Magnetic Alignment of Poly(carbonate)

Hisashi Aoki, Masafumi Yamato, and Tsunehisa Kimura*
Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397

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An external magnetic field was applied to poly(carbonate) undergoing melt crystallization under a chemical reaction with organic salts. The solidified sample exhibited crystal orientation with the *c*-axis aligned parallel to the applied magnetic field.

Owing to the diamagnetic anisotropy of chemical bonds, organic molecules have a potential ability to align under a magnetic field.[1] Organic crystals[2,3] and polymeric fibers,[4–8] which exhibit anisotropic diamagnetic susceptibility, can undergo magnetic alignment in suspension, if their size is large enough to exceed the thermal energy. The minimum size required for the magnetic alignment ranges from micrometers to tens of nanometers depending on the values of the diamagnetic anisotropy (typically 10^{-5}–10^{-7}) of the material and the field strength used (5 – 10 T).

Crystal alignment is also possible during the crystal formation from solutions[9,10] and melts.[11,12] In these cases, the orientation proceeds during the concomitant crystal formation, which makes the phenomenon complicated in comparison to the simple case of the crystal alignment in the suspension. Especially in the case of polymers, it is believed that anisotropic structures occurring in a very initial stage of crystallization play an important role, but this stage remains poorly understood. We have so far found that some crystalline polymers can undergo magnetic alignment, but some others do not. Even for a same polymer, the alignment condition depends on the molecular weight and the thermal history.[13] For example, a low molecular weight isotactic poly(propylene) undergoes magnetic alignment, but a high molecular one does not.[13] In addition, this low molecular-weight sample, once heated above the equilibrium melting point, does not exhibit magnetic alignment.

Poly(bisphenol-A-carbonate) (PC) are usually used in amorphous state and hence regarded as an amorphous polymer. PC, lacking in anisotropic structures necessary for the magnetic alignment, therefore would not be aligned by a simple solidification of its melt under a magnetic field. However, it is reported that PC crystallizes under some conditions. For example, a heating at 190 °C for 9 days causes cold crystallization of PC;[14] a casting from a solution produces crystallites;[15] a heating under a chemical reaction with organic salts brings about crystallization.[16] These reported facts lead us to expect that we will be able to attain the magnetic alignment of PC if we apply a magnetic field to the PC under some of these conditions encouraging crystal formation. In this study, we report that the magnetic alignment is attained by melt crystallization of PC under the reaction with organic salts.

Poly(bisphenol-A-carbonate) used in this study was Panlite® L-1250WP (Teijin Chemicals Ltd.). The sample powder was dried at 120 °C for 15 h under vacuum before use. A 10 wt% methylene dichloride solution of the PC powder was poured into a laboratory dish of 4 cm in diameter, covered, and slowly evaporated to obtain a cast film.

Two organic salts were used according to the reference.[16,17] Sodium phenoxide purchased from Aldrich was used as received. Sodium *o*-chlorobenzoate was prepared by neutralization of the corresponding acid (Tokyo Kasei Kogyo Co., Ltd) with sodium hydroxide and dried at 120 °C for 15 h under vacuum before use.

The PC powder was mixed with a 0.1 wt% sodium salt, stirred in an Imoto micro-mixer at 35 rpm at 250 °C for 5 min, followed by extrusion into air. The extruded mixture was hot-pressed at 190 °C for 30 s to obtain a film sample of 400 μm thickness.

The film sample obtained was placed in a home-built heating unit and the unit was put in the center of a room-temperature bore of an Oxford superconducting magnet generating a 6 T vertical magnetic field, then was heated at 300 °C for 5 min followed by crystallization at 225 °C for 1 h and cooled slowly to ambient temperature. The same thermal history was applied to obtain a sample prepared without the magnet field. The cast film was heated at 250 °C for 5 min followed by quenching. This procedure was carried out both inside and outside the magnet.

Differential scanning calorimetry (DSC) was carried out on a SEIKO Instruments Inc. DSC200 at a heating rate of 5 °C/min. Wide-angle X-ray diffraction measurements were carried out with a MAC Science M18XHF-SRA equipped with an imaging plate.

