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Study on the Structure and the Tensile Property of a 60 mol % *p*-Hydroxybenzoic Acid/40 mol % Ethylene Terephthalate Liquid Crystalline Copolyester Oriented in a Magnetic Field

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ABSTRACT: A thermotropic liquid crystalline copolyester, one from the Rodrun series, consisting of 60 mol % *p*-hydroxybenzoic acid and 40 mol % ethylene terephthalate was aligned under a magnetic field of 6 T and by mechanical methods. The tensile properties of the aligned films were different depending on the orientation degree and the means used for the orientation. The magnetically oriented films exhibited a lower ultimate tensile strength than the mechanically oriented films, but their elastic modulus was as high as that of the mechanically oriented films, suggesting that magnetic fields could provide an additional means for orientation in processing thermotropic liquid crystalline copolyesters. The difference in tensile properties was discussed in relation to the oriented structures examined by wide-angle X-ray measurement, the high-resolution solid-state ^{13}C NMR technique, Fourier transform infrared spectroscopy, and polarizing microscopy.

Introduction

The orientation is an important factor which determines the physical and the mechanical properties of thermotropic liquid crystalline copolyesters in their final products. Mechanical methods, including the application of shear or elongation, are usually used to attain the orientation but there are difficulties in using these methods to finely control the orientation. For example, injection molding could cause orientations through shear, but in some cases, skin−core structures are formed, leading to inhomogeneous orientations. On the other hand, it is well-known that liquid crystalline copolyesters are susceptible to magnetic fields[1−4] due to the diamagnetic anisotropy of their backbone structures and to the propensity to form mesophases. Since the magnetic field is easier to control and it penetrates into the materials, we could take advantage of using the magnetic fields to attain a fine control of orientation.

A number of studies have been reported on the magnetic orientation of liquid crystalline copolyesters,[5−9] as well as the tensile properties of mechanically oriented liquid crystalline copolyesters,[10−16] but there are few studies reporting the structures and the physical properties of magnetically oriented liquid crystalline copolyesters.[17−20] Following our study on the physical properties of the magnetically oriented thermotropic liquid crystalline copolyesters,[19,20] we report here the tensile properties of a magnetically oriented thermotropic liquid crystalline copolyester (Unitika Rodrun LC-3000) composed of 60 mol % *p*-hydroxybenzoic acid/40 mol % ethylene terephthalate. The comparison is made with the tensile properties of the mechanically oriented samples, and the difference is discussed in terms of the structures observed by means of X-ray diffraction, high-resolution solid-state ^{13}C NMR, Fourier transform infrared spectroscopy, and polarizing microscopy.

Experimental Section

Sample Preparation. The sample is a Unitika random copolyester Rodrun LC-3000 composed of 60 mol % *p*-hydroxybenzoic acid (PHB) and 40 mol % ethylene terephthalate (ET). Pellets as received were dried at 90 °C under vacuum for 12 h, hot-pressed between two polyimide sheets at 220 °C for 5 min, quenched in ice−water, and dried at 90 °C under vacuum for 12 h to obtain a pressed film. A heat-treated film was prepared by heat-treating the pressed film at 250 °C for 30 min and cooling under the nitrogen atmosphere.

The pressed film was heat-treated in a magnetic field (6 T) under nitrogen gas atmosphere and slowly cooled in the magnet. The heat-treatment temperature was between 231 and 251 °C, and the heat-treatment time was between 15 and 120 min. Details are reported elsewhere.[19]

The oriented film of the lowest orientation was supplied by Unitika. This film was elongated at 95 °C in the tensile test machine to obtain a film of a higher orientation. The dried pellet was melted at 280 °C and elongated by rapidly drawing the polymer by pulling it up with a glass rod to obtain the mechanically oriented film with the highest orientation.

Tensile Test. Mechanical properties of the sample were investigated by using a TMC-500-1 (Tokyo Koki Co. Ltd.) tensile test machine[21] with a chuck distance of 40 mm and an elongation rate of 1 mm/min at room temperature.

