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Influence of Entanglements on Crystallization of Macromolecules

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Single- and pauci-chain collective particles were prepared by a freeze-drying method from dilute solutions of isotactic polystyrene (*i*-PS) in benzene. Thermal analysis revealed that the collective particles crystallize much faster than bulk polymer, which can be attributed to much fewer interchain entanglements within and between particles, thus proving experimentally for the first time that entanglements are a barrier to the crystallization of polymers.

The *i*-PS solution was put into a rotating flask which was immersed in liquid nitrogen to ensure quick freeze of the solution, and then vacuum was applied to sublimate solvent at −15 to −10 °C in an ice−salt bath. After complete sublimation of the solvent, fluffy particles were collected at the bottom of the flask and stored in a refrigerator until use.

Thermal analysis of the collective particles was carried out with a Du Pont 910 DSC at a heating rate of 8 °C/min in a nitrogen atmosphere. DSC traces of the collective particles prepared from solutions of various concentrations are shown in Figure 1. As the concentration decreases, the cold crystallization temperature (T_{ch}) significantly depresses. For collective particles from 1×10^{-3} wt % solution, the T_{ch} is about 40 °C lower than bulk polymer, indicating the crystallization of the collective particles to be quite easy and faster. Figure 2 shows the half-time of crystallization measured from isothermal crystallization of bulk polymer and collective particles. Clearly, collective particles crystallize much faster in both cases of low and high supercooling.

Polymer solution theory indicates that there is an overlap concentration, C^*, where physical contact among macromolecular coils starts as proposed by de Gennes.[1] Below C^*, it is generally assumed that macromolecules exist as isolated single-chain coils in solution. However, Qian, Cheng et al.[2,3] suggested a dynamic contact concentration (C_s), at which coils have already contacted due to molecular motion, and they argued that only below C_s, coils are well-separated in solution. C_s is usually 1−2 orders of magnitude lower than C^*. It would be possible to obtain particles containing one single chain from an extremely dilute solution with concentration below C_s, if the solvent could be removed with the coils remaining isolated from each other. Single-chain single crystals were prepared by spreading the extremely dilute solution on a water surface with quick evaporation of solvent, followed by crystallization.[4]

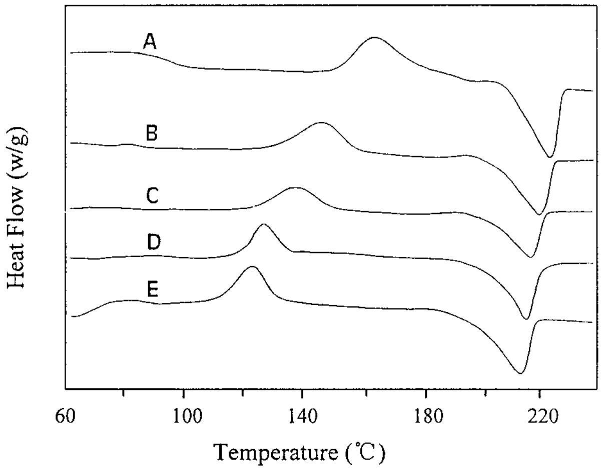

Figure 1. DSC traces of collective particles prepared from solutions of various concentrations: (A) bulk isotactic polystyrene; (B) 1×10^{-1} wt % solution; (C) 1×10^{-2} wt % solution; (D) 2×10^{-3} wt % solution; (E) 1×10^{-3} wt % solution.