A cast film exhibits a number of spherulites under optical microscope. The DSC thermogram of this film shown in Figure 1(a) indicates that the melting point of the crystal is ca. 245 °C. As-received powder exhibits a thermogram almost identical

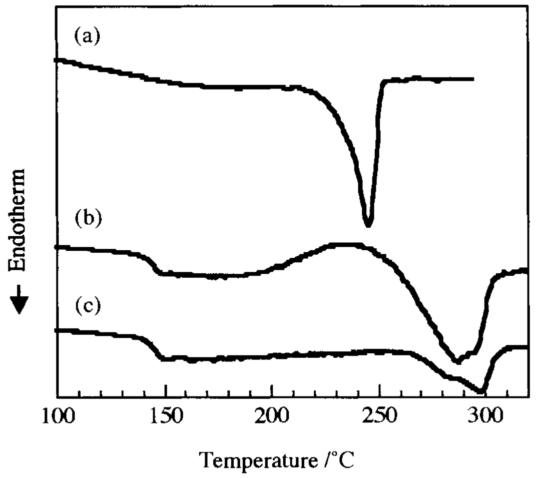

Figure 1. DSC thermograms of PC: (a) PC film cast from a 10 wt% methylene dichloride solution, (b) hot-pressed film of PC/SOCB, (c) hot-pressed film of PC/SP.

with that in Figure 1(a). Since the PC powder does not crystallize once it is melted, a possible way of the magnetic alignment is the thermal treatment just above the melting point for a short time before the crystalline order is completely relaxed, leading to the alignment of the residual ordered structure. This is the condition that has been applied successfully to some crystalline polymers.[13] However, this is not the case for PC in this study. Heating the cast film in the vicinity of the melting point (245–255 °C) followed by quenching did not give rise to orientation detectable by observation under crossed polars.

Figure 1(b) and (c) display the DSC thermograms for the hot-pressed films containing sodium *o*-chlorobenzoate (SOCB) and sodium phenoxide (SP), respectively. Both exhibit the melting point of ca. 290–300 °C, which is much higher than those for the cast film and as-received powder.

In Figure 2 is shown the X-ray diffraction patterns obtained for the hot-pressed film with 0.1 wt% SOCB heat-treated outside and inside the magnet. The thermal history applied is similar to that applied to attain the magnetic alignment of poly(ethylene-2,6-naphthalate), isotactic poly(styrene), and poly(ethylene terephthalate), namely, the melting just above the melting point followed by isothermal crystallization. The thermal treatment outside the magnet only gives rings corresponding to the (020) and (202) diffraction of the PC crystal.[18] It is evident that there is no crystal orientation. On the other hand, the alignment is clearly observed when the magnetic field is applied. The diffraction pattern indicates that the PC crystallite aligns with its *c*-axis parallel to the applied magnetic field. The same result is obtained for the PC mixed with SP.

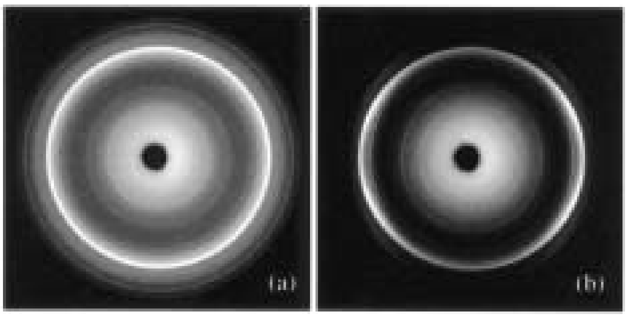

Figure 2. Wide-angle X-ray diffraction patterns of PC/SOCB heat-treated (a) outside the magnet and (b) in the magnet (6 T).

The reason why the magnetic alignment is possible only for the PC/salt systems could be as follows. According to Bailly et al.,[16] the organic salts react with PC to produce ionic chain ends, resulting in high crystallization rates, high melting points, and lack of spherulite formation. Though in the present study we only confirmed the increase in melting point, the same effect reported by Bailly et al. might be true to our PC/salt system. Three effects described above are all in favor of magnetic alignment. If the crystallization does not occur in an acceptably short time, we need a long time before the magnetic alignment is detected. Thick lamellae, reflected by high melting point, are important because the larger the lamella size, the larger a magnetic torque acting on the lamella, resulting in a quick and high orientation. The lack of spherulite formation is also important. Because of its symmetrical nature, a spherulite does not have diamagnetic anisotropy and hence it does not align.

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