X-ray Diffraction. A MAC Science MXP (40 kV, 250 mA) was used. The orientation degree (OD) was estimated according to the equation, $(180° - H)/180°$, where H is the width at half-height of the azimuthal scan of the peak at $2\theta = 20°$. The equatorial direction is taken to be perpendicular to the orientation direction.

^{13}C Solid-State NMR. Cross polarization/magic angle spinning ^{13}C solid-state nuclear magnetic resonance was carried out by using a JEOL EX270 at a spinning rate of 5750 Hz, a ^{1}H 90° pulse of 4 μs, a contact time of 2 ms, a repetition time of 10 s, and 400 scans.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) spectra were obtained by using a Nicolet Magna-750 with a resolution of 2 cm^{-1} and 100 scans. Microscope FTIR spectra were obtained by using a Nicolet-760 equipped with a microscope system. The resolution was 4 cm^{-1}, and the number of scans was 512.

Polarizing Optical Microscopy. Microscope observations were carried out by using an Olympus BH-2 microscope equipped with a polarizer and an analyzer.

Results and Discussion

Tensile Properties. Since the mechanically oriented films used here for the tensile tests are as thin as 30−50 μm, we expect that these films are free from skin−core structures usually arising in thick sheet

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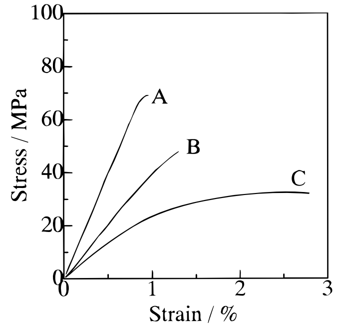

Figure 1. Stress-strain curves for the magnetically oriented films with the various orientation degrees: (A) 0.88, (B) 0.63, and (C) 0 (pressed film).

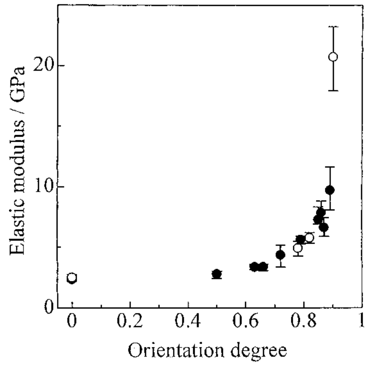

Figure 2. Elastic modulus of the magnetically (●) and mechanically (○) oriented films as a function of the orientation degree. The error bars indicate the maximum and the minimum values of four to six experiments. The data point at the origin of the orientation degree is of the pressed film.

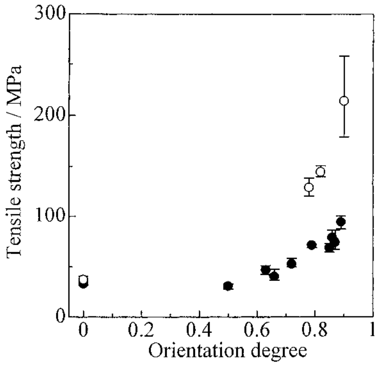

Figure 3. Tensile strength of the magnetically (●) and mechanically (○) oriented films as a function of the orientation degree. The error bars indicate the maximum and the minimum values of four to six experiments. The data point at the origin of the orientation degree is of the pressed film.

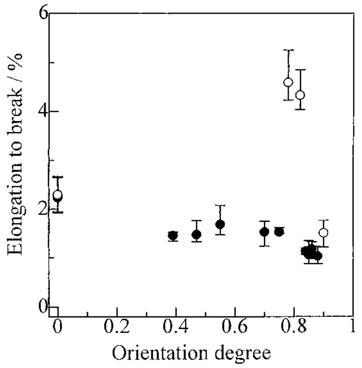

Figure 4. Elongation to break of the magnetically (●) and mechanically (○) oriented films as a function of the orientation degree. The error bars indicate the maximum and the minimum values of four to six experiments. The data point at the origin of the orientation degree is of the pressed film.

samples or molds[22] and hence provide tensile properties corresponding to the skin structure, which might be close to the "intrinsic" tensile properties of mechanically processed films of a given orientation degree. The magnetically oriented films used in this study, which are ca. 100 μm in thickness, also provide the "intrinsic" tensile properties attainable by means of the magnetic orientation because the magnetic field penetrates uniformly into the film. We use the term "intrinsic" simply to indicate that the orientation degree is homogeneous throughout the film. Of course, the "intrinsic" tensile properties could depend on the preparation conditions.

