# Communications to the Editor

## Concentration Dependence of Crystalline Poly(ethylene terephthalate) Prepared by Freeze-Extracting Solutions

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**Introduction.** Poly(ethylene terephthalate) (PET) is a slow-crystallizing material. A solution-cast PET film quenched from the melt is in the amorphous state, which is usually crystallized by annealing at temperatures above the glass transition. However, it takes as long as 2 days to anneal PET to a semicrystalline state at 200 °C.[1,2] Degrees of crystallinity in an annealed PET are generally in the vicinity of 50% measured by the X-ray diffraction method.[1−3] Annealing PET bristles in the drawn state at a temperature as high as 250 °C for 268 min could yield 56% crystalline phase in the sample.[4] The degradation of the amorphous region of a drawn PET fiber with aqueous methylamine resulted in 66% crystalline phase of the PET residual.[5] But this etching procedure made the sample lose more than 80% of its original weight.[5]

In this paper, we describe a new method for the crystallization of PET. By dropping the PET/phenol solution into ice water followed by freeze-extracting the frozen solvent with ethanol, we obtained a PET powder which exhibits much higher crystallizability than a solution cast film. The crystallinity of the freeze-extracted PET depends on the concentration of solutions and on the freezing speed of the solution. There is a concentration boundary in dilute solution for crystallizability of PET: near the boundary concentration the chain coils contain a considerable amount of segments with few chain entanglements. By annealing the freeze-extracted PET prepared from the 0.2% solution, we obtained a highly crystalline PET with 65% crystallinity. The purpose of this communication is to report some experimental results in conformational and thermal properties of these freeze-extracted PET and to propose an explanation for their high crystallizability in terms of chain entanglement.

**Experimental Section.** A commercially available poly(ethylene terephthalate) with an intrinsic viscosity of 0.6 dL $g^{-1}$ determined in *o*-chlorophenol at 25 °C corresponding to an average molecular weight, $M_v$ = 21 000, was supplied by Yizheng Chemical Co. The freeze-extracted samples were prepared by dissolving the commercial PET in phenol and heating to 150 °C for 1 h to obtain solutions of different concentrations (0.03−60 wt %). The solutions were then cooled to 80 °C. After these solutions were frozen by dropping them into ice water, the frozen phenol was extracted with cold ethanol at 20 °C, and then the sample was separated by ultracentrifugation and dried under vacuum at room temperature. The resulting PET powder was designated as freeze-extracted PET. This procedure was simpler than the freeze-drying method which took much longer to sublime the frozen phenol.

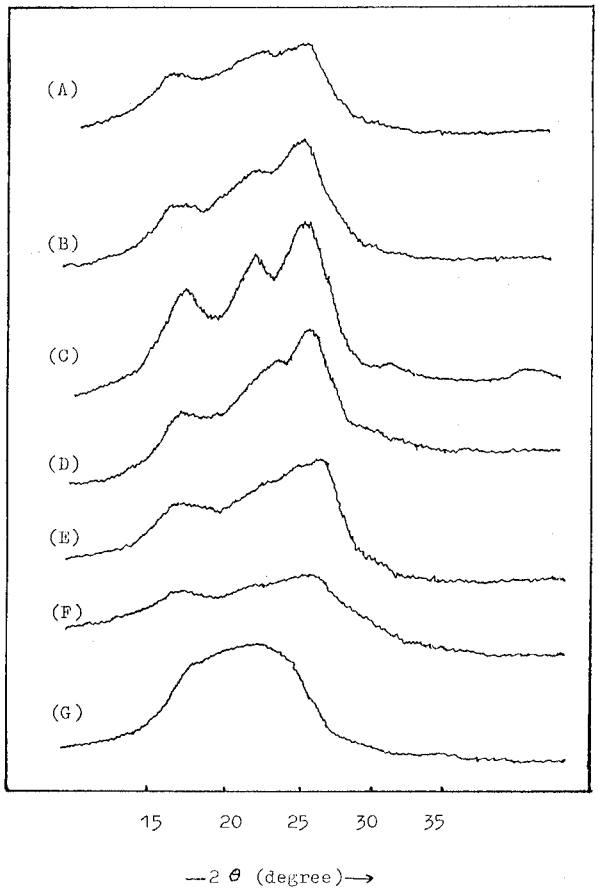


**Figure 1.** Wide-angle X-ray diffraction curves of PET prepared by ice water-cooling and freeze-extracting: (A) 0.03% solution; (B) 0.05% solution; (C) 0.2% solution; (D) 5% solution; (E) 20% solution; (F) 40% solution; (G) a film quenched from the melt.

For comparison, a solution-cast PET film quenched from the melt was studied.

The resulting PET samples were examined by means of a wide-angle X-ray diffractometer (Rigaku D/Max-Ra) using Ni-filtered Cu Kα radiation detected by a scintillation counter with single-channel discrimination. 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.

