Concentration Dependence of Crystalline Poly(vinylidene fluoride) Prepared by Freeze-Extracting Solutions

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Poly(vinylidene fluoride) (PVDF) is a polymeric material characterized by its piezoelectric and pyroelectric effects, nonlinear optical susceptibility, and an unusually high dielectric constant. Degrees of crystallinity in PVDF are generally in the vicinity of 50%.[1-5] PVDF is usually crystallized from solution and from the melt at atmospheric and elevated pressures. In this paper, we describe a new method for the crystallization of PVDF. By rapidly freezing a very dilute solution in dioxane (0.05% by weight) of PVDF in liquid nitrogen followed by freeze-extracting the frozen solvent with ethanol, we obtained a highly crystalline PVDF glass with 71% crystallinity. There is a concentration boundary in very dilute solution for crystallizability of PVDF: near the boundary concentration the chain coils contain a considerable amount of segments with few chain entanglements.

The poly(vinylidene fluoride) used in this study was supplied by Shanghai Chemical Co. The number-average degree of polymerization was stated to be approximately 1000 and the amount of head-to-tail structure approximately 95.5%. Infrared spectroscopy and the X-ray diffractogram showed that its crystalline phase was mostly phase II.

The freeze-extracted samples were prepared by dissolving the original PVDF in dioxane and refluxing for 1 h to obtain solutions of varying concentration. After freezing these solutions in liquid nitrogen, the frozen solvent was extracted with cold ethanol at a temperature below the melting point, and then the sample was separated by ultracentrifugation and dried under vacuum at room temperature. The resulting PVDF powder was designated as shock-cooled and freeze-extracted PVDF. This procedure was simpler than the freeze-drying method which took a much longer time to sublime the frozen dioxane.[6]

For comparison, PVDF samples were also prepared by freezing the solution at relatively slow rate in a refrigerator followed by freeze-extracting.

Infrared spectra were measured with a Fourier transform infrared spectrometer, Nicolet FT-IR 170 SX. All of the spectra were taken with 4 cm^{-1} resolution. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer Model DSC-2C system with a data station. Data processing was carried out with the software furnished by the instrument manufacturer. The heating rate was 10 °C/min.

Figure 1 illustrates FT-IR spectra recorded from PVDF freeze-extracted from solutions with varying concentration. These spectra show that the samples have two concentration-dependent properties: one is the phase transition, and the other is the degree of crystallizability. In dioxane solvent PVDF normally crystallizes in form III shown in parts A, B, and D of Figure 1. But some bands such as 763, 795, and 975 cm^{-1} [7] also indicate a significant amount of phase II. As to Figure 1C, the relative intensity of the peaks around 532 and 510 cm^{-1} and the bands at 975, 795, 763, and 614 cm^{-1} shows that the freeze-extracted 0.05 g/dL sample is mostly form II. On the basis of the DSC curve in Figure 3A and also according to the method used in our previous paper,[6] we obtained 71% for the crystallinity of the freeze-extracted 0.05 g/dL PVDF. The "crystalline" vibrational bands at 613, 763, 795, and 975 cm^{-1} of the freeze-extracted sample from 0.05 g/dL are more intense than those prepared from other solutions, while the 842 cm^{-1} "amorphous" band decreases in intensity. Moreover, WAXD results also confirm this conclusion. All these findings suggest that there is a concentration boundary for the crystallizability of PVDF by the freeze-extracting method.

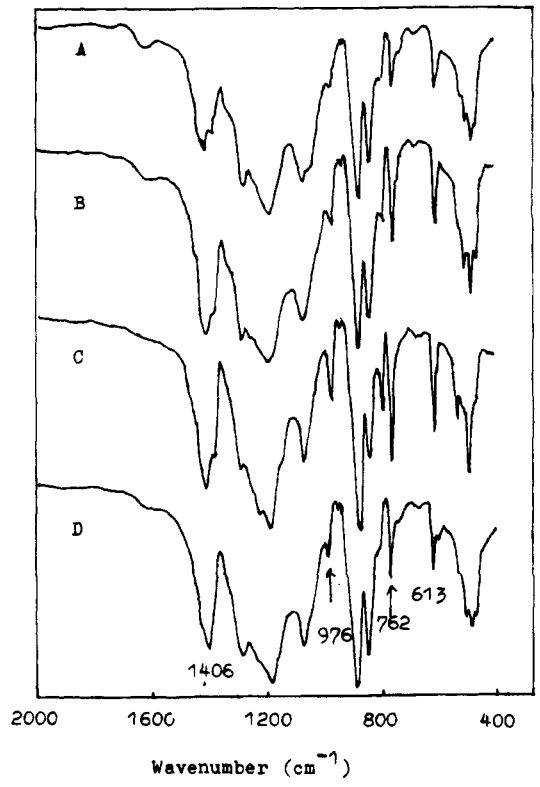

Figure 1. FT-IR spectra of freeze-extracted PVDF from (A) 5, (B) 0.5, (C) 0.05, and (D) 0.02 g/dL solutions.