Figure 1 shows typical stress−strain curves obtained for the magnetically oriented films with various orientation degrees. In Figure 2, the elastic modulus of the magnetically and mechanically aligned films are displayed as a function of the orientation degree. The data points obtained for the two different orientation methods lie on a single curve except for the mechanically oriented one with the highest orientation degree. Lee *et al.*[23] has reported in their study on the mechanical properties of thermotropic liquid crystalline polymers that the elastic modulus increases gradually with increasing draw ratio, while the orientation degree increases very slightly except for a sharp increase at a relatively small draw ratio: they attributed this observation to a high aspect ratio of the nematic domains attained under a large draw ratio. In terms of their description, our observation of a high elastic modulus for the mechanically oriented sample at a higher orientation degree could indicate that deformation of the nematic domains occurs under the mechanical orientation. Of course, the magnetic field could deform the nematic domain,[18] but our observation here indicates that the effect of the magnetic field is less compared to mechanical orientation.

The ultimate tensile strengths are compared in Figure 3. In contrast to the elastic modulus, the ultimate tensile strengths of the mechanically oriented films are 2−3 times larger than those of the magnetically oriented films. Figure 4 compares the elongation to break. The magnetically oriented films show lower values than that of the mechanically oriented films. Because of the lack of data points for the mechanically oriented film at lower orientation degrees, we cannot say much about the behavior in this region. However, we might expect that the decrease at higher orientation degrees is preceded by an initial increase at lower orientation degrees since it is reported[10] that the elongation to break of the fiber samples of the same material exhibits a sharp increase and a subsequent decrease (almost a discontinuity) when plotted against the draw ratio. In contrast, such a phenomenon does not seem to occur for the magnetically oriented films.

X-ray Diffraction. Figure 5 shows the equatorial scans of the magnetically oriented film (OD = 0.88), the mechanically oriented film (OD = 0.89), and the pressed film. The main peak around $2\theta = 20°$ is close to the (110) diffraction of the crystalline part of the PHB homopolymer[24,25] and hence might reflec the mean chain spacing of the mesophase. A closer look at the peak position reveals that the mean chain spacing depends on the samples: the spacing for the magnetically oriented sample and the pressed sample is about 4.50 Å, while that for the mechanically oriented one is about 4.44 Å. This observation leads to that the magnetic

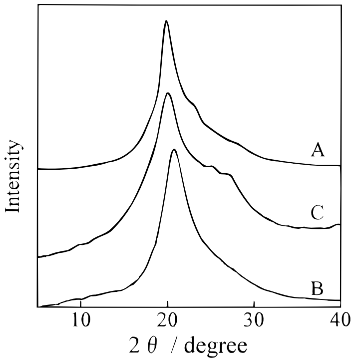

Figure 5. X-ray diffraction patterns obtained for the equatorial direction, which is perpendicular to the orientation direction, of the magnetically oriented (A), mechanically oriented (B), and pressed (C) films.

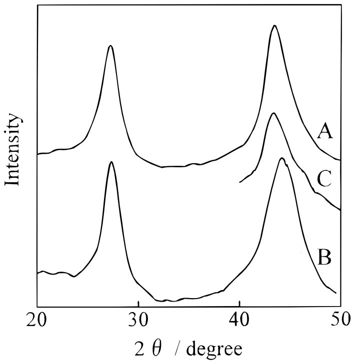

Figure 6. X-ray diffraction patterns obtained for the meridional direction, which is parallel to the orientation direction, of the magnetically oriented (A), mechanically oriented (B), and pressed (C) films.

orientation occurs without changing the initial chain packing of the pressed sample, whereas the mechanical process alters the packing. A narrower peak width for the magnetically oriented film, in comparison to the mechanically oriented film, indicates that the packing homogeneity is better in the magnetically oriented film.

