Metastable Isotactic Poly(methyl methacrylate) Prepared by Freeze-Extracting Solutions in Poly(ethylene glycol)

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Introduction. Stereo-regular poly(methyl methacrylates) have received considerable attention due to the ability to form helix and double-stranded helix structures,[1] which are often encountered in biological systems. The crystallization of isotactic poly(methyl methacrylate) (i-PMMA) is a very slow process. It takes many days or even weeks to develop a semicrystalline morphology in melt or in a solution-cast i-PMMA film by annealing at elevated temperature.[2] Some recent measurements have focused on the consequences of rapidly taking polymers from the dilute solution regime to a concentrated state.[3−5] This was interpreted as an indication that during rapid freezing the extent of chain interpenetration which had existed in the solution would be preserved. It was found that the thermal behavior of a freeze-dried polymer sample depends strongly on the concentration of the original solution.[3−5] There is a concentration boundary for the original solution: below the boundary, due to much fewer interchain entanglements within and between particles, the freeze-dried polymer samples could crystallize quickly upon heating; above the concentration boundary, the freeze-dried polymer is in completely disordered amorphous conformation.[3−5] By wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) measurements, in this Communication we find that the freeze-extracted i-PMMA sample from a concentrated poly(ethylene glycol) (PEG) solution is in a metastable phase, which is poorly crystallized but can be easily transferred to crystalline state upon heating. It has a higher glass transition temperature than the raw i-PMMA, but this difference disappears after melting at 160 °C. The metastable i-PMMA sample freeze-extracted from concentrated solutions in PEG shows a desirable crystallization tendency comparable with that of the i-PMMA sample freeze-extracted from very dilute solutions in dioxane, in which solution regime that less interchain entanglements is generally assumed to be favorable of crystallization.

Experimental Section. The i-PMMA and PEG (M_w = 400) were purchased from Aldrich Co. ^{13}C NMR spectra showed that the i-PMMA sample contained more than 90% isotactic triads. The viscosity-average molecular weight (M_v) of this highly stereoregular i-PMMA was about 69.0×10^4, measured in chloroform at 25 °C. A desired amount of i-PMMA and PEG was added into a 10 mL Erlenmeyer flask. The mixture was initially heated to 150 °C while being stirred in a silicon oil bath and then held at this temperature for 6 h to ensure that all of the i-PMMA had fully dissolved in the PEG and to make a homogeneous solution with concentrations of 15 wt %. The hot solution was then added directly into a large amount of liquid nitrogen so that it was frozen in a fraction of a second. The frozen solution was then extracted by the cold ethanol with magnetic agitation for 1 day. After high-speed centrifugal separation, the PEG-rich ethanol solution was removed. The i-PMMA sediment was vacuum-dried to constant weight and then ready for the next cycle of freeze-extracting. The above process was repeated until no weight loss of PEG was observed during the two successively dried i-PMMA samples. The collective powders from concentrated solutions by freeze extraction were designated as sample freeze-extracted i-PMMA. For comparison, a freeze-extracted i-PMMA sample from solution in dioxane was prepared. The M_v of the freeze-extracted i-PMMA powders was measured to be 63.6×10^4 and 65.0×10^4, respectively, which were only slight lower than that of the raw polymer. The freeze-extracted samples were examined by WAXD (Rigaku D/Max-Ra diffractometer) and DSC (Perkin-Elmer model DSC-2C system with a data station) measurements.

Results and Discussion. In Figure 1 are shown the WAXD recorded from the freeze-extracted i-PMMA from PEG (top) and dioxane (bottom). Curves A were recorded at room temperature from the freshly freeze-extracted i-PMMA, and curves, B, C, D, and E were recorded from the samples after they had been heated to 60 °C for 15, 22, 37, and 44 h, respectively. Curves A in Figure 1 exhibit broad and intense bands, with the center at $2\theta = 13.8°$. This shows that i-PMMA freshly freeze-extracted from concentrated solutions in PEG and in dioxane are mainly in the amorphous phase. After annealing the freeze-extracted i-PMMA recovered from PEG at 60 °C for 15, 22, and 37 h, several crystalline peaks appeared gradually in the range of $2\theta = 5°-30°$, which could be clearly observed in the upper curves in Figure 1. However, WAXD patterns in Figure 1 (bottom) show broad haloes even after annealing the sample for many hours, indicating that the i-PMMA freeze-extracted from dioxane is difficult to crystallize at 60 °C.

Crystallinities are obtained by dividing the crystalline intensity by the total diffracted intensity. A Fortran program was edited to resolve the band and to calculate the crystallinity content. Different sets of fitting parameters are tried; they all give relative uncertainty below 10% (as shown in Figure 1). After the computer calculation, the degree of the crystallinity of i-PMMA freeze-extracted from PEG before and after heating treatment was 0.09 and 0.4, respectively. Curves in Figure 1 (bottom) indicate that the crystallinities of i-PMMA recovered from dioxane were very low.