The crystallinity of the prepared samples can be measured from wide-angle X-ray diffractograms, IR spectra, and DSC curves. Figure 2 shows two plots of the crystallinity versus the concentration of solutions from which the PVDF samples were prepared by shock-cooled and slow-cooled and freeze-extracting methods, respectively. The crystallinity is low in the semidilute and dilute regimes, while it increases rapidly as the concentration becomes more dilute. Near 0.05 g/dL, the crystallinity reaches a maximum near 71%. The crystallinity of PVDF prepared by the freeze-extracting method is much higher than those prepared by normal solution crystallization and thermal annealing techniques.[1-6]

It has been established that the chain configuration of the form II PVDF is tg^+tg^- and that of the form III is $tttg^+tttg^-$. Welch[8] had studied the dilute solution

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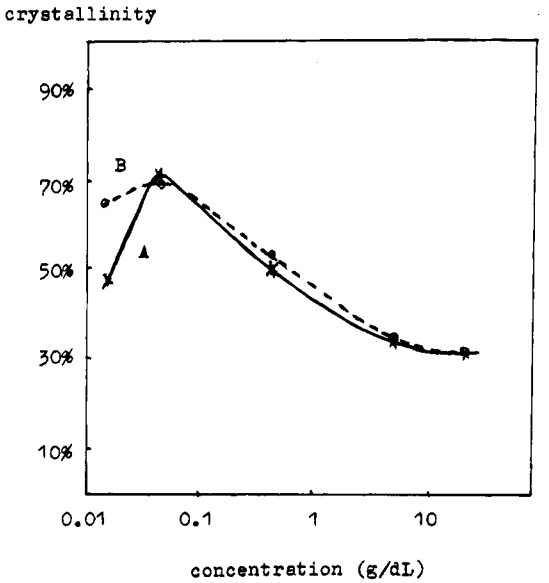

Figure 2. Plots of crystallinity versus concentration of the original solutions: (A) PVDF prepared by rapid-cooling and freeze-extracting. (B) PVDF prepared by slow-cooling and freeze-extracting.

properties of PVDF, and Tonelli[9] had calculated the unperturbed dimensions of isolated PVDF chains. Tonelli's calculation shows that there are strong electrostatic interactions in the chains of isolated PVDF. On the basis of these conceptions, we suggest that, because of the strong electrostatic interactions, the PVDF chains take a much more ordered or extended arrangement in the 0.05 g/dL solution, with less entanglements than in the 0.5 and 5 g/dL solutions. Since at a high dilution the distances between chains become too great for the coils to crystallize, the shock-cooled and freeze-extracted PVDF is less crystalline if the concentration is lower than 0.05 g/dL as illustrated in Figure 1 and Figure 2A. However, when the very dilute solution (c = 0.02 g/dL) was frozen relatively slowly, the chain coils could aggregate, resulting in a high crystalline PVDF as shown in Figure 2B.

Some recent measurements have focused on the consequences of rapidly taking polymers with flexible chains from the dilute solution regime to a concentrated state. Measurements of nonradiative energy transfer between a mixture of donor- and acceptor-labeled polystyrene freeze-dried from a dilute solution suggested that the neat polymer obtained is comprised of nonoverlapping collapsed coils.[10,11] The concentration of the solution for polystyrene used in these reports was 0.83 g/dL. This is 4 times more dilute than the critical concentration, C^*, at which overlap of the polystyrene chains would commence.[12] However, NMR experiments indicated that substantial interpenetration exists among polystyrene chains freeze-dried under the same conditions.[13,14] Further experimentation is desirable to explain the curious contradictions between the NMR and fluorescence experiments. Our study of PVDF, another flexible chain glass prepared by freeze-extracting varying solutions, indicates that the flexible chain coils expanded as the solution became more dilute and reached a maximum expansion in 0.05 g/dL solution. This boundary is in the very dilute regime. As the expanded chain coils were frozen in a fraction of a second in liquid nitrogen followed by removal of the solvent, a more ordered or extended chain state persisted, yielding a highly crystallized polymer. But

