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Crystallization of poly(vinylidene fluoride) by freeze-extracting method

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Summary

High crystallinity poly(vinylidene fluoride) (PVF_2) has been achieved by freezing its very dilute solution and followed by freeze-extracting the frozen solvent. FT-IR, WAXD, and DSC studies indicate that the freeze-extracted PVF_2 has higher crystallinity than those samples prepared by solution crystallization or by thermal annealing techniques.

Introduction

Poly(vinylidene fluoride) is a polymeric material with interesting scientific and technological properties. It is characterized by its piezoelectric and pyroelectric effects, non-linear optical susceptibility and an unusually high dielectric constant.

Degrees of crystallinity in PVF_2 are generally in the vicinity of 50%.[1-5] The usual crystallization methods of PVF_2 are crystallization from solution and from the melt at atmospheric and elevated pressures. In this paper, we describe a new method for the crystallization of PVF_2. By freezing a very dilute solution (0.05% by weight) of PVF_2 in a refrigerator followed by freeze-extracting the frozen solvent, we obtain a highly crystalline PVF_2 sample.

Experimental

The poly(vinylidene fluoride) used in this study was supplied by Shanghai Chemical Company. The number average degree of polymerization was stated to be approximately 1000, and the amount of head-to-head structure approximately 5.5%. Infrared spectroscopy and X-ray diffractogram showed that the crystalline phase was mostly form II.

The freeze-extracted sample was prepared by dissolving the original PVF_2 in purified dioxane and refluxing for 1h to obtain a 0.05wt.-% solution. After freezing the solution in a refrigerator, the frozen solvent was then extracted by cold ethanol at a temperature below the melting point. Separate the sample by ultracentrifugation and dry it under vacuum at room temperature. The resulting PVF_2 powder was designated as

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freeze-extracted PVF_2.

For the sake of comparison, two other samples were prepared by crystallization from a dilute solution (0.05wt.-%) in monochlorobenzene/dimethylformamide (9:1) [6] and by thermal annealing at 158 °C for 22 h.[7]

Results and Discussion

Figure 1 shows the IR spectrum of the freeze-dried PVF_2.

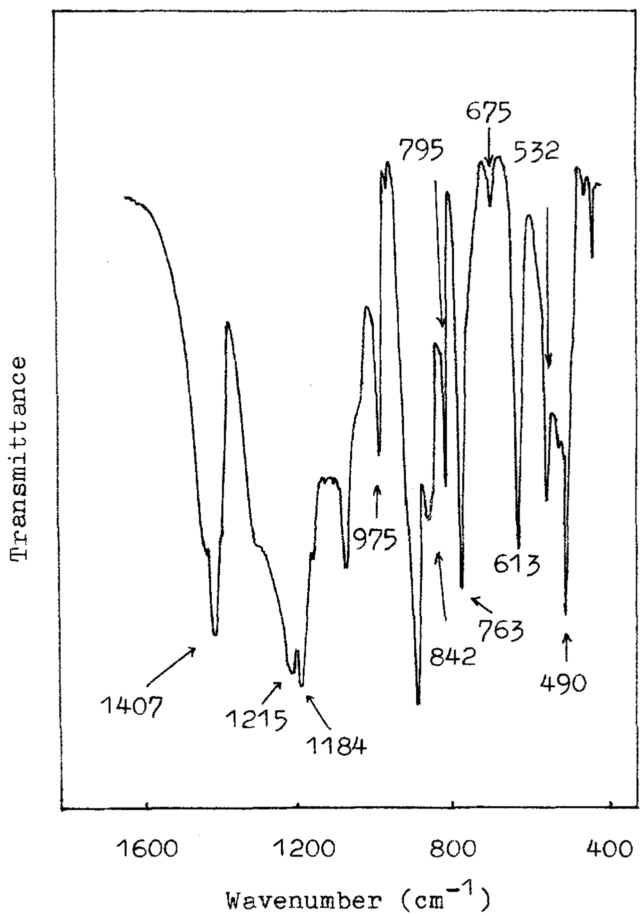

Figure 1. IR spectrum of the freeze-extraxted poly(vinyldiene fluoride)

