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Concentration dependence of crystallinity of polycarbonate by shock-cooling and subsequent freeze-drying of its various solutions

Gending Ji, Gi Xue*, Jianlin Ma and Chenyu Dong
Department of Chemistry, The Institute of Coordination Chemistry, Nanjing University, Nanjng 210093, China

and Xinhong Gu
Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA
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Polycarbonate (PC) can be easily crystallized by injecting a very dilute benzene solution of PC directly into liquid nitrogen, and then freeze-drying to remove the solvent. The crystallinities of these prepared samples were characterized by wide-angle X-ray diffraction (WAXD). The results of WAXD studies showed that there is a concentration boundary in very dilute solution for crystallizability of PC: near the boundary concentration, the solution has a lower chain entanglement level, and as a result, crystallizes more quickly and completely than more highly entangled PC. By annealing these fewer-chain-entanglement samples at 190°C for 289 h, crystallinity reaches a maximum value of 79.6%, which is much higher than that of annealing ordinary or other solution-crystallized samples. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polycarbonates (PCs) are distinguished not only by their excellent mechanical properties, dimensional stability and self-extinguishing nature; but also by their considerably slow crystallization behaviour which corresponds to their chain rigidity and difficulty of transfer to a crystalline structure. The thermal crystallization of PC is a time-consuming business. At 190°C 1 day is necessary for the first crystallite of simple PC to develop[1] and 1 week or even more to obtain a crystalline material with a well-developed spherulite structure[2]. Compared to other polymers at the temperature of maximum spherulitic growth rate, PC is a thousand times slower than poly(ethylene terephthalate) (PET) and 5×10^5 times slower than polyethylene (PE)[3]. Its half-crystallization time is around 12 days (18 000 min)[4]. The resulting value of its crystalline fraction is modest, typically less than 25%[5,6].

In this paper we report a new method to crystallize PC samples. By rapidly freezing a very dilute benzene solution ($0.05\,\mathrm{g\,dl^{-1}}$) of PC in liquid nitrogen, followed by freeze-drying the frozen solution under high vacuum condition, some white, opaque powder was left in the bottom of the flask. It was found that there is a considerable amount of crystalline structure in this resultant material. Annealing the shock-cooled and freeze-dried PC could further crystallize it, resulting in a much higher degree of crystallinity than annealing an ordinary PC sample. There is also a concentration boundary in very dilute solution for crystallizability of PC: near the boundary concentration the polymer chain coils contain a considerable number of segments with much chain disentanglement.

EXPERIMENTAL

Bisphenol-A polycarbonate was kindly supplied by Changchuo Chemical Company. The supplier claimed that the material contained no additives and had a weight-average molecular weight of 30 000 obtained by light scattering. The transparent property showed that the sample was in amorphous state. The benzene was commercially purchased and distilled before use.

The shock-cooled and freeze-dried polycarbonate samples were prepared by dissolving the desired amount of the original PC in distilled benzene, refluxing these mixtures for 1 h to make homogeneous solutions with varying concentrations. The resulting hot solutions were injected directly into liquid nitrogen for shock-cooling so that they were frozen in a fraction of a second. The frozen solvent was sublimed at 0°C under high vacuum for 3 days, and then were kept at room temperature under vacuum for another 3 days to remove any residual solvent. The resulting PC powder, designated as freeze-dried PC, was annealed and examined by wide-angle X-ray diffraction (WAXD).

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* To whom correspondence should be addressed

The annealing of the freeze-dried PC samples was carried out by wrapping in Al foil and placing in glass ampoules which were immersed in a thermostatted silicon oil bath. The Al foil was required to prevent the polymer powder from flowing excessively during crystallization at the desired temperature. The temperature was regulated with a precision better than 0.1°C. The ampoules were evacuated for 24 h and then backfilled with argon to protect the samples from oxidation and to facilitate thermal equilibration.

The WAXD patterns of such prepared samples were obtained using the copper/graphite-filtered Kα radiation of copper at an exciting voltage of 30 kV and an exciting current of 60 mA. The diffractograms were recorded by use of a rotating anode X-ray diffractometer (Rigaku D/Max-Ra). An IBM personal computer was used for band resolving and for crystalline degree calculation.

RESULTS AND DISCUSSION

Figure 1 illustrates WAXD recorded from freeze-dried PC from shock-cooled solutions with varying concentration. A survey of the WAXD curves of these samples is revealing. The shape of these patterns is not beyond the observation of any other researchers[7,8]. The prepared PC samples show stronger, sharper reflections out of the amorphous part, with the centre at $2\theta = 17.5°$. The shape of this kind of pattern suggests that there is a considerable amount of crystalline structure after the shock-cooled and then freeze-dried treatment. For the purpose of comparison, the WAXD curve of the crystallized PC sample prepared by hot precipitation as described in reference 8 was measured and is shown in *Figure 1E*.