It is well-known that i-PMMA is considered as a semicrystalline polymer characterized by very slow crystallization rates and relatively low crystallinity.[2] Both de Boer et al.[2a] and Konnecke et al.[2b] found that the optimal temperature with respect to crystallization rate was about 120 °C. Crystallization at lower temperature would be greatly retarded owning to the restricted motion of chain segments. Scheider et al.[2c] arrived at a degree of crystallinity of 0.15 for the cast

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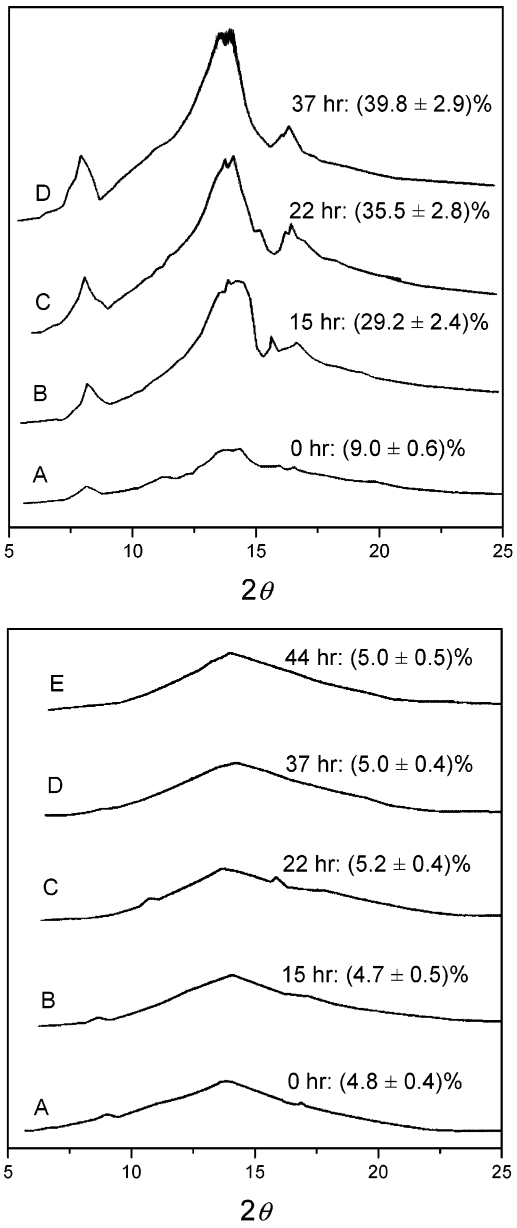

Figure 1. Wide-angle X-ray diffraction curves recorded from i-PMMA freeze-extracted from PEG solution (top) and from dioxane solution (bottom) after annealing at 60 °C for various times.

film from acetonitrile solution after annealing at 120 °C for 14 days. The maximum degree of crystallinity of 0.58 was obtained by Konenecke et al.[2b] and Buyse et al.[2d] after annealing the i-PMMA gel for over 2 weeks.[2c] In this study, we find that the fresh i-PMMAs (solvent-free samples) freeze-extracted from the concentrated solution both in dioxane and in PEG were nearly in an amorphous state. But the latter became a phase of 0.4 crystallinity after annealling at 60 °C for 44 h, showing a much faster crystallization rate.

Figure 2 shows the DSC thermograms of freeze-extracted i-PMMA samples from 15 wt % solution in PEG and in dioxane. Before the DSC measurement they had been annealed at 60 °C for 44 h, which is a temperature near the glass transition of amorphous i-PMMA. The DSC curve for i-PMMA freeze-dried from dioxane shows a glass transition at 59 °C and no melting peaks, while the DSC curve for i-PMMA freeze-extracted from PEG shows a higher glass transition temperature at 67 °C and endothermic peaks near 129 °C, indicating the melt of a crystalline phase formed during annealing. The increase in crystallinity upon annealing is in good agreement with the WAXD study in Figure 1. The increase in T_g indicates a more rigid amorphous phase for the freeze-extracted sample from PEG. The increase in T_g could be maintained even after heating above T_m for a short time. The sample had been kept at 140 °C for 1 min and then quenched to room temperature. The DSC heating scans for these heat-treated samples are shown in Figure 3 (the lower curves), where one can see that T_g for the sample recovered from PEG is 6 deg higher than the raw i-PMMA sample. However, after the samples were heated at 160 °C for 10 min, they show the same T_g at 58 °C (the upper curves), indicating that the structure in i-PMMA recovered from PEG had been disordered after melting at higher temperature for a longer time.