In Figure 6 the meridional scans for the magnetically oriented film (OD = 0.88), the mechanically oriented film (OD = 0.89), and the pressed film are shown. The peak around $2\theta = 43°$ is assigned to the contribution of PHB by comparison of the copolyester samples with different PHB contents.[16] Also, in the study[26] of a copolyester of PHB and hydroxynaphthoic acid, it is reported that this peak is attributed to PHB, and the distance corresponds to one-third of the repeating unit of PHB. Here again, the peaks for the magnetically oriented sample and the pressed sample are located at almost the same position around $2\theta = 43.4°$, while the peak for the mechanically oriented one is located around $2\theta = 44.1°$. The values $2\theta = 44.1$ and 43.4° give repeating distances of 6.15 and 6.24 Å, respectively. Coincidentally, these values are close to the repeating length of the PHB unit measured along the chain direction, when the unit is connected in the *cis* and *trans* forms, respectively, as shown in Figure 7. In the magnetically oriented film and the hot-pressed film, the poly-PHB chain takes a more extended conformation than in the mechanically oriented film. The low-angle shift of the peak on heating of the mechanically oriented sample is also reported by Takahashi *et al.*[27] It could be said that the magnetic orientation does not alter the chain conformation nor the chain packing of the mesophase.

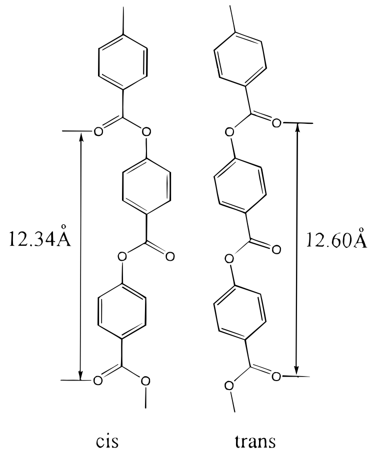

Figure 7. Connection of the PHB repeating unit in the *cis* and *trans* forms.

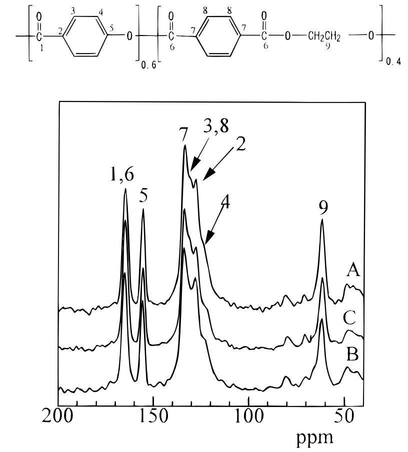

Figure 8. CP/MAS ^{13}C NMR spectra for the magnetically oriented (A), mechanically oriented (B), and pressed (C) films, with the assignment.

^{13}C Solid-state NMR. Solid-state ^{13}C NMR spectra are shown in Figure 8 for the same samples as used in the X-ray measurement. The assignment is given on the basis of the literature data[28] and of the comparison of the spectrum of the sample used here (PHB/ET = 60/40) with that of another sample (PHB/ET = 80/20). The line shape around the peak assigned to phenyl rings is different between the mechanically oriented film and the other two. To make the difference clear, the difference spectrum between the mechanically and magnetically oriented samples is taken as shown in Figure 9. The residual peaks are the contributions of the tertiary carbons of phenyl rings of PHB (C3 and C4) and ET (C8) units. An explanation for the observed difference is that the structural inhomogeneity around the phenyl carbons are larger in the mechanical films, resulting in the line broadening of 3-, 4-, and 8-carbons. Another explanation would be the difference in the chemical shifts of these carbons arising from the different electromagnetic circumstances. These explanations are in agreement with the X-ray observation that the magnetically oriented film exhibits a higher homogeneity in packing than the mechanically oriented one and that its chain conformation and the chain packing are different from those of the mechanically oriented one.

