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RAPID CRYSTALLIZATION OF POLYCARBONATE BY SHOCK-COOLING AND FREEZE-DRYING METHOD

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ABSTRACT

Rapid crystallization of a polycarbonate has been achieved by shock-cooling its very dilute benzene solution and then by sublimation of the solvent under vacuum. The degree of crystallinity of this treated polycarbonate is 42.5% or 46.4% by differential scanning calorimetry (DSC) or wide-angle X-ray diffraction (WAXD) studies respectively. These values are significantly higher than that of the sample prepared by hot precipitation technique.

INTRODUCTION

The polycarbonate of bisphenol-A (poly(oxy-carbonyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene) is one of the crystallizable polymers. But it is hard to crystallize and usually has amorphous structure because of its chain rigidity and is difficult to transfer to a crystalline

structure. The thermal crystallization of polycarbonate is time-consuming. At 190°C, one day is necessary for the first crystallite to develop [1] and one week, or even more, to obtain a crystalline material with a well-developed spherulite structure [2]. Its crystalline fraction is modest, and typically less than 25% [3,4].

Many efforts have been made in the past decade to induce a rapid crystallization of polycarbonate. Some of them were based on the action of plasticizers, which increases the mobility of polymer chain and which may promote, in principle, both nucleation and spherulite growth. Conix and Jeurissen [5] were the first to propose the use of plasticizers to accelerate the crystallization rate of polycarbonate. The solvent-induced crystallization studied by Kambour, et al. [6] and by Mercier, et al. [7] may be considered as a variant of the same procedure. Another possible way to modify the kinetics of crystallization is to incorporate the crystallization promoter such as nucleating agents to polycarbonate matrix [8]. All these methods are time consuming or harmful to material and of initiation of the degradation of polymer chain.

In this paper, an interesting phenomena was reported that much higher content of crystallinity and a more perfect crystalline structure of bisphenol-A polycarbonate could be obtained by pouring a very diluted benzene solution (0.05% by weight to volume) of polycarbonate into liquid nitrogen and followed by freeze-drying the frozen solution under high vacuum conditions. This shock-cooling and freeze-drying method has been proven to be a fruitful way to rapidly crystallize the iso-PS [9].

EXPERIMENTAL

Bisphenol-A polycarbonate was obtained commercially from Changchuo Chemical Company. Its melt index is 8.0 at 300°C under the loading of 2.16 Kg. The benzene was purchased commercially and redistilled before use.

Polycarbonate was dissolved in distilled benzene by refluxing this mixture for 1 hr to make a very dilute homogeneous solution with a concentration of 0.05-w/v %. The resulting hot solution was poured directly into liquid nitrogen for shock-cooling. It was frozen in a fraction of a second. The frozen solution was dried at 0°C under high vacuum for three days. It was then kept at

room temperature under vacuum for another three days to remove any residual solvent. The resulting polycarbonate powder, designated as freeze-dried polycarbonate, was further examined by DSC, WAXD and FT-IR.

The melting behavior of samples was measured using a differential $20^{\circ}\text{C min}^{-1}$. A refrigeration unit was attached to the DSC block for controlled cooling to subambient temperature. Sealed aluminum cup containers were employed. The T_g and melting endothermic of sample was of interest.

The wide-angle X-ray diffraction patterns of such prepared samples were obtained using the copper/graphite-filtered $K\alpha$ radiation of copper at exciting voltage of 30kV and exciting current of 60 mA. The diffractograms were recorded by the use of an Rotating Anode X-ray diffractometer (Rigaku D/Max-Ra). An IBM pc was used for resolution of band and calculation of crystallinity degree.