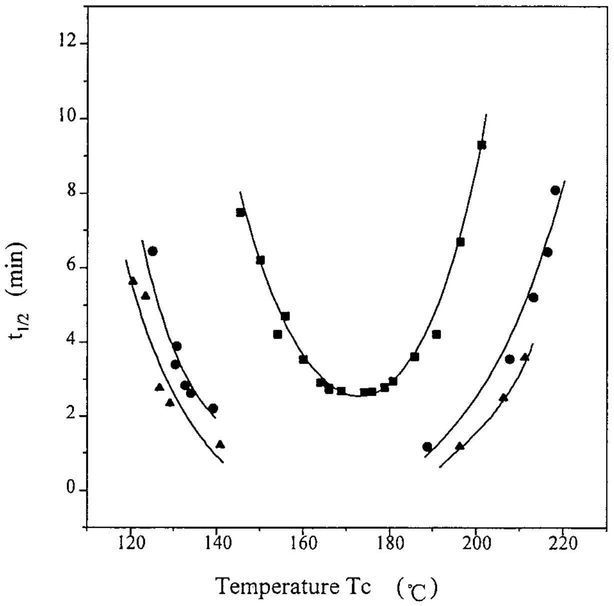

Figure 2. Half-time of crystallization as a function of crystallization temperature: (■) bulk *i*-PS; (●) 1×10^{-1} wt % solution; (▲) 1×10^{-2} wt % solution.

Assuming the chain conformation of *i*-PS in solution is similar to atactic polystyrene (a-PS), the C^* of the solution of *i*-PS ($\bar{M}_n = 6 \times 10^5$ used in our research) in benzene can be estimated to be around 1 wt % using the unperturbed dimension of an a-PS coil,[1] and C_s is about 6×10^{-2} wt %.[2,3] At a concentration between C_s and C^*, it is reasonable to propose that aggregates of coils would be temporarily formed in solution when coils collide and there should exist a distribution of the sizes of aggregates. The amount of single-chain coils would

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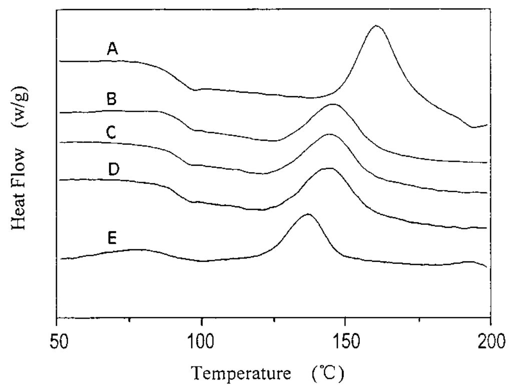

Figure 3. DSC traces of collective particles prepared from 1 × 10^{-2} wt % solution after annealing at 100 °C for various times: (A) bulk sample; (B) 10 h; (C) 5 h; (D) 1 h; (E) virgin sample.

increase as the concentration moves toward C_s, while aggregates of various sizes dominate as the concentration increases toward C^*. On the other hand, phase separation could occur during the freezing process if the cooling rate was not sufficiently fast, thus producing more aggregates.[5] Therefore, the resulting collective particles from the solution of concentration < C^* would be a mixture of single-chain particles and pauci-chain particles. However, a limitation of single-chain particles seems to be reached; as is seen in Figure 1, the crystallization behavior of the collective particles from 2 × 10^{-3} wt % solution is close to the case of 1 × 10^{-3} wt % solution.

Single-chain coils gradually shrank to form compact globules due to the interaction of segments after the solvent was moved. But the compact globules still contain voids and have a lower density;[6,7] even pauci-chain particles are also less dense. Consequently, the molecular motion of segments within collective particles is relatively easy, leading to an increase in crystallization rate. However, the density of the collective particles was reported to be only about 3% below bulk polymer.[7] Annealing of collective particles from 1 × 10^{-2} wt % solution was performed at the glass transition temperature of *i*-PS (100 °C) for various times. As illustrated in Figure 3, T_{ch} was found to go up continually to 144 °C from 136 °C until 10 h of annealing, most likely due to further dense packing of particles and segments in particles, but it is still 20 °C below that of the bulk polymer.

For single- and pauci-chain particles, there are no or far fewer interchain entanglements, which must be a main reason for the acceleration of crystallization rate. Holding the collective particles at a temperature above the equilibrium melting temperature of *i*-PS for 15 min resulted in recovery of crystallization and melting behavior characterized by bulk polymer. It seems that the coils in the melt could be interpenetrated easily, at least at surface of particles, resulting in formation of a continuous entangled network of chains as in the bulk melt. Therefore, entanglements must have a great retardation effect on the crystallization of polymers, as shown for the first time on the experimental grounds.