**Results and Discussion.** Figure 1A illustrates wide-angle X-ray diffraction patterns recorded from a PET film quenched from the melt and from freeze-

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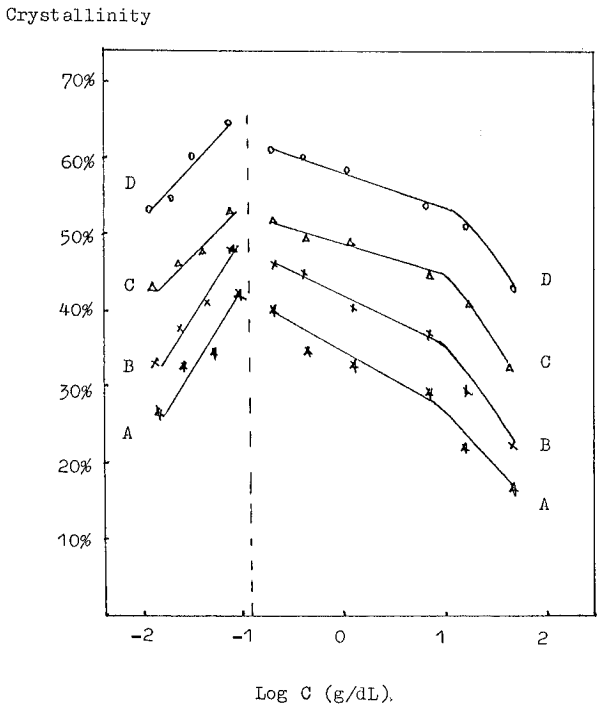


**Figure 2.** Plots of crystallinity versus concentration of the original solutions: the freeze-extracted PET (A) before annealing, (B) after annealing at 150 °C for 1 h, (C) after annealing at 150 °C for 5 h, and (D) after annealing at 200 °C for 24 h.

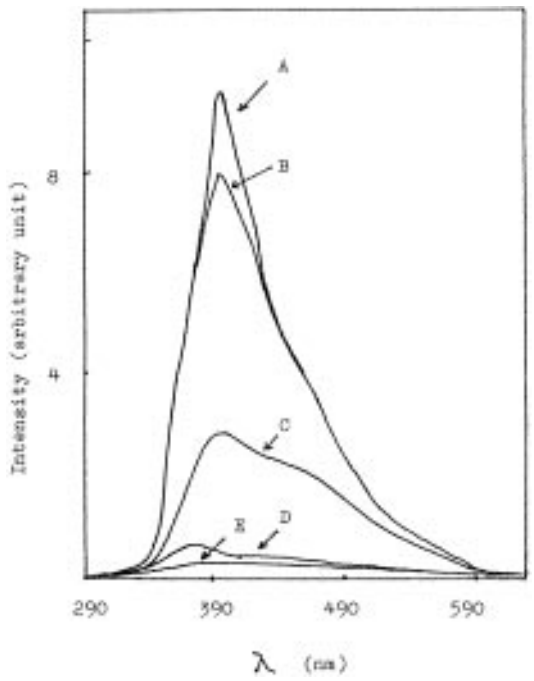


**Figure 3.** Fluorescence spectra recorded on a PET film (A) and on freeze-extracted PET from 20% (B), 0.5% (C), 0.2% (D), and 0.05% (E) solutions.

extracted PET samples from 0.03 to 40 wt % solutions. These patterns show that the samples have a concentration-dependent crystallinity. The quenched film from the melt seems to be amorphous. The PET sample prepared by quenching the 80 °C solution in ice water followed with freeze-extracting the solvent contains a considerable amount of crystalline phase. The melting point of phenol is about 41 °C. Freezing the PET–phenol solution in ice water at 0 °C seems to create numerous nuclei of solvent which might induce the nucleation of the PET solute. The macromolecules of PET in dilute solutions are in an expanded state depending upon the interaction between polymer and solvent, which are supposed to contain fewer chain entanglements than the normal PET in the solid state. As the entire solution was frozen and subsequently the solvent was extracted below its melting temperature, the PET macromolecules would remain in their expanded state to a certain extent. During the extracting process, a partially crystalline phase could be formed, as shown by the wide-angle X-ray diffractogram pattern in Figure 1A. After annealing the freeze-extracted PET, the crystallization will proceed very fast since there are many nuclei in the sample and there are fewer chain entanglements. The ice water-cooled and subsequently freeze-extracted PET is highly crystallizable, as shown by the wide-angle X-ray diffraction curves in Figure 1.

Figure 2 illustrates plots of the crystallinity of PET samples before and after annealing versus the concentration of solutions from which the PET samples were prepared by the freeze-extracting methods, respectively. The crystallinity is low in the concentrated regimes, while it increases rapidly as the concentration becomes more dilute. Near 0.2 wt %, the crystallinity reaches a maximum near 45% before annealing and near 65% after annealing at 200 °C for 24 h.