FTIR. The conformation of the spacer region, the ethylene group of ethylene terephthalate moiety, is investigated by means of Fourier transform infrared spectroscopy. The spectra are shown in Figure 10

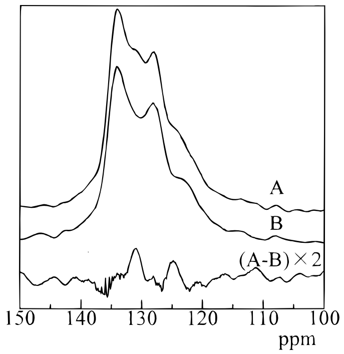

Figure 9. Difference spectrum obtained by subtraction of the spectrum of the mechanically oriented film (B) from that of the magnetically oriented film (A). The residual peaks in the difference spectrum correspond to C3, C8, and C4.

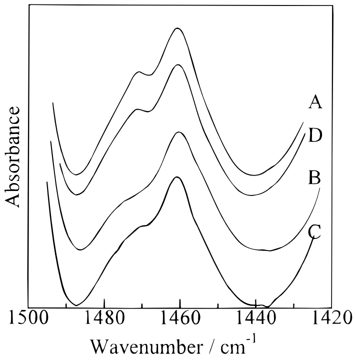

Figure 10. FTIR spectra of the magnetically oriented (A), the mechanically oriented (B), pressed (C), and heat-treated (D) films.

including the spectrum of the heat-treated sample. Though the difference in spectral shape is not clear enough, it could be said that the spectrum of the magnetically oriented film is similar to that of the heat-treated sample, and the spectrum of the mechanically oriented film is similar to the pressed sample. The bands at 1473 and 1460 cm^{-1} are assigned to the bending vibration of *trans* and *gauche* conformations of the ethylene group, respectively.[29,30] Since the peaks are broad in this region and might include many components, further investigations would be required to assign correctly these two peaks to the specific conformations. However, the *trans* content seems slightly higher in the magnetically oriented sample than in the mechanically oriented sample. The comparison of the spectrum of the magnetically oriented film with that of the heat-treated film indicates that the specific conformation of the magnetically oriented film is not due to the effect of the magnetic field but is instead due to the effect of the heat-treatment.

Difference in Morphology. In Figure 11 are compared the micrographs of thin films aligned by means of the magnetic field and of mechanical stretching. The mechanically oriented film shows a band-like structure running parallel to the stretching direction, but a uniform orientation is indicated by a uniform dark sight observed under crossed polars. On the other hand, the morphology of the magnetically oriented film is quite different. Though the orientation is confirmed by the measurement under crossed polars, we observe in addition dark spots (Figure 11). Since these dark spots remain dark under a 360° rotation of the specimen under crossed polars, they are assigned to be isotropic. A similar observation of the dark spots are reported for the same material,[31] and the origin of the isotropic nature is attributed to a partial segregation of an ethylene terephthalate rich region out of the anisotropic region.

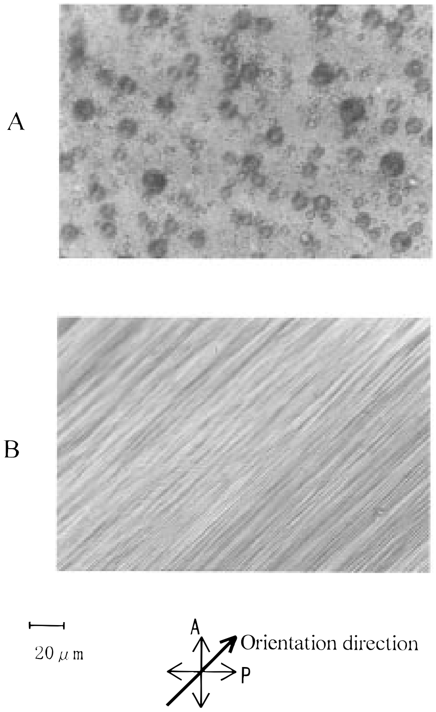

Figure 11. Micrographs of the magnetically (A) and mechanically (B) oriented films taken under crossed a polarity.