Based on the characteristic bands at 532, 614, 763, 795 and 975 cm^{-1},[8,9] the freeze-extracted PVF_2 sample is determined to be α phase form (form II), just in the same phase as the solution-crystallized PVF_2.[6] The spectra of original PVF_2, thermal annealed treated PVF_2 and a freeze-extracted PVF_2 are illustrated in Figure 2(A)- (C). The "crystalline" vibrational bands at 975, 795, 763 and 613 cm^{-1} of the freeze-extracted sample are more intense than those of the thermal annealed sample and the original sample; while the 842 cm^{-1} "amorphous" band decreases in intensity. All these finding suggest that the freeze-extracted PVF_2 has a higher crystallinity than the annealed PVF_2 sample.

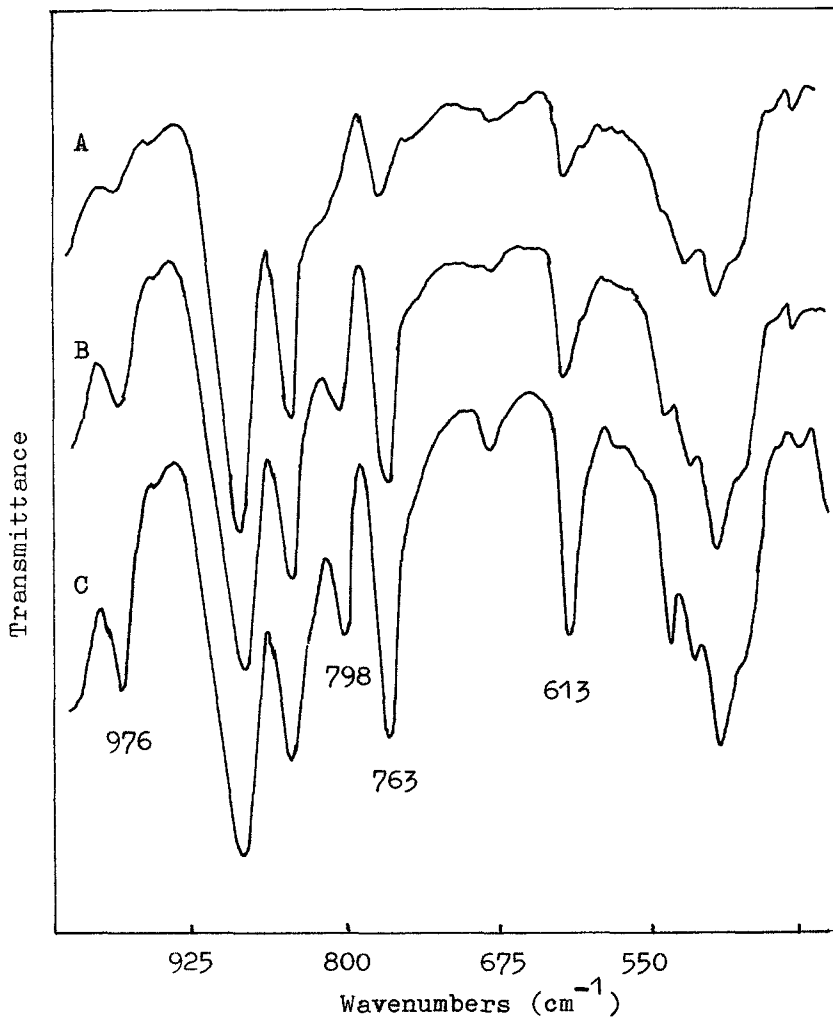

Figure 2. IR spectra of PVF_2; (A) solution crystallized sample; (B) annealed sample; (C) freeze-extracted sample.

Figure 3 displays DSC curves of PVF_2 samples.