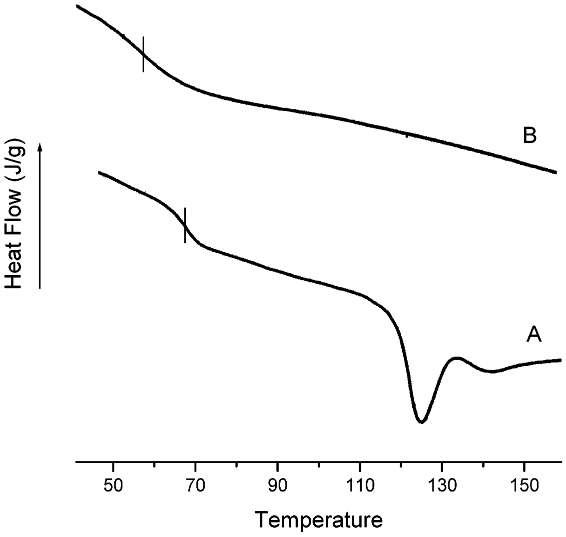

Figure 2. DSC thermograms of freeze-extracted i-PMMA after annealing at 60 °C for 44 h: (A) prepared from PEG solution; (B) prepared from dioxane solution.

For a normal amorphous sample below T_g, only the smaller units such as pendant groups and branched groups can move, but the chain conformation is frozen. Upon heating to T_g, the movement of chain segments is activated, and conformational transitions can be realized. The shift of T_g to a higher temperature indicates the formation of certain organization between i-PMMA segments that restricts their motion.[6] The organization may form as mesomorphic layer or mosaic block structures that precedes the formation of crystallites.[7] Recent time- and temperature-resolved small-angle X-ray diffraction (SAXS) and WAXS obervations have indicated that the organization at local scale contributes mainly to the SAXS intensity before they are detected as Bragg peaks in WAXS.[7] Such an intermediate state between the crystalline and the usual amorphous phase is sometimes generalized as the rigid amorphous fraction or the metastable state in several polymers such as polypropylene[8] and poly(oxymethylene)[9] and in polymers with less flexible structures such as poly(phenylene sulfide).[10] Recently, Cheng and Keller pointed out the role of metastable states in polymer phase transitions.[11] To our knowledge, no papers have ever dealt with the rigid amorphous fraction of i-PMMA. Schneider et al.[2c] reported that the degree of crystallinity for the bulk sample was only 0.15 after annealing for 14 days at 120 °C.[2c] This was considered the

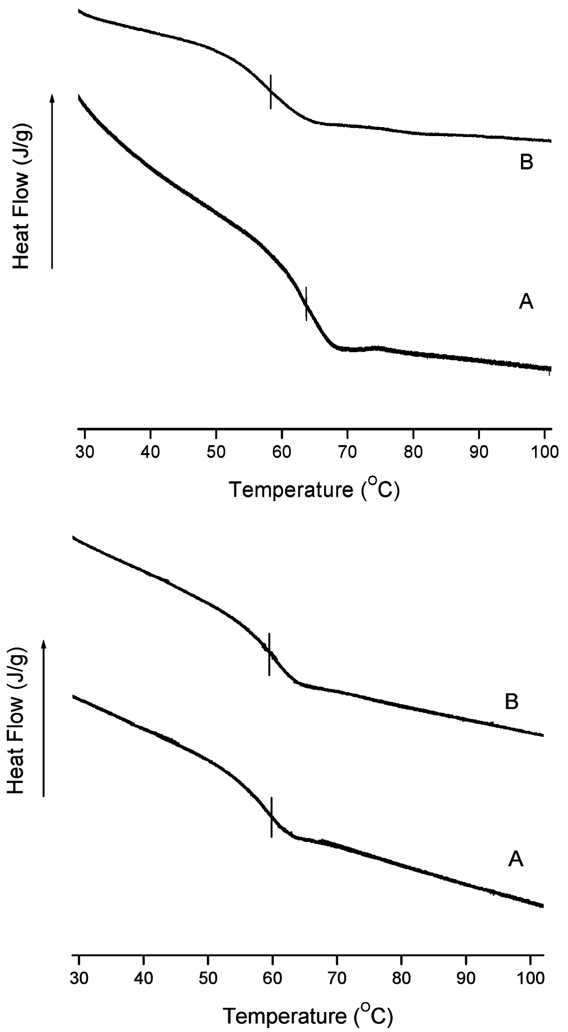

Figure 3. Top: DSC heating scan thermograms for i-PMMA after heating at 140 °C for 1 min. Bottom: DSC heating curves for i-PMMA after melting at 160 °C for 10 min. (A) Freeze-extracted from PEG; (B) the raw i-PMMA as received. The heating rate was 20 °C/min.