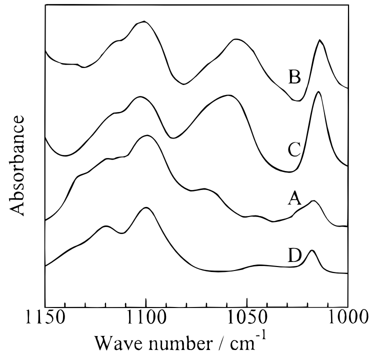

Figure 12. Microscope–FTIR spectra of the isotropic round spot region (A) and of the anisotropic region (B) of the magnetically oriented film, in comparison to the FTIR spectra of the pressed film (C) and of a poly(ethylene terephthalate) film (D).

In order to confirm this, we conducted microscope FTIR measurements. Figure 12 displays the microscope FTIR spectra for the anisotropic region and the isotropic round region, together with the transmission spectra of the pressed film and a poly(ethylene terephthalate) (PET) film. The difference is seen in the bands at 1100 and 1050 cm^{-1}. Similarity in the spectra is evident between the anisotropic region and the bulk pressed film, as well as between the isotropic region and the PET film. It is therefore concluded that the isotropic region is rich in the ethylene terephthalate moiety. The microscope FTIR measurements were also conducted on the mechanically oriented film. In contrast, no significant difference is observed for the spectra measured at different sites. This indicates that there is no conformational inhomogeneity over a range of 5 μm, the resolution of the microscope FTIR spectroscope.

The difference in morphology between the magnetically and mechanically aligned samples observed with the polarizing microscope might be attributed to the effect of the thermal annealing. In the case of the magnetic orientation, the sample undergoes a long thermal history including heat-treatment in the molten state and subsequent slow cooling in the magnet, during which the partial phase separation of ethylene terephthalate rich region could proceed. The segregation process might not be connected with the magnetic orientation because the isotropic regions also arise from heat-treatment alone. A similar observation has also been reported.[31] In the case of the mechanically oriented sample, on the other hand, there is not enough time for the sample to develop the segregation. In addition, even if there is a segregation structure in the melt, it would be destroyed or elongated during the stretching process and would disappear. The segregation structure could cause the reduction of tensile properties such as the ultimate tensile strength and the elongation to break.

Conclusions

The tensile properties of the magnetically oriented liquid crystalline copolyester have been studied in comparison to those of mechanically oriented one. Since the mechanically oriented films used here are considered to be thin enough to be free from unoriented core structures, the elastic modulus obtained here could represent the contribution solely due to the orientation. Also, since the magnetic field penetrates the material, the magnetically oriented films are assumed to be oriented throughout the whole thickness. Therefore, the results of the tensile tests enable us to compare the intrinsic tensile properties attained by the two different alignment methods.

The elastic modulus of the magnetically oriented film is comparable to that of the mechanically oriented film over a wide range of orientation degree. This implies that the application of a magnetic field during the fabrication process of thick films or molds could help improve their elastic modulus.[32] The tensile strength is about 2 times lower than that for the mechanically oriented sample. A similar tendency has been reported in our previous study[20] on the mechanical properties of another thermotropic liquid crystalline copolyester.

The structure analyses have revealed that the structure of the magnetically oriented sample is close to that of the pressed or the heat-treated sample rather than to that of the mechanically oriented sample. The packing of the mesogen group is higher in the mechanically oriented sample, but the packing homogeneity is higher in the magnetically oriented sample. Microscope analyses show a clear difference in morphology. The mechanically oriented film shows a band structure, while the magnetically oriented film shows ethylene terephthalate rich isotropic spots segregated from the anisotropic matrix. This difference of the morphology could be responsible for the lower value of the tensile strength of the magnetically oriented film.

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