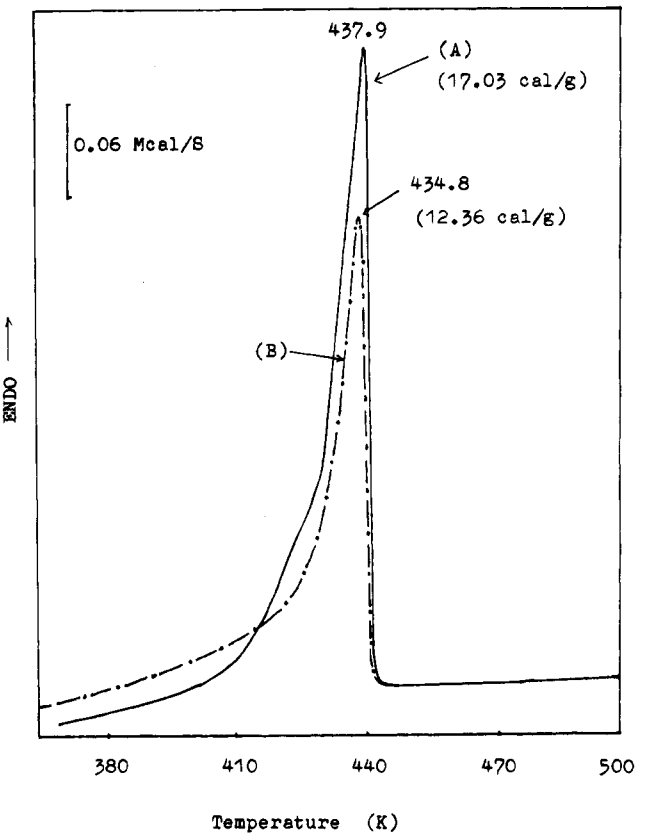

Figure 3. DSC curves of the freeze-extracted PVDF: (A) the first scan from 20 to 260 °C. (B) the second scan.

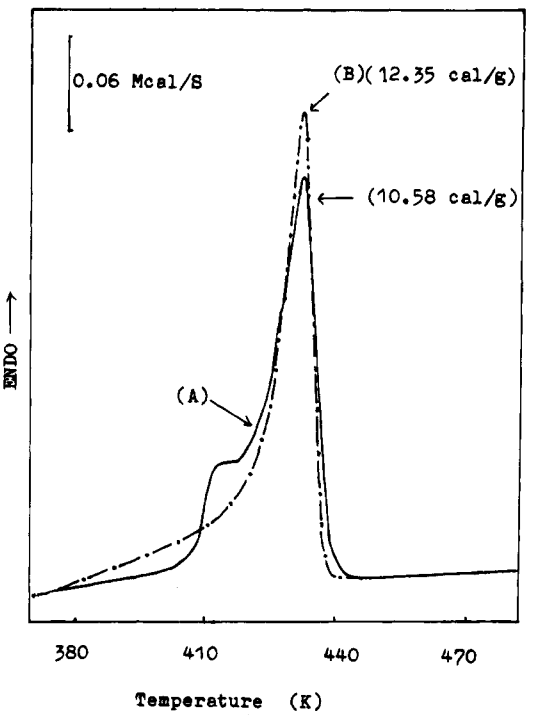

Figure 4. DSC curves of a commercial PVDF as received: (A) the first scan from 20 to 260 °C. (B) the second scan.

PVDF freeze-extracted from a 0.50 g/dL solution seems to contain less crystallinity. Our finding about the concentration boundary near 0.05 g/dL for PVDF is in good agreement with Qian's results about the concentration boundary in dilute polystyrene solution studied by excimer fluorescence experiments.[15] The unambiguous conclusion drawn from the FT-IR experiments is

that the coils of PVDF in a very dilute solution (near 0.05 g/dL) contain a considerable amount of segments with a few chain entanglements. As the solution was rapidly frozen, the segments aggregated to crystals resulting in a freeze-extracted PVDF with considerable crystallinity. The crystallinity of PVDF prepared by freeze-extracting a 0.05 g/dL solution is much higher than that prepared by the conventional solution precipitation and annealing methods.[1-5]

Figures 3 and 4 show DSC curves of the commercial PVDF and the freeze-extracted PVDF from a 0.05 g/dL solution. The sample was first scanned from 20 to 260 °C (curve A), followed by air cooling to 20 °C at 2 °C/min. A second scan from 20 to 260 °C was then carried out (curve B). The initial scan in Figure 3 shows a strong exothermic peak due to the melting of the crystallites. Based on the heat of fusion, the freeze-extracted PVDF is calculated to have 71% crystallinity. But the curve of the second scan shows that the sample has only 52% crystallinity after melting, which is exactly the same as the second scan of the commercial sample, as illustrated in Figure 4. This phenomenon suggests that the initial freeze-extracted PVDF is in a highly crystalline phase with less chain entanglements, and after the melting at 260 °C, the chain coils return to the normally entangled state. As a result, the freeze-extracted PVDF after melting shows a thermal property similar to that of ordinary commercial samples crystallized from the melt.

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