Some recent measurements have focused on the consequences of rapidly taking polymers with flexible chains from the dilute solution regime to a concentrated state.[6–10] Our study of the crystallizability of freeze-extracted PET from solutions with different concentrations found that there is a concentration boundary in the dilute region. For each annealing treatment, with increasing polymer concentration the crystallinity first increases and then decreases after reaching a maximum. It is clear that there is a concentration boundary near 0.2% for the crystallizability of PET: near the boundary concentration the macromolecular chains contain a considerable amount of segments with few chain entanglements. At concentrations above 0.2%, chain overlap leads to more entanglements, and as a result the freeze-extracted PET samples from concentrated solutions exhibit less crystallizability. In a polymer solution with a concentration that is higher than the critical concentration, where the crystallinity is highest, the molecular weight between neighboring entanglements, $(M_c)_{soln}$, is given approximately by[11]

$$(M_c)_{soln} = (\rho/C)M_c = M_c/\phi$$

where $\rho$ refers to the bulk density of polymer and $\phi$ is the polymer volume fraction in the solution. $M_c$ is the molecular weight between entanglements in the undiluted polymer melt. This equation shows that $(M_c)_{soln}$ is inversely proportional to the volume fraction of the polymer, and hence the number of entanglements per molecule for a given molecular weight is proportional to it. This means that the number of entanglements per molecule can be controlled by the concentration of the polymer solution. Above the critical polymer concentration, crystallinity decreases with increasing polymer concentration due to the increasing entanglement density. But at high dilution the distances between chains become too great for them to crystallize, the freeze-extracted PET is less crystalline if the concentration is lower than 0.1 wt %, as illustrated in Figure 2.

Fluorescence studies of intra- and interchain excimers in PET and poly(ethylene-2,6-naphthalenedicarboxylate) (PEN) have been reported previously.[12,13] In a

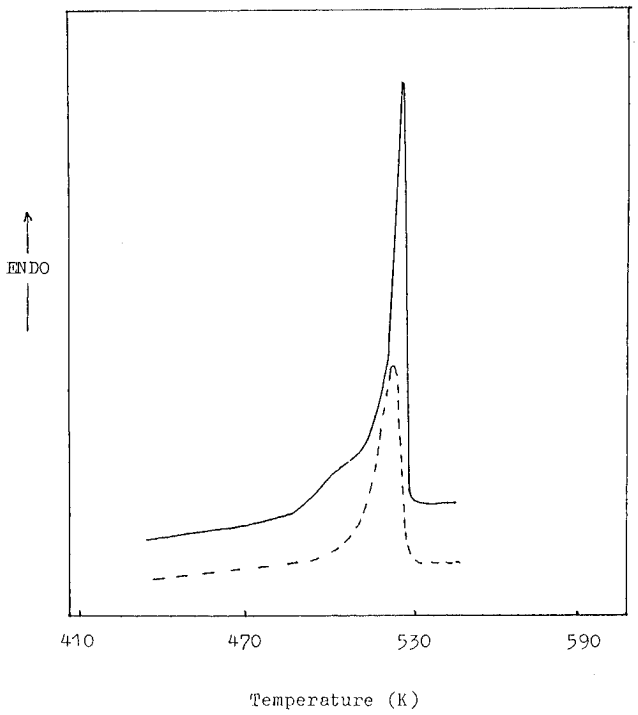


**Figure 4.** DSC curves of the freeze-extracted PET prepared from 0.2% solution. The dotted line was recorded in the second scan.

solid PEN film, excimer fluorescence was observed before and after stretching. In the biaxially stretched film, the naphthalene rings in PEN will tend to orient along the plane of the film so as to increase the probability of naphthalene rings favorable for excimer formation.[12] We measured fluorescence spectra of the excimer for the freeze-extracted PET with excitation at 338.7 nm. Figure 3 shows the fluorescence spectrum of an amorphous PET film (Figure 3A) and the spectra of freeze-extracted PET from various solutions (Figure 3B−E). Of particular interest here is the observation that the fluorescence spectral intensities decrease rapidly on reducing the concentration of the solutions from which the PET samples were prepared by freeze-extracting methods. Hence, it appears that the interchain distance in the freeze-extracted PET from a dilute solution is larger than that in a PET film, resulting in a faster crystallization.

Figure 4 shows DSC curves of the freeze-extracted PET from the 0.2% solution and the annealed PET films. The samples were first scanned from 20 to 260 °C (solid lines), followed by air cooling to 20 °C at 2 °C/min. A second scan from 20 to 260 °C was then carried out (dotted lines). The initial scan in Figure 3 shows a strong exothermic peak due to crystal melting. The shoulder in the curve of Figure 4 is probably due to the melting of crystallites containing partially extended chains.[14] On the basis of the heat of fusion, the freeze-extracted PET is calculated to have high crystallinity. But the curve of the second scan shows that the samples have a lower crystallinity after melting. This phenomenon suggests that the initial freeze-extracted PET is highly crystalline with fewer chain entanglements, and after the melting at 260 °C, the chain coils return to the normally entangled state. As a result, the freeze-extracted PET after melting shows a thermal property similar to that of an ordinary PET film.

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