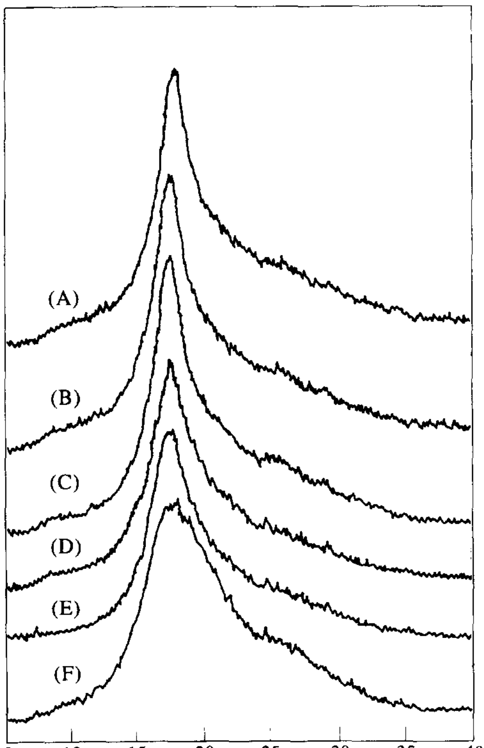

Figure 1 WAXD curves recorded from freeze-dried PC samples from following solutions: (A) 0.01 g dl^{-1}; (B) 0.05 g dl^{-1}; (C) 0.1 g dl^{-1}; (D) 0.05 g dl^{-1}; (E) 1 g dl^{-1} hot-precipitated; (F) amorphous PC sample

From WAXD data, there are several different methods to calculate the content of crystallinity. One can distinguish between two kinds:

1. The procedures evaluating the relative content of crystallinity by means of crystalline and amorphous standards.
2. The procedures deriving the absolute degree of crystallinity based upon the ratio of the integrated intensity under the crystalline peaks to the integrated intensity under the complete X-ray diffraction trace.

Here the first method was employed to derive the degree of crystallinity of samples. The standard of amorphous PC was prepared by the following procedure. PC pellets were heated to 280°C, pressed into thin films between two layers of aluminum foil, and plunged into ice water for rapid cooling, and then annealing at their glass transition temperatures T_gs to remove the moisture and release the inner stress. Differential scanning calorimetry (d.s.c.) studies show that this sample has an amorphous structure. The WAXD pattern of the amorphous sample was also measured and is shown in *Figure 1F*. The amorphous PC shows only one broad and intensive band at $2\theta = 17.3°$.

After the computer calculation, we found the crystallinity degree of various samples. The crystallinity of hot-precipitated PC sample is 30.2%, which was almost the same as that determined by G.A. Adam and coworkers[8]. This result suggested that our computer program works correctly and is suitable for band resolution and crystallinity calculation. *Figure 2* shows the plots of the level of crystallinity *versus* the concentration of solutions from which the PC samples were prepared by the method of shock-cooling and then freeze-drying. The crystallinity is low in the semidilute and dilute regimes, while it increases rapidly as the concentration becomes more dilute. At the vicinity of 0.05 g dl^{-1}, the crystallinity degree reaches a maximum near 46.4%. These values of PC prepared by the shock-cooling and freeze-drying method are higher than those prepared by hot-precipitation crystallization[8] and normal thermal annealing techniques[5,6].

Some recent characterizations have focused on the consequence of rapidly taking polymers with flexible chains from the dilute solution regime to a concentrated state. Measurements of non-radiative energy transfer

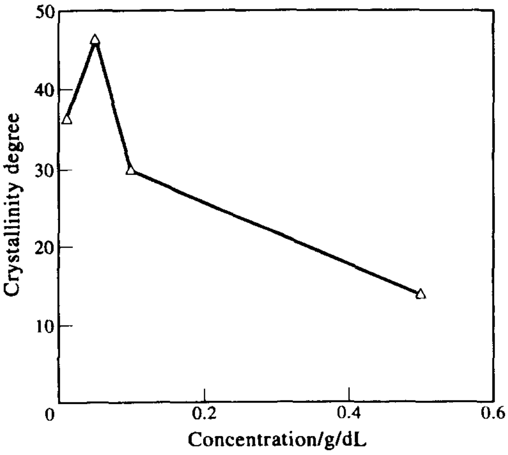

Figure 2 The relationship between crystallinity degree and, concentration of solution

between a mixture of donor- and acceptor-labelled polystyrene freeze-dried from a dilute solution suggested that the neat polymer obtained comprised non-overlapping collapsed coils[9,10]. 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 chain would commence[11]. However, nuclear magnetic resonance (n.m.r.) study has suggested that substantial interpenetration exists among polystyrene chains freeze-dried under the same conditions[12,13]. Further experiment is desirable to elucidate the curious contradictions between the n.m.r. and fluorescence experiments. Our study on PC, a rigid-chain class prepared by the freeze-drying method, indicates that the rigid-chain coils expanded as the solution became more dilute and reached a maximum expansion in 0.05 g dl^{-1} 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 sublimation of the solvents at frozen state under high vacuum, a more ordered or expanded chain state persisted, resulting in a highly crystallized polymer. Our finding about the concentration boundary near the 0.05 g dl^{-1} for PC is in good agreement with Qian *et al.*'s results about the concentration boundary in dilute polystyrene solution studied by excimer fluorescence experiments[14]. The chain coils of PC in a very dilute solution (near 0.05 g dl^{-1}) contain a considerable amount of segments with much chain disentanglement. As the solution was rapidly frozen, the segments aggregated to crystals resulting in a freeze-dried PC with considerable crystallinity. The crystallinity of PC prepared by freeze-drying a 0.05 g dl^{-1} solution is much higher than that prepared by the conventional solution precipitation and annealing method.