Flory and Yoon[8] argued that macromolecules in the melt cannot disentangle from each other during the time scale required for the crystallization front to advance across these selfsame molecules. In other words, disentanglement cannot take place during crystallization and so entanglements have no effect on crystallization rate. On the contrary, Hoffman et al.[9] also estimated the time needed to reel in a macromolecule from the melt onto the growing crystal surface, using both reptation and sea snake models. It is about 3 orders of magnitude faster than the estimate by Flory and Yoon, and is consistent with crystallization rate data. They concluded that there is no barrier to reeling-in of macromolecules due to entanglements during crystallization. Moreover, Hoffman et al.[10] introduced the reptation concept into nucleation theory and proposed that reeling-in of molecules is fast enough to keep up with the substrate completion rate in regime I (a temperature region of low supercooling), unless different parts of the same molecule are simultaneously incorporated into different niches such as in regime III (a temperature region of high supercooling). Therefore, the effect of entanglements on the crystallization can be negligible for macromolecules with moderate molar mass in regime I. However, according to our experimental results, entanglements would have a large barrier to the crystallization of polymers and may control the crystallization rate, even in regime I. For the crystallization of the collective particles, the particle may crystallize itself and may not initiate other particles to crystallize if the particles are kept separated from each other. As a result, the overall crystallization rate seems to be mainly dependent on the primary nucleation rate. If the close packing of the collective particles is reached after annealing at 100 °C, the density of segments should be similar to that in the melt, and then the overall crystallization rate is related to both of nucleation rate and growth rate. In both cases, DSC analysis has indicated the retardation effect of entanglements on the crystallization of polymers.

On the basis of the observation of annealing effects, the interpenetration between compact globules is a very slow process at low temperature. On account of their fast crystallization, it seems impossible for collective particles to amalgamate before crystallization during the cold crystallization process. Therefore, crystallization is assumed to occur in-situ within compact globules and nano crystals are produced. As is seen from Figure 1, T_m of freeze-dried samples depresses as the solution concentration decreases (10 °C below that of bulk *i*-PS in the case of 1 × 10^{-3} wt %); this T_m depression is attributed to the decreasingly small size of the resulting nanocrystal. Equation 1 gives a correlation between T_m and the volume (V) of a crystal:[4a]

$$T_m = T_m^0[1 - (6/\Delta h_f)(\gamma_e \gamma^2/V)^{1/3}] \qquad (1)$$

Here T_m^0 is the equilibrium melting temperature, Δh_f is the heat of fusion per cubic centimeter, γ and γ_e are the side and fold surface free energies, respectively. For the crystals from 1 × 10^{-3} wt %, the T_m is 484.4 K. With the values[11] of $T_m^0 = 516.2$ K, $\Delta h_f = 9.678 \times 10^8$ erg/cm^3 and $\gamma^2\gamma_e = 1.48 \times 10^4$ erg^3/cm^6 and adopting the observed thickness of 11.4 nm,[4b] the average particle diameter of nano crystals is 38 nm. For the number-average molar mass ($\bar{M}_n = 6 \times 10^5$) and the highest molar mass ($M_i = 4 \times 10^6$) in the distribution of the used sample, it can be estimated to have average particle diameters of 10 and 24 nm, respectively, when using the observed thickness in combination with the density data (1.13 g/cm^3) of *i*-PS. Apparently, the average particle diameter from eq 1 is larger than that of the single-chain crystals of average molar mass, even larger than the size of the crystals from the highest molar mass fraction. However, in recognition of uncertainties of $\gamma^2\gamma_e$ of *i*-PS,[12] the size calculation based on eq 1 is only an approximate estimate. On the other hand, such a larger size may be produced from the growth of crystals. Once a molecule crystallizes, it initiates other molecules to crystallize on the growing crystal surface, leading to a crystal larger than a single-chain crystal, unless the separation of single-chain particles is at a distance far beyond the molecular scale so that other chains cannot reach the crystal through diffusion. In addition, the larger crystal dimension may also be caused by phase separation during the freeze-drying process because of an insufficient cooling rate and by reorganization of crystals during the DSC scan. Nevertheless, the initial particles from a 1×10^{-3} wt % solution should be a mixture of single-, pauci-, and even multi-chain particles. A detailed investigation of crystallization and melting behavior of the collective particles will be published later.

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