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Highly crystallizable poly(ethylene terephthalate) prepared by freeze-extracting solutions

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Poly(ethylene terephthalate) (PET) solutions in phenol were crystallized together by dropping the solution into ice water. The solvent was subsequently extracted at a temperature below its melting point with ethanol. Wide-angle X-ray diffraction study indicates that the freeze-extracted PET powder exhibits a much higher crystallizability than a solution cast PET film. The crystallization speed and the ultimate crystallinity for the freeze-extracted PET depend on the concentration of the solution from which the sample was prepared. There is a concentration boundary in the dilute region for crystallizability of PET: near the boundary concentration, the chain coils contain a considerable amount of segments with few chain entanglements. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Poly(ethylene terephthalate)(PET) is a slow crystallizing material. In the fabrication of articles, films, and fibers, the slow crystallization properties of PET will influence the dimension stability of these products, and thus will limit their application range. 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 X-ray diffraction method[1–3]. Annealing PET bristles in the drawn state at the 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 could increase the crystallinity up to 66% in the PET residual[2].

In this paper, we describe a new method for the crystallization of PET. By dropping PET solution in phenol into ice water followed by freeze-extracting the frozen solvent with ethanol, we obtained a PET powder which exhibits much higher crystallizability than a cast film. The crystallinity of the freeze-extracted PET depends on the concentration of solutions and on the freezing speed. There is a concentration boundary in dilute region for crystallizability of PET: near the boundary concentration, the chain coils contain a considerable amount of segments with few chain entanglement. By annealing the freeze-extracted PET prepared from 0.2% solution at 150°C for 250 min, we obtained a highly crystalline PET glass with 65% crystallinity. The purpose of this paper 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

A commercial available poly(ethylene terephthalate) with an intrinsic viscosity of 0.6 dl g^{-1} determined in o-chlorophenol at 25°C corresponded to an average molecular weight, $M_v = 19\,000$ was supplied by Yizheng Chemical Co. The freeze-extracted samples were prepared by dissolving the commercial PET in phenol and heating to 100°C for 1 h to obtain solution of different concentrations (0.03–40%). The solutions were then cooled to 60°C. After freezing these solutions by putting them drop by drop into ice water, the frozen solvent was extracted with ethanol at a temperature below the melting point, and then the sample was separated by ultracentrifugation and dried under a 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 a much longer time to sublime the frozen phenol.

For comparison, one PET sample was also prepared by freezing the solution at a relatively slow rate by naturally cooling it as a whole from 60°C to room temperature (20°C). Another sample was prepared by shock-cooling solution in liquid nitrogen followed by freeze-extracting the frozen solvent at 20°C. A solution cast PET film quenched from the melt and a solution precipitated PET were also studied.

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

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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 manufacture. The heating rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

Figure 1A illustrates a wide-angle X-ray diffraction pattern recorded from freeze-extracted PET from 5 wt% solution. The solution was frozen by putting it drop by drop into ice water. Subsequently, the solvent was extracted with ethanol at 20°C. *Figure 1B* was recorded from an amorphous PET sample quenched from its melt. The diffraction pattern of *Figure 1B* exhibits a broad and intensive band, with the centre at $2\theta = 21.3°$. *Figure 1* indicates clearly that the PET prepared by freezing in ice water and subsequent freeze-extracting from 5 wt% solution is partially crystalline. Annealing the freeze-extracted PET at 150°C for 3 h resulted in a significant increase in crystallinity, as shown by the wide-angle X-ray diffractograms in *Figure 2A*, while the curve of *Figure 2B* for the quenched film after annealing at 150°C for 3 h shows less morphological changes. Further annealing the freeze-extracted PET sample at 200°C for 24 h resulted in a highly crystalline phase as shown in *Figure 3A*. The wide-angle X-ray diffractogram pattern shows several crystalline peaks which could be indexed according to Johnson[1] and Kilian *et al.*[5]:

$$0\bar{1}1 \quad 010 \quad \bar{1}11 \quad 1\bar{1}0 \quad 100 \quad 1\bar{1}1 \quad 101$$

Figures 2 and 3 show the comparison of wide-angle X-ray diffractogram patterns recorded from the annealed freeze-extracted PET and from the annealed PET film quenched from the melt. *Figure 3A* recorded from the PET, which had been freeze-extracting treated and then annealed at 200°C for 24 h, exhibits sharp peaks in the range of $2\theta = 10–35°$ of the diffractogram, indicating that the sample was highly crystallized. The sample of *Figure 3B* was crystallized by annealing the quenched film at 200°C for 48 h. Comparison of the intensity and the sharpness of crystalline peaks of the diffractograms in *Figures 2 and 3* indicates that annealing the ice water cooled and freeze-extracted PET could result in much higher crystallinity than annealing the PET film.

