM) using a Leica DMLP apparatus with a Linkam THMSE-600 type hot stage. The sample prepared by freeze-drying process was put evenly between two glass pieces on the hot stage. The temperature was increased to 516.3 K at a heating rate of 20 K/min and kept for 1 min for melting of the sample and then decreased to the crystallization temperature at a cooling rate of 50 K/min.

3 Results and discussion

1. DSC studies on the crystallization behavior of *i*-PS prepared by freeze-drying process

The polymer solution theory of de Gennes [2] indicates that there is a critical concentration (overlap concentration), c^*, below which it is generally assumed that macromolecules exist as isolated single-chain coils in the solution. The overlap concentration c^* of *i*-PS with $\overline{M}_\eta = 5.8\times10^5$ used in this study could be approximately estimated to be 2.2×10^{-2} g/mL based on the formula $c^* = \overline{M}\Big/\left[(4/3)\pi\tilde{N}\left(R_\theta^2\right)^{3/2}\right]$.

Moreover, the dynamic contact concentration c_σ proposed by Qian et al. [6] was estimated to be 5.8×10^{-4} g/mL according to the formula $c_s = K_\alpha \overline{M}^{-0.1}$. The concentration of solutions used in this work for sample preparation by freeze-drying process was in the range of 1×10^{-3} – 2×10^{-5} g/mL. Therefore, the degree of separation of *i*-PS coils in the solution increases with the decrease in its concentrations, and so the interchain entanglements decrease. Clearly, when the concentration is below c^*, *i*-PS coils can be separated entirely, so that they cannot feel the existence of each other. In these cases, the samples prepared by freeze-drying are amorphous single chain coil aggregates. Therefore, single-, few-, and multi-chain particles can be prepared by freeze-drying process, using solutions of various concentrations. DSC traces of samples prepared from solutions of various concentrations are shown in Fig. 1. It is clear that the crystallization temperature (T_c) of samples from their glassy state decreases with the decrease in the concentration of solutions used in the freeze-drying process. These results indicate that the crystallization is easier for samples with more single and pauci chain particles and less entanglements between chains. The correlation between melting point (T_m) and thickness of lamellae (l) is given by Hoffmann as

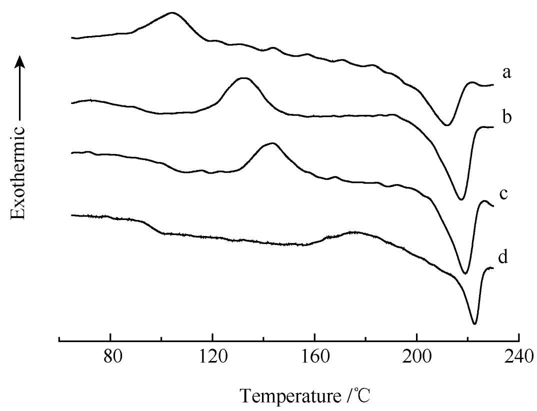

Fig. 1 DSC results of bulk *i*-PS and samples freezing-dried from solutions of various mass concentrations

a. 2×10^{-5} g/mL; b. 1×10^{-4} g/mL; c. 1×10^{-3} g/mL; d. bulk sample

$T_m = T_m^0(1 - \frac{2\sigma_e}{l\Delta H_f})$, Where T_m^0 is the equilibrium melting temperature, σ_e is the fold surface free energy of lamellae, ΔH_f is the enthalpy of fusion per unit volume. The values of *i*-PS are as follows: $T_m^0 = 516.3$K, σ_e=34.8 erg/cm^2, ΔH_f=9.11×10^8 erg/cm^3. According to the above formula and the T_m values from DSC measurements, the lamella thickness (l) of *i*-PS obtained by freeze-drying from solutions of various concentrations was calculated (Table 1). The results indicated that the thickness of *i*-PS lamellae became thinner as the concentration of the freeze-drying solutions was decreased.

Table 1 The results obtained from DSC measurements of bulk *i*-PS and freeze-dried samples prepared from solutions of various concentrations

Parameter	Bulk	Concentration/(g·mL^{-1})		
		1×10^{-3}	1×10^{-4}	2×10^{-5}
T_m/K	495.8	492.2	490.6	485.1
l/nm	19.3	16.4	15.3	12.6
$t_{1/2}$/s (468.3 K)	360	95	36	–
G/(μm·s^{-1}) (478.3 K)	0.18	0.24	0.26	0.28

