Graded Alignment of Polymer Liquid Crystalline Film Prepared under Magnetic Field

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A liquid crystalline polymer film with a graded alignment was prepared using a magnetic field with a field gradient. The graded alignment was confirmed by X-ray diffraction.

Liquid crystalline polymers (LCPs) align in magnetic fields.[1] Alignment by magnetic fields has several advantages over the mechanical methods including the injection molding, etc. First, the magnetic field can penetrate materials so that the alignment is achieved throughout the whole sample, while the alignment is limited only in the surface area, for example, in the case of the injection molding. Second, it is possible to choose the direction of the magnetic field in a desired manner, and hence we can design a variety of alignments, accordingly. Even the alignment perpendicular or inclined to the film surface is possible. Third, not only the direction of the alignment but also the distribution of the alignment, that is, graded alignments (GAs), or more generally, three-dimensionally controlled alignments, become possible by use of the magnetic field.

The orientation direction of the polymer chains with respect to the magnetic field depends on the molecular structure of the polymer. LCPs having aromatic rings in their main chain usually align with the chain direction parallel to the magnetic field because in their nematic phase there is a cylindrical symmetry along the chain axis. Hence, the magnetic alignment has the same effect as the mechanical stretching with respect to the orientation direction. We reported[2,3] that the degree of alignment attained by the magnetic field for a main chain aromatic-ring-containing LCP is as high as that obtained by a mechanical method. It was also shown that the Young's modulus obtained by the magnetic alignment is as high as that obtained by the mechanical stretching. Thus, unique mechanical properties are expected for the LCP films with GA.

The GA technique is also promising for the fabrication of GA crystalline polymers because crystalline polymers also align under magnetic fields, as we have demonstrated for some crystalline polymers including poly(ethylene 2,6-naphthalate),[4–6] isotactic polystyrene,[7] isotactic polypropylene,[8] and poly(ethylene terephthalate).[9] A project in this line is under way.

In the present study, we demonstrate a GA of an LCP, consisting of 60 mol% *p*-hydroxybenzoic acid and 40 mol% ethylene terephthalate (Unitika Rodrun® LC-3000) on which we have reported in detail the magnetic orientation[2,10] and some physical properties.[2,11]

Pellets of the sample were pressed at 280 °C for 5 min and allowed to quenching in ice water to obtain a film with 200 mm thick. A sample strip (1 cm × 5 cm) was cut from the film and sandwiched between Kapton films then screwed tightly between two aluminum plates. This set of the aluminum plates was set in a heating cell. The sample was then heated at 280 °C for 20 min in a gradient magnetic field.

The magnet used was a Tamagawa TM-WTF6215C electromagnet with two pole pieces of different sizes (Figure 1a). The detail of the magnetic field profile is not available, but the asymmetrical configuration of the pole pieces insures the profile of the filed direction schematically sketched in the figure. The sample position is shown in Figure 1b. The field strength at the sample center was ca. 2.4 T as measured by gauss meter.

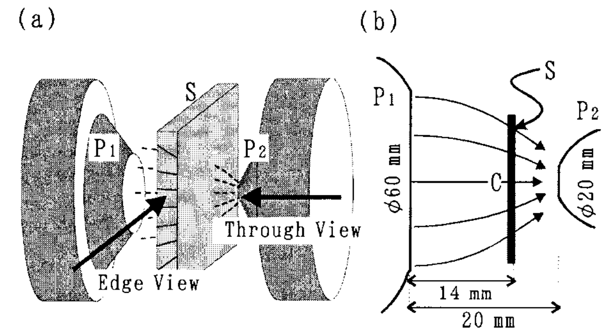

Figure 1. (a) Schematic diagram of an electromagnet with pole pieces P_1 and P_2 with different sizes. Dotted lines indicate a direction profile of the magnetic field. This profile is neither a calculated one nor a measured one, but just one expected from the asymmetric configuration of the pole pieces used. S indicates the sample strip with an expected alignment drawn on the edge. Definition of the through and edge views are indicated. (b) The detail of the experimental setting. P_1 and P_2: pole pieces; S: sample; C: the center of the sample, and the origin of the sampling position.

A MAC Science MXP system, equipped with an imaging plate was used for X-ray diffraction measurements. The edge and through directions are defined in Figure 1a. Prior to the heat treatment in the magnet field, a narrow (ca. 1 mm width) strip was cut from the original strip and the X-ray measurements were carried out on 8 points on the strip. After the heat treatment in the magnet, another narrow strip was cut from the same edge and the same X-ray measurements were carried out on 8 points in the vicinity of the original sampling points chosen for the measurement before the heat treatment.