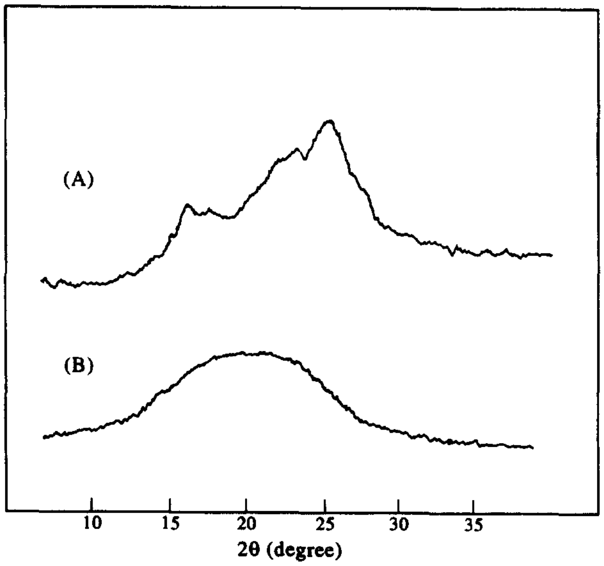

Figure 1 Wide-angle X-ray diffraction curves recorded from (A) an ice water-cooled and freeze-extracted PET from 5% solution, (B) an ice water-quenched PET film from the melt

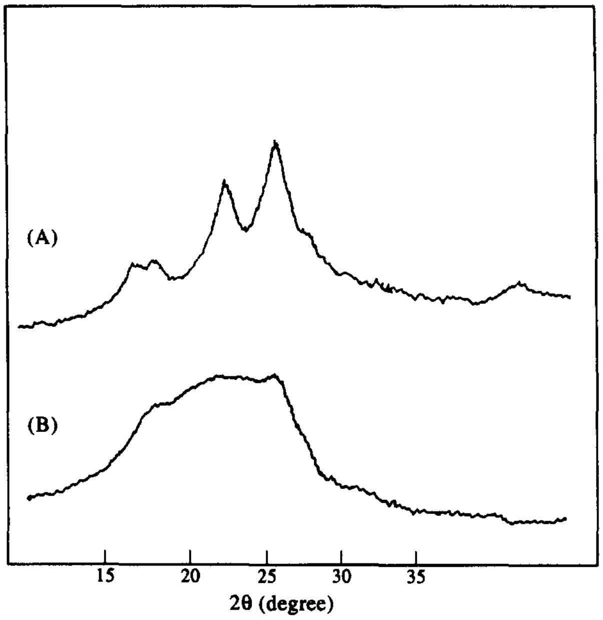

Figure 2 Wide-angle X-ray diffraction curves recorded from (A) an ice water-cooled and freeze-extracted PET annealed at 150°C for 3 h, (B) a quenched PET film annealed at 150°C for 3 h

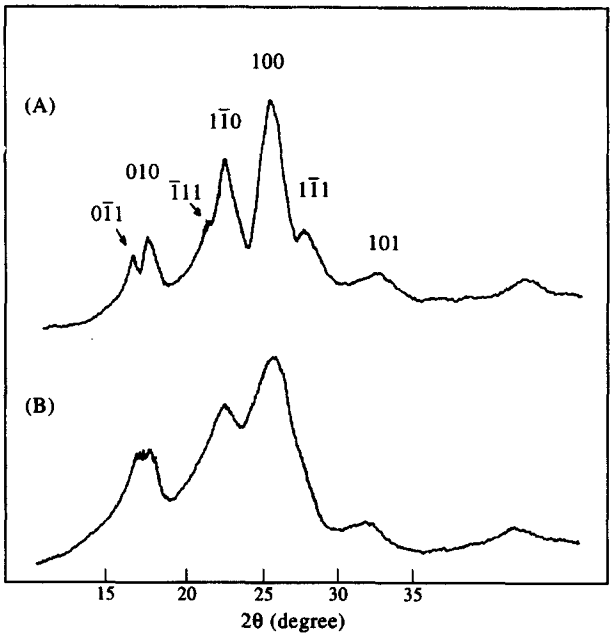

Figure 3 Wide-angle X-ray diffraction curves recorded from (A) an ice water-cooled and freeze-extracted PET annealed at 200°C for 24 h, (B) a quenched PET film annealed at 200°C for 48 h