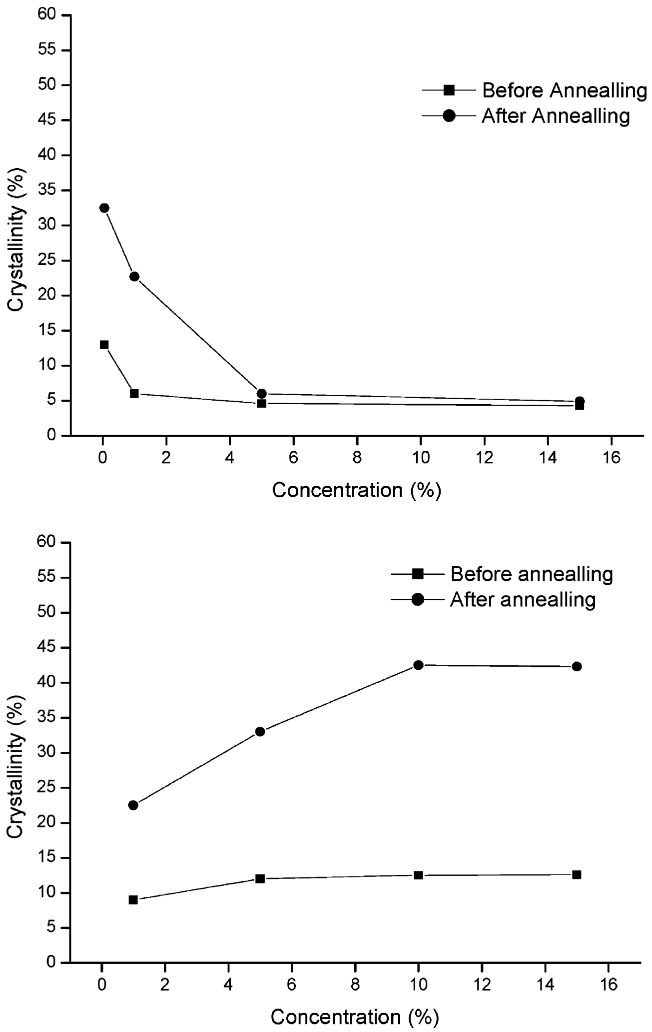

Figure 4. Concentration dependence of crystallinity measured by wide-angle X-ray diffraction for (top) i-PMMA freeze-extracted from dioxane and (bottom) i-PMMA freeze-extracted from PEG.

optimum temperature with respect to crystallization rate for i-PMMA. Compared with the yet slow crystallization rate at the optimal temperature (120 °C) proposed by Schneider et al.,[2c] the growth of crystalline i-PMMA freeze-extracted from PEG at a lower temperature (60 °C) indicates that little heat is required to induce crystallization of this metastable i-PMMA. The top DSC patterns in Figure 3 show no difference in T_g between these i-PMMA freeze-extracted from PEG and the raw polymer, indicating that the original freeze-extracted i-PMMA turned back into the ordinary state after melting at higher temperature for enough time.

The equilibrium and hydrodynamic properties of the polymer solution and the freeze-dried sample are known to depend strongly on the concentration of the original solution in small-sized molecules.[3,4] The crystallization or recrystallization rate is particularly susceptive to the degree of interchain entanglements that is determined by the concentration of the parent polymer solution.[3−5] There is a concentration boundary (about 0.04−0.2 wt %) for the parent solution: below the boundary, due to much fewer interchain entanglements within and between particles, the freeze-dried polymers i-PS, PET, and PVF_2 samples could crystallize quickly upon heating; above the concentration boundary, the total solution space can no longer accommodate the polymer coils without some chain entanglement, and the freeze-dried polymers are in completely disordered amorphous conformation.[3−5] Figure 4 (top) shows the plots of the level of crystallinity vs concentration of solutions in dioxane from which the i-PMMA samples were freeze-extracted. The crystallinity is low in the concentrated and semidilute regimes, while it increases rapidly as the concentration becomes very dilute. At the vicinity of 0.05 wt %, the crystallinity degree reaches a maximum near 35% after annealing at 120 °C for 10 h. In this study, we demonstrated that i-PMMA freeze-extracted from concentrated solutions (10−16 wt %) in PEG showed crystallization tendency comparable with that of i-PMMA sample freeze-extracted from very dilute solutions in dioxane. This may suggest that freeze-extracting semidilute or concentrated solution in solvents of middle molecular size produced i-PMMA powders with the same level of chain disentanglement as that was recovered from a very dilute solution in small-sized solvent dioxane. Additionally, we reported recently that PET, PVC, and i-PS could be also easily crystallized in some middle-sized solvent such as PEG oligomer or DOP.[12] The complexity of the solvent effect, including its molar volume and solvophobical effect, on the conformation of nonbiological polymers in solution is currently under further systematic investigation in this lab.

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