It was reported that PC could crystallize by annealing the polymer at 190°C for a certain time[1] or by precipitation from hot solution[8]. The comparison of WAXD patterns recorded from an annealed shock-cooled and freeze-dried PC and from an annealed normal amorphous sample is shown in *Figure 3*. The 'normal' sample means a sample the same as the shock-cooled ones in every respect, but the shock-cooling and subsequent freeze-drying. The curve of *Figure 3A* recorded from the PC which had been freeze-dried and then annealed at 190°C for 287 h exhibits sharp peak in the range of $2\theta = 5$–$40°$ of the diffractogram, indicating that the sample was highly crystallized. *Figure 3B* shows the diffractogram of normal amorphous polycarbonate sample which was crystallized at the same condition and time period. Comparison of the intensity and the sharpness of WAXD curves in *Figure 3* indicates that the annealing of the shock-cooled and subsequent freeze-dried PC could result in much higher crystallinity than annealing the normal sample.

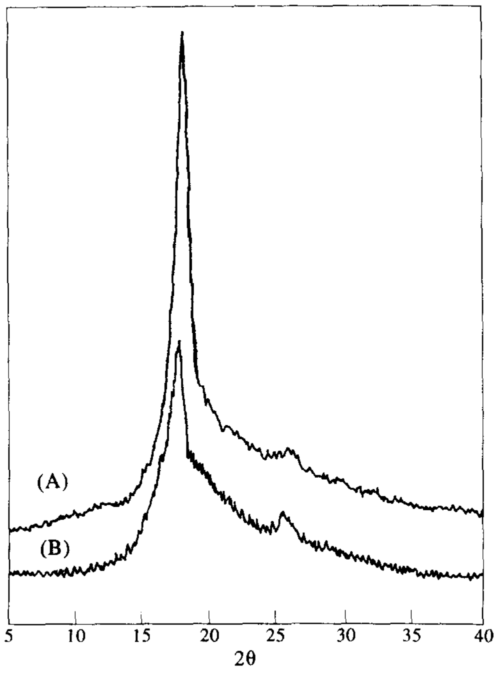

Figure 3 WAXD patterns recorded from: (A) annealed freeze-dried PC for 287 h; (B) annealed amorphous PC for 287 h

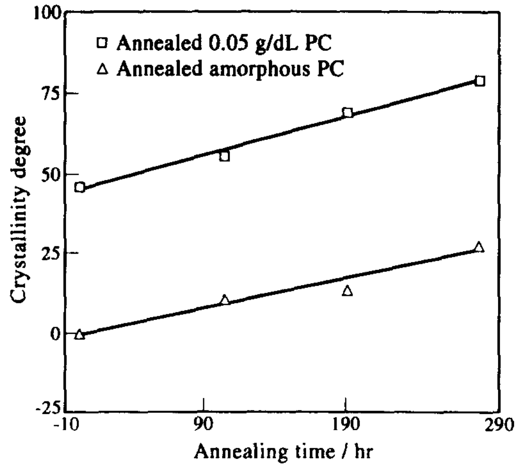

Figure 4 The crystallinity degree *versus* annealing time

At this annealing experiment, the change of the degree of crystallinity of the treated and the normal samples with annealing time was also characterized. *Figure 4* shows two plots, of the crystallinity content *versus* the annealing time of different samples. From *Figure 4* it was found that the crystallinity increases linearly with annealing time. But the crystallinity of the treated PC at 0.05 g dl^{-1} solution increases rapidly and reaches a maximum value of 79.6% at the end of 289 h annealing time. Annealing of the normal sample results in only 28.4% crystallinity which is almost the same as the previous reported value[4,5]. This result suggests that the expanded and disentangled chains can easily crystallize and result in high crystallinity.

Although Galez *et al.*[4] reported crystallinity of 60% of PC samples in the presence of a nucleating agent, the weight-average molecular weight of the samples had been decreased during the crystallization course. So at the time we started this investigation, there was no PC known to have this high degree of crystallinity without being chain-degraded. The Fourier transform infra-red (*FT*i.r.) experiment was performed to check on the stability of PC to the shock-cooling and freeze-drying method and to the annealing procedures. All materials were first dissolved in methylene chloride, then cast from dilute solutions onto NaCl salt plates. The highly-crystallized samples had to be first melted before they would totally dissolve in this good solvent for amorphous PC. *FT*i.r. spectra showed that there were no differences for freeze-dried and annealed PC. This result suggested that the freeze-drying method had no effect on molecular weight, just as the conclusion of Abbas and Porter's[15] studies on polystyrene samples whose molecular weight was less than 2 000 000. The unambiguous conclusion drawn from the above experiments is that it constitutes an example of high crystallinity degree PC samples without molecular weight degradation.

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