In all above-mentioned experiments, the polymer sample is found unchanged by its treatment. The proofs are (1) maintenance of molecular weight by determining the intrinsic viscosity of PET before and after treating and (2) constancy of the chemical displacement of the treated polymer sample by using solid nuclear magnetic resonance spectrocopy.

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 PET solution. The PET macromolecules in solution are in expanded state which are supposed to contain less chain entanglements than the normal PET in solid state. As the entire solution was frozen and subsequently the

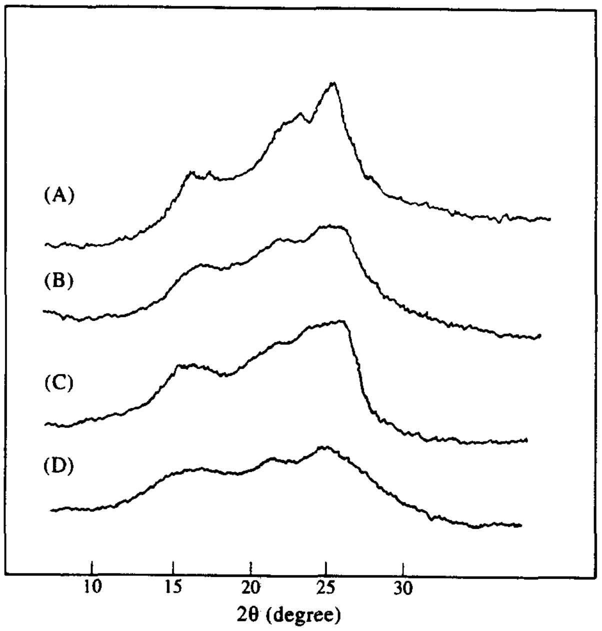

Figure 4 Wide-angle X-ray diffraction curves of freeze-extracted from 5% solution by different cooling methods: (A) freezing in ice-water, (B) shock-cooled in liquid nitrogen, (C) naturally cooled at room temperature, (D) solution precipitation

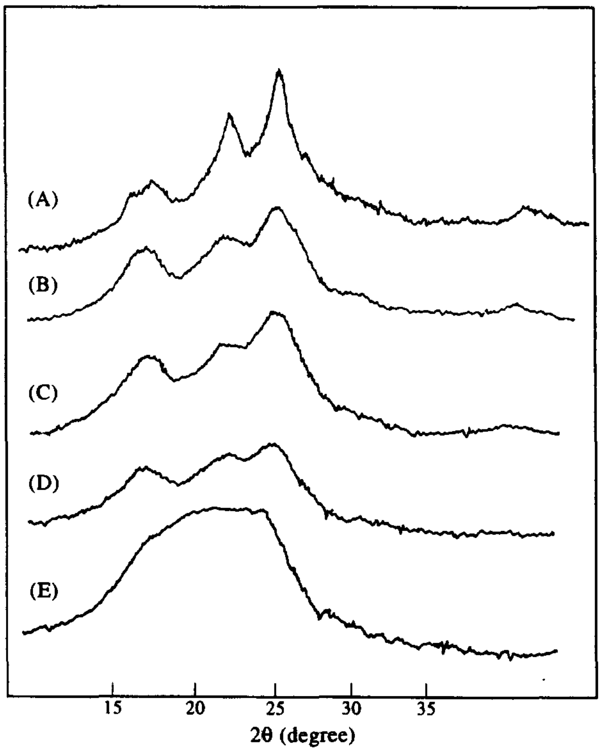

Figure 5 Wide ange X-ray diffraction curves of PET after annealing at 150°C for 2 h. Samples (A–D) are the same as those in *Figure 4*, (E) is a quenched film