2. Effect of entanglements on the melt crystallization rate of *i*-PS samples

The radial growth rate of spherulites of melt crystallization of polymers, G, can be described by the equation [7, 8]: $G = G_0 \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right]\exp\left[\frac{K_g}{T_c(T_m^o - T_c)f}\right]$, where G_o is a pre-factor related with molecular weight of samples, U^* is the free energy of activation for a polymer chain crossing the barrier from melt to the crystal, T_c is crystallization temperature, T_∞ is expressed as $T_g - (30 \sim 50)$ (K), K_g is a constant related with the rate of second nucleation, T_m^o is the equilibrium melting temperature, R is the gas constant, f is a factor indicating the correction of the heat of fusion during crystallization in various temperatures which is given by $f = 2T_c/(T_m^o + T_c)$. Therefore, polymer crystallization kinetics is influenced by two energy barriers, which are the nucleation free energy and migration activation energy, respectively.

It is well known, when polymer crystallizes in the Regime II region, the rate of nucleation is fast, so that the growth rate of lamellae is dependent on the diffusion rate of polymer chains from the subcooling melt onto the growing crystal surface. Hoffman considers that the diffusion rate of crystallization chains is related to the frictional resistance to chain movements in the subcooling melt. As the molecular weight increases, the chain will be longer, there will be more entanglements among chain coils, and the diffusion rate of chains onto lamellae will be decreased. So the growth rate of lamellae decreases. Meanwhile, Hoffman thought that the influence of entanglements on crystallization can be proved by the crystallization of ultra-high molecular weight polymers ($\overline{M}_n \geq 10^7$). For crystallization of normal molecular mass polymers, as the rate of disentanglement is faster than the rate of diffusion in the melt, the interchain entanglements have no influence on the rate of diffusion.

The result of our research indicated that the growth rate of spherulite of *i*-PS ($\overline{M}_\eta = 5.8\times10^5$) samples prepared by freeze-drying process (dr/dt) was intimately related to the concentration of solutions used in the freeze-drying process. Figure 2 shows the time dependence of spherulite radius under annealing at 478.3 K for *i*-PS samples obtained from solutions of various concentrations. The spherulite growth rate of freeze-dried *i*-PS samples increases with decreasing the concentration of the original solutions, while the growth rate of freeze-dried samples are all larger than that of the normal bulk samples. Calculated from Fig. 2, the spherulite growth rate of the sample from the solution of 2×10^{-5} g/mL is about 0.28 μm/s, while that of the bulk sample is only about 0.18 μm/s. On the other hand, from DSC measurements the data of half-crystallization time ($t_{1/2}$) of various *i*-PS samples under annealing at 468.3 K can be obtained and are listed in Table 1. When the concentration of the solution was diluted to 1×10^{-4} g/mL, the $t_{1/2}$ of the sample was about 36 s, which was about one tenth of that of the normal bulk sample. These data also indicated that the crystallization rates of freeze-drying samples greatly increased compared with that of the bulk sample. During crystallization the polymer molecules tend to move to the crystal surface, and the driving force is the difference in free energy between the subcooled melt and the crystal. At the same time, the entanglements among the polymer chains may impede the diffusion of chains from approaching the crystal

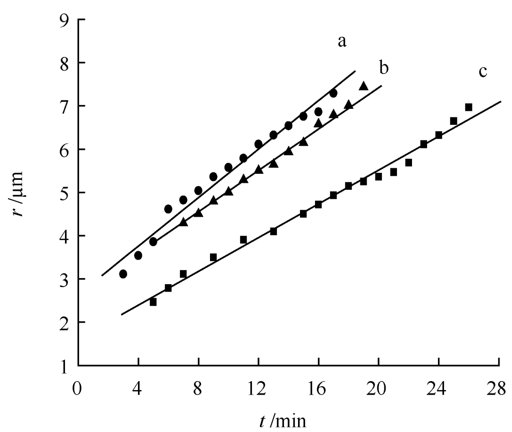

Fig. 2 Plot of the radius of the spherulite of samples freeze-dried from solutions of various concentrations and bulk *i*-PS with annealing at 478.3 K.

a. 2×10^{-5} g/mL; b. 1×10^{-4} g/mL; c. bulk sample surface and influence the crystallization rate. The density of the interchain entanglements of freeze-dried samples should be much lower than that of conventional bulk samples and also decreases with the decrease in the concentration of solutions used for sample preparation, especially when the concentrations are less than c^* and c_s of the polymer solution system. So our results present experimental evidence on the influence of interchain entanglements on the crystallization of polymers.

Acknowledgements The authors would like to thank Professor Rongshi Cheng at Nanjing University for the use of POM equipment and valuable discussions. This work was supported by the National Natural Science Foundation of China (Grant No. 20474013).

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