RESULTS AND DISCUSSION

It has been well accepted that FT-IR spectroscopy can be used to characterize the crystalline structure and to measure the degree of crystallinity since the molecule conformations in crystalline is different from that in its amorphous counterpart. Different conformations give rise to bands with different widths or frequencies of absorption in IR spectrum [11]. Figure 1 illustrates the FT-IR transmittance spectroscopy of polycarbonate samples from 400 to 2000 cm^{-1} recorded in NICOLET 170SX by KBr disc technique. In order to minimize the error of sample preparation, the concentrations of PC in KBr is 4% and kept unchanged during the preparation. Figure 1A shows the IR spectrum of a commercial polycarbonate as received.

Most of its bands are more diffuse and wider than those of its counterpart. Most of the bands at 1780, 1507, 1014, 554 cm^{-1} in IR spectrum of Figure 1B, recorded from the freeze-dried polycarbonate sample, are sharper than those in Figure 1A. The bands at 1160, 1191 cm^{-1} are more intense and better defined referring to its counterpart. This suggests that the polycarbonate sample is in a more ordered state after shock-cooling and freeze-drying treatment.

Polycarbonate is usually crystallized by thermal annealing at 190°C for several days, or by the addition of a small amount of plasticizers, or by a hot-precipitation method from its solution[11].

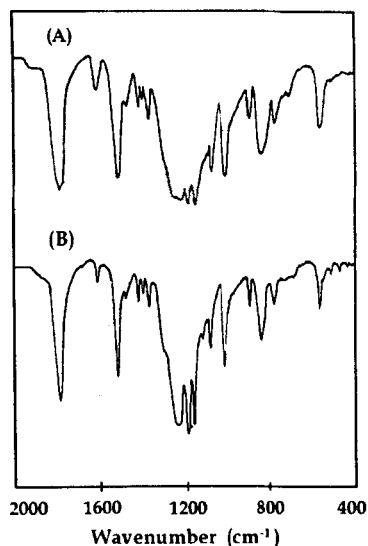


Fig.1 FT-IR spectra of PC recorded from
 A: a commercial sample
 B: a freeze-drying prepared PC

It was reported that about 30% crystallinity can be obtained for polycarbonates after the hot precipitation from 1,2-dichloroethane and treatment with acetone [11]. Figure 2 shows the DSC curves of a freeze-dried polycarbonate and a hot-precipitated sample. The width of the melting band can be used to characterize the perfectness of the crystalline structure. The exothermic band of the DSC curve in Figure 2A appears to be significantly narrower. The detailed value of FWHM (full width at half maximum) of the freeze-dried sample (Figure 2A) is 15K, another FWHM of the hot-precipitated form (Figure 2B) is 21K. The lower value of FWHM corresponds to the fact that the polycarbonate sample prepared by shock-cooling and freeze-drying method possesses a more perfect crystalline structure than that prepared by a hot-precipitation technique.

The apparent fusion heat provided by DSC is based on the sample mass and the energy consumed during the melting of that mass. The area covered by the exothermic peak in Figure 2A is larger than that of Figure 2B, indicating that the heat of fusion of the freeze-dried polycarbonate is larger than that of the hot-precipitated polymer. The degree of the crystallinity value, expressed in weight, refers to the whole material, can be calculated by the following equation, where X_c is the

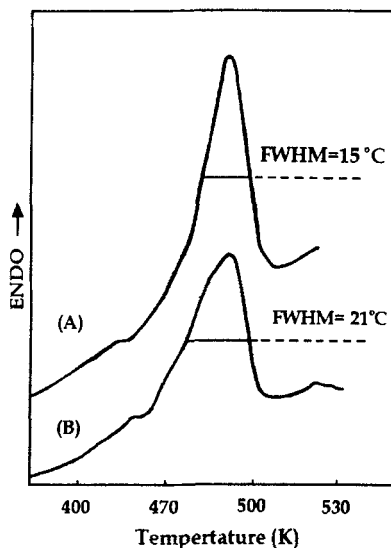


Fig.2: DSC curves of PC
 A: freeze-dried sample
 B: a hot-precipitated PC

percentage of crystallinity, H the apparent heat of fusion, and H_f the literature value of the heat of fusion:

$$X_c \text{ (in \%)} = \frac{H}{H_f} * 100 \quad (1)$$

In Figure 2A and 2B, the H values of apparent heat of fusion are 5.7 cal/g and 4.5 cal/g respectively, which were integrated from 445K to 519K. According to Conix and Jeurissen, the heat of fusion of Polycarbonate crystalline is 13.4 cal/g [3]. Therefore, the extent of crystallinity of freeze-dried polycarbonate is 42.5%, while the degree of crystallinity of the hot-precipitated sample is 33.6%. These results suggest that the crystallinity of PC samples prepared by the shock-cooling and freeze-drying method is higher than that of samples prepared by the hot-precipitation technique.

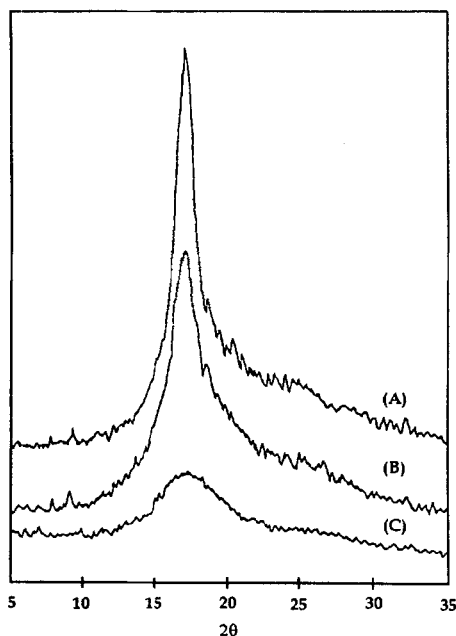


Fig. 3: Wide-angle X-ray diffractogram of PC recorded from
 (A): a freeze-drying prepared PC (B): a hot-precipitated PC
 (C): amorphous PC

The degree of crystallinity can also be determined by wide-angle X-ray diffractograms (WAXD) in which scattered intensities are plotted as a function of the Bragg angle 2θ . The WAXD curves of shock-cooled and then reeze-dried polycarbonate samples and hot-precipitated ones are shown in Figure 3A and 3B respectively. It has a similar shape as that reported in Reference 11.

In order to obtain the degree of crystallinity of samples, the amorphous polycarbonate was prepared by the following procedure: heating polycarbonate pellets to 280°C , pressing it into a thin film between two aluminum foil sheets, and throwing it into iced water for rapid cooling, and then annealing it at its glass transition temperature to remove the moisture on it and to release the inner stress. DSC studies show that this sample has amorphous structure. The WAXD pattern of amorphous sample was also measured and displayed in Figure 3C.

A BASIC computer program was edited to resolve the band and to calculate the crystallinity content. After the computer calculation, the extent of crystallinity of shock-cooled and freeze-

dried polycarbonate was 46.4%. This value was significantly higher than 30.2%, the degree of crystallinity of hot-precipitated polycarbonate. This calculation result was consistent with DSC value.

Based on the experimental results, it can be concluded that a considerable amount of crystallization formed in a fraction of a second by shock-cooling a very dilute solution of polycarbonate in liquid nitrogen and further freeze-drying under vacuum. It may be the reason for this phenomena that, due to strong intramolecular interaction, the polycarbonate chains take a well ordered arrangement in very dilute benzene solution with few chain entanglements. As the solution is frozen rapidly, this interaction forces the isolated chains to aggregate to form crystals, resulting in a freeze-dried polycarbonate sample with a considerable amount of crystallinity, as evidenced by the FT-IR spectra, DSC studies and WAXD curves. The present findings will encourage us to seek a systematic approach to the specification of crystallization mechanism and kinetics of polycarbonate in this treatment method and their optimization relation to the production of high-performance composites.

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