solvent was extracted below its melting temperature, the PET macromolecules would remain 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 process very quickly, 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 diffractogram patterns in *Figures 2 and 3*. We tried to freeze the PET-phenol solution by different methods to compare the effect of cooling rate on crystallization. *Figures 4 and 5* illustrate wide-angel X-ray diffractogram patterns recorded from freeze-extracted PET which were cooled by different methods and the annealed freeze-extracted PET, respectively. Shock-cooling the solution by putting it drop by drop into liquid nitrogen rendered it frozen in a fraction of second. Naturally cooling the solution to room temperature (20°C) seems to freeze it in a slower rate than dropping the solution into ice water. By comparing the intensities and the sharpness of the crystalline peaks in *Figures 4 and 5*, we concluded that cooling in ice water resulted in more crystallizable PET than shock-cooling in liquid nitrogen and slow cooling at room temperature. The solution precipitation method yielded PET with lower crystallizability than the ice water cooled and freeze-extracted PET as shown in *Figures 4 and 5*.

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 non-radiative energy transfer between a mixture of donor and acceptor labelled polystyrene freeze-dried from a dilute solution suggested that the neat polymer obtained is comprised of non-overlapping collapsed coils[6,7]. The concentration of the solution for polystyrene used in these reports was 0.83 g dl^{-1}. This is four times more dilute than the critical concentration, C*, at which overlap of the polystyrene chains would commence[8]. However, n.m.r.

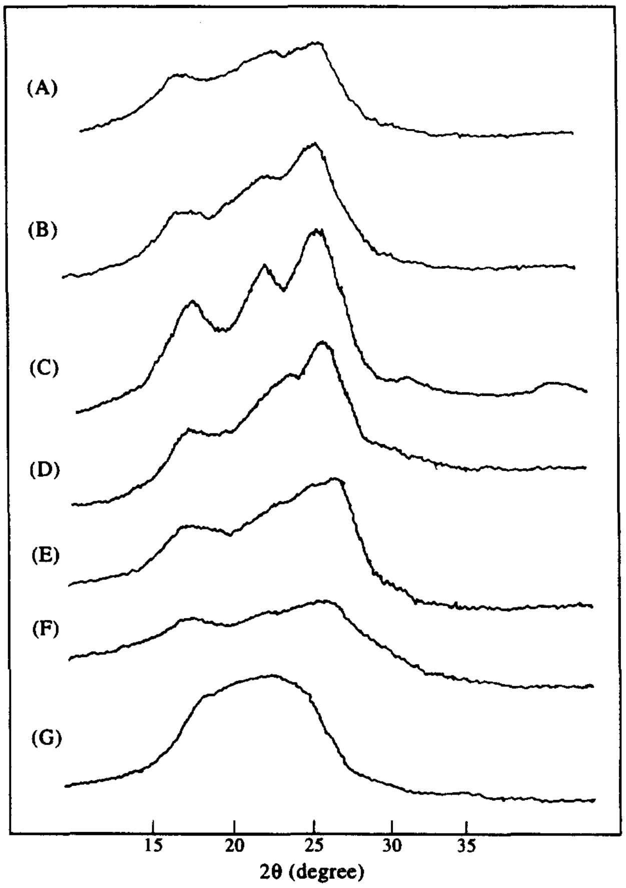

Figure 6 Wide-angle X-ray diffraction curves of PET prepared by ice water-cooling and freeze-extracting: (A) 0.03% solution, (B) 0.05% solution, (C) 0.2% solution, (D) 5% solution, (E) 20% solution, (F) 40% solution, (G) a film quenched from the melt