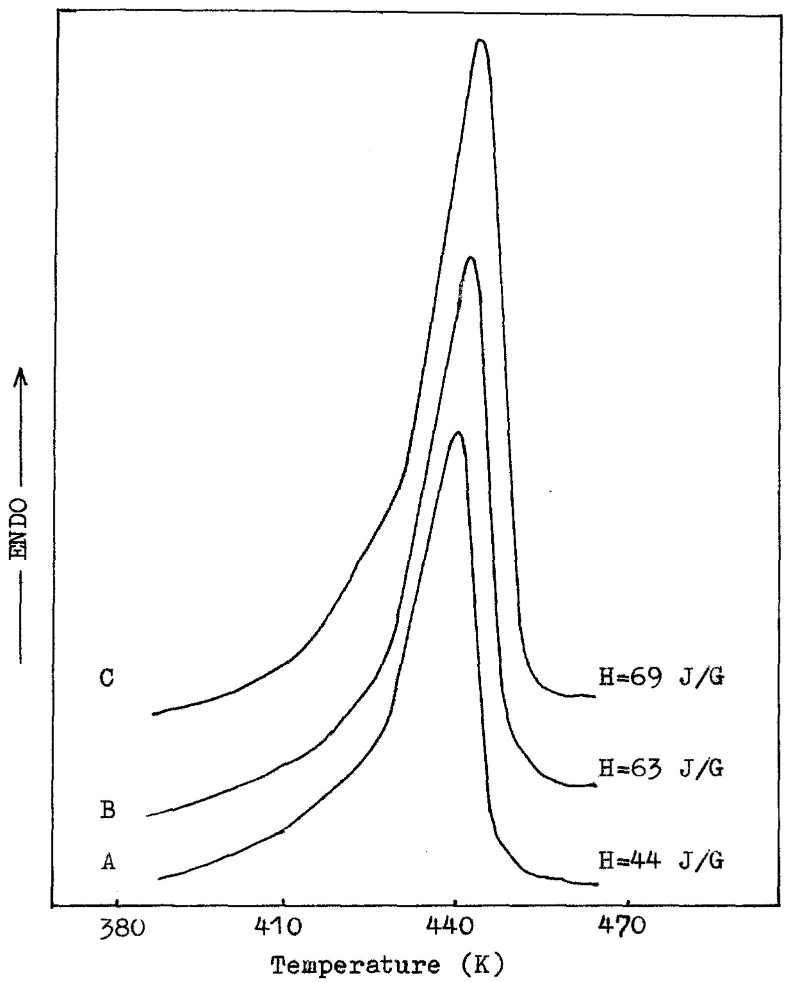

Figure 3. DSC curves of PVF_2 samples; (A) commercial sample as received; (B) annealed sample; (C) freeze- extracted sample.

The apparent heat of fusion is provided by the thermal analyzer and is based on the mass of the sample and the energy consumed during the melting of that mass. The percent crystallinity value can be calculated by the following equation, where C = percent crystallinity, H = the apparent heat of fusion, and H′ = the literature value heat of fusion:

$$C\ (\text{in}\ \%) = (H/H')\quad 100\%$$

According to Kofer et al., the heat of fusion of the α phase PVF_2 is 100 J/g. Therefore, the freeze-extracted PVF_2 is calculated to have 69% crystallinity, while the thermal annealed PVF_2 has about 63%, and the original PVF_2 has 44% crystallinity.

The preceding IR and DSC studies have shown that freeze-extracted PVF_2 has a higher crystallinity than solution-crystallized and thermally annealed PVF_2. This was further confirmed by wide-angle X-ray diffractograms.