Figure 2a shows the X-ray diagrams taken from the edge at various sampling positions before the heat treatment. The ring at $2\theta = 19.5°$ corresponds to the mean chain spacing in the nematic phase. The arcs on the ring centered at the equatorial direction indicate that the chain axes lie parallel to the film surface. Though they are not shown, through views exhibit arcs centered at the equatorial direction, which is due to the radial flow exerted during the hot pressing process. These orientations are frequently observed for the pressed LCP film samples.

Figure 2b shows the edge views taken after the heat treatment in the magnetic field. These edge views exhibit intense arcs located approximately in the meridional direction. These arcs were in the equatorial direction before the heat treatment in the field. This shift of the arcs is due to the change in align-

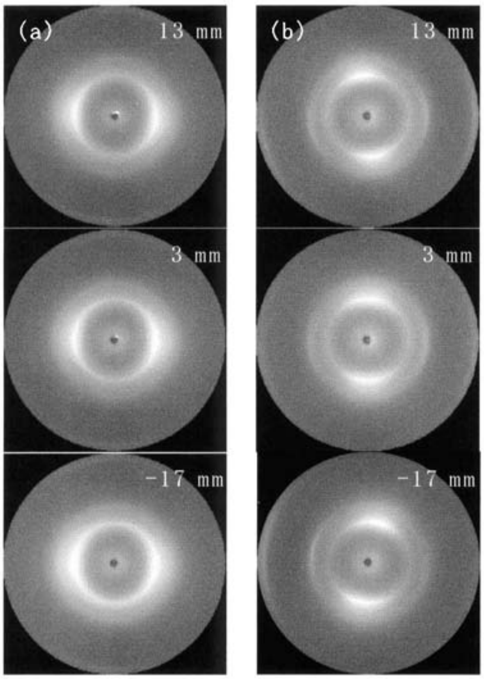

Figure 2. X-Ray diagrams (edge views) of the samples obtained at various sampling positions indicated in the figure, taken (a) before and (b) after the heat treatment in the magnetic field. Sampling position of 0 mm indicates the center of the sample.

ment of the chain from the parallel direction to the perpendicular direction with respect to the film surface. However, since there is a field gradient, the arc centers are deviated from the exact meridional direction depending on the sampling positions on the sample strip.

On the other hand, the through views exhibit almost a uniform ring though they are not displayed. However, a closer observation by the azimuthal scan along the ring reveals that there are weak arcs corresponding to a slight orientation in the strip direction especially for the sampling points away from the sample center. Disappearance of the strong arcs in the through view upon heat treatment is explained by the alignment of the chains in the field direction. Due to the perpendicular alignment by the magnetic field, the anisotropy disappears when viewed from the perpendicular direction, resulting in disappearance of the arcs in the through view. Since the field direction is deviated from the perpendicular direction at sampling points off from the center, some orientations remain in the strip direction, giving rise to a weak arc in the through view.

In Figure 3, the location of the arcs in the edge view obtained after the heat treatment is plotted as a function of the sampling position. At the center of the sample, the chains align in the direction perpendicular to the film surface. With sampling points going off from the center, the tilt angle from the normal direction increases by 15° on one end of the sample strip.

The half width of the arc is a measure of the degree of orientation. The detail analyses of the half width by means of

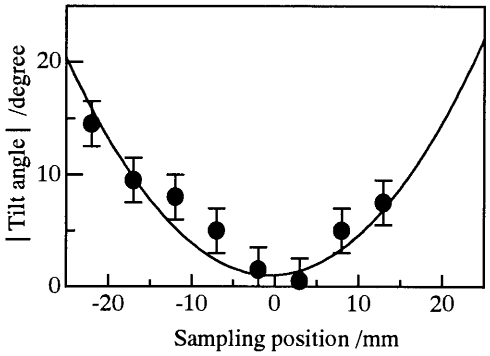

Figure 3. The tilt angle of the chain direction measured with respect to the direction perpendicular to the film surface, plotted as a function of the sampling position. The sampling position of 0 mm indicates the center of the sample. The tilt angle 0° at the sample center indicates that the direction of the chain is perpendicular to the film surface.

azimuthal scan at $2\theta = 19.5°$ show that the degree of orientation is lower at off-center sampling points than those near the center. This might be due to the lower field strength at off-center positions.

In conclusion, the graded alignment (GA) of a liquid crystalline polymer (LCP) was demonstrated by use of a field gradient provided by an electromagnet with asymmetrical pole pieces. It will be possible even to obtain three-dimensionally controlled alignment provided that a magnet with a well-defined field profile is available. This technique could also be applied to crystalline polymers.

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