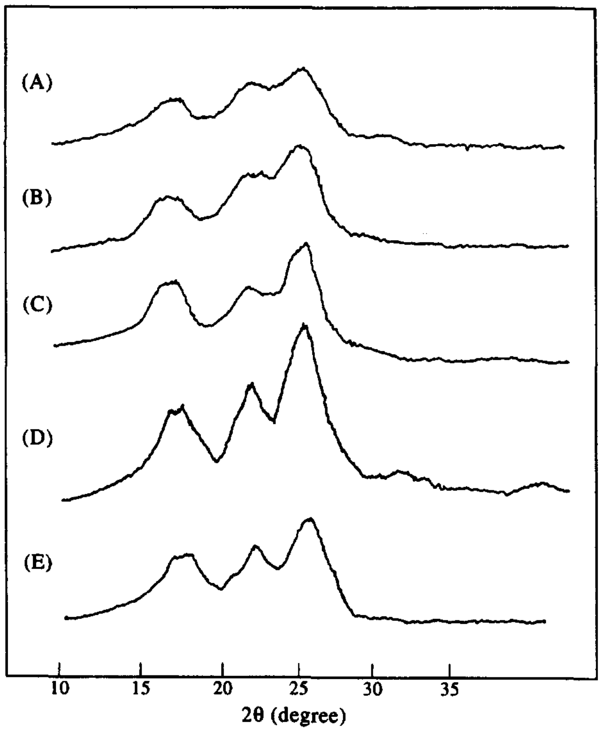

Figure 7 Wide-angle X-ray diffraction curves recorded from freeze-extracted PET and then annealed at 150°C for 1 h. The original concentration of the solutions from which the samples were prepared is (A) 0.03%, (B) 0.05%, (C) 0.1%, (D) 0.2%, (E) 0.5%

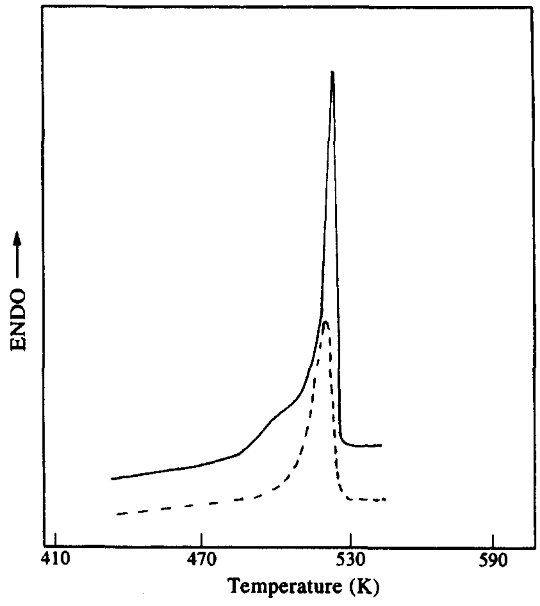

Figure 8 DSC curves of the freeze-extracted PET prepared from 0.2% solution. The dotted line was recorded in the second scan

experiments indicated that substantial interpenetration exists among polystrene chains freeze-dried under the same conditions[9,10]. Further experimentation is desirable to explain the curious contradictions between the n.m.r. and fluorescence experiments. Our study of the crystallizability of freeze-extracted PET from solution with different concentrations found that there is a concentration boundary in dilute region. *Figure 6* shows the wide-angle X-ray diffractogram patterns of ice water cooled and subsequent freeze-extracted PET from solutions from very dilute (0.03 wt%) to concentrate (40 wt%) regions. *Figure 7* illustrates that annealing these samples at 150°C for 1 h resulted in increase of the crystallinity. *Table 1* shows the crystallinity of the freeze-extracted PET before and after annealing. The diffractogram patterns in *Figures 6 and 7* and the data in *Table 1* clearly indicate that 0.2 wt% solution yielded the highest crystallizable PET after cooling in ice water and subsequent freeze-extracting. Annealing the freeze-extracted PET from 0.2 wt% solution at 150°C for 5 h could result in 64% crystalline phase, while the quenched film could form only 57% crystallinity after annealing at 200°C for 48 h. This improvement in crystallizability of PET by freeze-extracting method is significant since it was reported in literature that high crystalline PET could be obtained only by etching the amorphous region of an

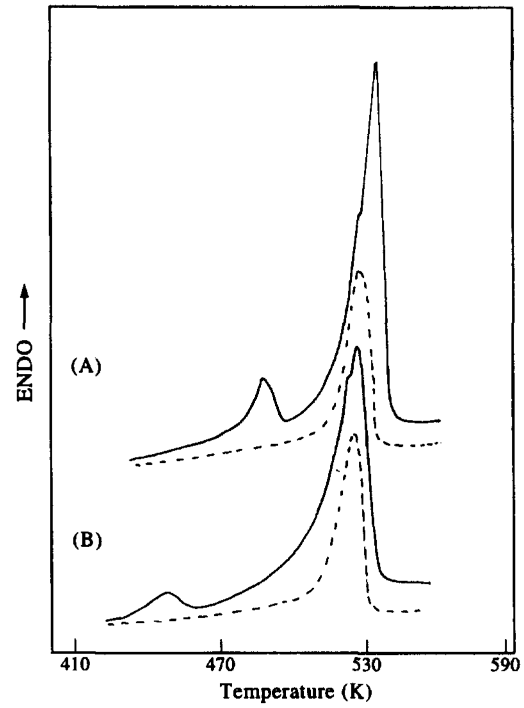

Figure 9 DSC curves of a spin casting film of PET after annealing (A) at 200°C for 48 h, (B) at 150°C for 5 h. The dotted lines were recorded in the second scan