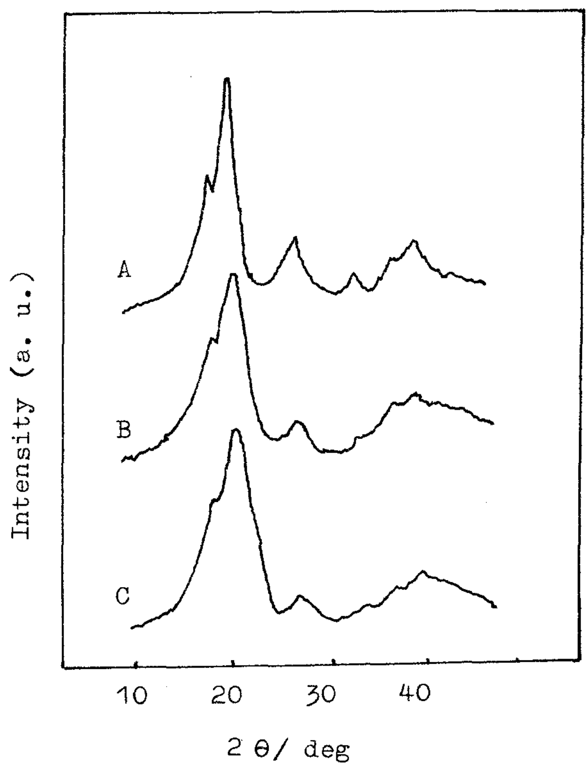

Figure 4. Wide-angle diffractograms of PVF_2 prepared by (A) freeze-extracting method; (B) solution crystallization; (C) annealing at 158 °C for 20 h.

WAXD patterns from three PVF_2 samples prepared are shown in Figure 4(A)-(C). Comparing the X-ray diffraction data with that of Newman and Scheinbeim's,[11] we are able to index the crystalline peaks of freeze-extracted PVF_2 as 100, 020, 110, 021, and 002 respectively. In consideration of the intensity and the sharpness of "crystalline" peaks of the three diffractograms and applying the method of measuring the amorphous and crystalline contents to calculate crystallinity, we come to the same conclusion as through FT-IR and DSC, i.e., the crystallinity of freeze- dried PVF_2 is much higher than that achieved with the usually applied crystallization methods.

It has been established that the chain conformation of α phase of PVF_2 is a 2_1 helix.[12] Welch[13] had studied the dilute solution properties of PVF_2 and Tonelli[14] had calculated the unperturbed dimensions of isolated PVF_2 chains. Tonelli's calculations show that there are strong electrostatic interactions in the chains of isolated PVF_2. Based on these conceptions, we suggest that, because of the strong electrostatic interactions, the PVF_2 chains take a much ordered arrangement in the very dilute dioxane solution with few entanglements. As the solution is frozen rapidly, this interaction forces the isolated chains to aggregate to crystals, resulting in a freeze-dried PVF_2 with considerable amount of crystallite, as evidenced by the FT-IR spectra, DSC curves and WAXD patterns.

References

1. Nakagawa K, Ishida Y (1973) J. Polym. Sci., Polym. Phys. Ed. 11: 2153
2. Lando JB, Olf HG, and Peterlin A (1969) J. Polym. Sci., A-1 4: 941
3. Hasegawa R, Takahashi Y, Chatani Y, Tadokoro H (1972) Polym. J. (Tokyo) 3: 600
4. Enomoto S, Kawai Y, and Sugita M (1968) J. Polym. Sci.,A-2 6: 861
5. Lovinger AJ, Wang TT (1979) Polymer 20: 725
6. Osaki S, Ishida Y (1974) J. Polym. Sci., Polym. Phys. Ed. 12: 1727
7. Bachmann MA, Gordon WL, Koenig JL, Lando JB (1979) J. Appl. Phys. 50: 6106
8. Corrili G, Zerbi G (1967) Spectrochim.Acta 23A: 2216
9. Kobayashi M, Tashiro K, Tadokoro H (1975) Macromolecules 8: 158
10. Kofer U, Hirte R, Weigel P (1982) Acta Polym. 33: 486
11. Newman BA, Scheinbeim JI (1982) Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 23: 164
12. Doll WW, Lando JB (1970) J.Macromol.Sci.(B) 4: 309 13. Welch GJ (1974) Polymer 15: 429

14 Tonelli AE (1976) Macromolecules 9: 547