Table 1 Crystallinity of freeze-extracted PET prepared from diffeent solution and a cast film before and after annealing

Annealing time at 150°C (h)	Crystallinity (%) of PET from solutions with different concentrations								Cast film
	0.03%	0.05%	0.1%	0.2%	0.5%	5.0%	10%	40%	
0	26	33	34	47	30	32	28	6	0
1	45	46	54	53	46	44	41	13	9
3	48	49	55	56	47	47	43	36	28
5	52	54	61	64	54	52	51	40	36

annealed PET film in methylamine solution and that the ultimate crystallinity could reach 66%[2].

Table 1 shows the relation between the crystallinity for the annealed PET samples and the concentration of the solution from which the freeze-extracted PET samples were prepared. For each annealing treatment, with increasing the polymer concentration the crystallinity increases first and then decreases after reaching the maximum value. It is clear that there is a concentration boundary near 0.2% for crystallizability of PET: near the boundary concentration, the macromolecular chains contain a considerable amount of segments with few chain entanglements and could form the simplest coherent network, leading to nucleation on its strained arms of the network. At concentrations higher than 0.2%, the chain overlapping makes more entanglements, as a result the freeze-extracted PET samples from concentrated solutions exhibit less crystallizability. In a polymer solution with a concentration (C) that is higher than the critical concentration, where the crystallinity shows the highest value, the molecular weight between neighbouring entanglements, $(M_c)_{soln}$, is given approximately by[11]:

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

where ρ refers to the bulk density of polymer and ϕ 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 universely 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 a high dilution the distances between chains become too great for them to form a continuous network to nucleating; the freeze-dried PET is less crystalline if the concentration is lower than 0.05% as illustrated in *Figures 6 and 7* and *Table 1*.

Figures 8 and 9 show DSC curves of the freeze-extracted PET from a 0.2% solution and the annealed PET films. The samples were firsts scanned from 20 to 260°C (the solid lines), followed by air cooling to 20°C at 2°C min^{-1}. A second scan from 20 to 260°C was then carried out (the dotted lines). The initial scan in *Figure 9* shows a strong exothermic peak due to the melting of the crystallite. Based on 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 has lower crystallinity after melting, which is exactly the same as the second scan of the annealed PET films, as illustrated in *Figure 9*. This phenomenon suggests that the initial freeze-extracted PET is in a highly crystalline phase with less chain entanglements, and after the melting at 260°C, the chain coils return to the normally entangle state. As a result, the freeze-extracted PET after melting shows a similar thermal property as ordinary PET film samples crystallized by annealing above the glass transition temperatures.

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REFERENCES

1. Johnson, J. E., *Journal of Applied Polymer Science*, 1959, **2**(5), 205.
2. Farrow, G., Ravens, D. A. S. and Ward, I. M., *Polymer*, 1962, **3**, 17.
3. Rabiej, S. and Andrzei, W., *Die Angewandte Makromolekular Chemie*, 1990, **175**, 81.
4. Fakirov, F., Fischer, E. W., Hoffmann, R. and Schmidt, G. F., *Polymer*, 1977, **18**, 1121.
5. Von Kilian, H. G., Halboth, H. and Jenckel, E., *Kolloid-Zeitschrift*, 1960, **172**(2), 166.
6. Morawetz, H., *Science*, 1988, **240**, 172.
7. Chang, L. P. and Morawetz, H., *Macromolecules*, 1987, **20**, 428.
8. Doi, M. and Edwards, S. F., *The Theory of Polymer Dynamics*. Clarendon Press, Oxford, 1986.
9. McGrath, K. J. and Roland, C. M., *Macromolecules*, 1992, **0**, 1366.
10. McGrath, K. J., Roland, C. M. and Weiss, R. G., *Macromolecules*, 1993, **26**, 6127.
11. Huang, B., Ito, M. and Kanamoto, T., *Polymer*, 1994, **35**(6), 1210.