Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Tsunehisa Kimura, Svetlana Kossikhina, Toshiyuki Shimoda, Eiko Ito & Masanori Kawahara (1998): Structures and Tensile Properties of Magnetically Oriented Liquid Crystalline Copolyesters, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 318:1, 279-290

To link to this article: http://dx.doi.org/10.1080/10587259808045390

Mol. Cryst. Liq. Cryst., Vol. 318, pp. 279–289
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Structures and Tensile Properties of Magnetically Oriented Liquid Crystalline Copolyesters

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Structures and tensile properties were investigated for magnetically oriented commercial thermotropic liquid crystalline copolyesters, Xydar and Rodrun. The orientation dependence and the magnitude of the tensile properties were similar between these two copolyesters. Comparison was made with the results obtained for the mechanically oriented samples of these copolyesters. It was found that the ultimate tensile strength and the elongation at break obtained for the magnetically oriented samples were different from those obtained for the mechanically oriented samples. Structure analyses conducted by means of polarizing microscope and X-ray diffraction showed that the two different orientation methods provide different structures on macroscopic as well as microscopic levels. The difference in the tensile properties could be attributed to the difference in structures.

Keywords: liquid crystalline copolyesters; magnetic orientation; mechanical stretching; mechanical properties; structural analysis

INTRODUCTION

Mechanical means including the elongation and the shear is commonly used for the chain orientation of the commercially available liquid crystalline copolyesters. A number of studies have been reported on the tensile properties of mechanically oriented liquid crystalline copolyesters[1-6] and liquid crystalline copolyester-based blends[7-11]. Along with these traditional orientation methods, magnetic fields could be an alternative means to achieve high degrees of chain orientation in these materials. Because of the flexibility

in controlling the direction and the strength and of its capability to penetrate through materials, magnetic fields would provide a new means of finely controlling the chain orientation of liquid crystalline polymers (LCPs). Thus, the magnetic field would be used as an additional means of processing of commercially available liquid crystalline copolyesters. Studies on the kinetics of the magnetic orientation, the oriented structures, and physical properties of LCPs have been reported in the literature[12-17].

This study reports on the structures and the tensile properties of the magnetically oriented thermotropic liquid crystalline copolyesters composed of *p*-hydroxybenzoic acid (HBA), terephthalic acid (TA), and *p*, *p*'-biphenol (BP) (Xydar) and of HBA and ethylene terephthalate (ET) (Rodrun). The comparison is made with the results obtained for the mechanically oriented samples of these materials. Structural analyses are conducted by means of X-ray diffraction and polarizing microscopy.

EXPERIMENTAL

Materials

Xydar (SRT 900, Amoco Polymers, Inc.)[18] with T_m=346°C was supplied by Nippon Petrochemicals Co. Ltd. in the form of powder and uniaxially stretched film (80-90 μm). Rodrun LC-3000, composed of 60 mol % *p*-hydroxybenzoic acid and 40 mol % ethylene terephthalate was supplied by Unitika in the form of pellets and mechanically stretched film.

Mechanically Oriented Samples

Powder of Xydar was dried in vacuum at 100°C for 10 h, then it was hot pressed at 360°C for 5 min, followed by cooling to room temperature. The film (90-110 μm) exhibited a slight chain orientation. This film was used for the tensile test. The powder was also pressed at 320°C for 5 min to obtain the film for the treatment in the magnetic field. This film exhibited no chain orientation.

As received pellets of Rodrun were dried at 90°C under vacuum for 12 h, then they were hot pressed at 220°C for 5 min, followed by quenching in ice

water, and dried at 90°C for 12 h to obtain a pressed film. The mechanically stretched film supplied by Unitika was elongated at 95°C in the tensile testing machine to obtain films of higher chain orientation. The dried pellet was melted at 280°C and elongated by rapid drawing by pulling it up with a glass rod to obtain the mechanically stretched film of the highest orientation.

Magnetically Oriented Samples

An Oxford superconducting magnet of 6T was used. The experimental error of temperature control was ca. ±5°. Xydar samples were prepared by heat-treatment of the pressed films at 380°C for 5 or 10 min, and then at 390°C for 60 min followed by slow cooling (about 40 min) in the magnet. The pressed film of Rodrun was also heat-treated and slowly cooled in the magnetic field. The heat-treatment temperature was between 231 and 251°C, and the heat-treatment time was between 15 and 120 min.

Tensile Test

Tensile tests were carried out on a newly developed tensile testing machine, a TMC-500L of Tokyo Koki Co. Ltd.[19] at the strain rate of 2 mm/min (Xydar) or 1 mm/min (Rodrun). The direction of tensile force was parallel to the draw direction of the films. The reproducibility was within 10-15% for mechanically stretched films and 20-25 % for the magnetically oriented films.

X-ray Diffraction

A MAC Science MXP system (40 kV, 250 mA) generating CuK_α X-ray beam was used. The orientation degree (*OD*) was estimated by the equation, $(180°-H°)/180°$, where $H°$ is the width at half-height of the peak at 2θ=19.6° (Xydar) and 20.0° (Rodrun) of the azimuthal scan. The equatorial direction is taken to be perpendicular to the orientation direction.

RESULTS AND DISCUSSION

Kinetics of the magnetic orientation of Xydar and Rodrun has been reported elsewhere[20, 21]. The magnetically oriented films (100-130 μm) provide the

"intrinsic" tensile properties since the magnetic field penetrates uniformly into the material. Since the thickness of the mechanically stretched films used in this study was less than 100 μm, it could be expected that they did not exhibit skin-core structures either. Therefore, a uniform orientation is achieved throughout the film, also providing "intrinsic" tensile properties. We use the term "intrinsic" to indicate that the orientation degree is homogeneous throughout the film, and also to indicate that the tensile properties are dependent on, and hence intrinsic to, the orientation methods employed.

Tensile Properties

In Figs. 1a, b, and c are plotted the ultimate tensile strength, the elastic modulus, and the elongation at break measured at room temperature against the orientation degree (*OD*) for the magnetically and mechanically oriented Xydar and Rodrun samples.

Data points for the mechanically stretched samples shown by open symbols fall on single curves irrespective of the copolyesters used here. Data points for the magnetically oriented samples (shown by filled symbols) also seem to exhibit the same tendency though the elastic modulus of magnetically oriented Rodrun is slightly higher than that of Xydar. The effect of the orientation method on the tensile properties is clearly observed for the ultimate tensile strength and the elongation at break. The samples prepared in the magnetic field exhibit lower ultimate tensile strength and their values of the elongation at break are almost constant over the range of the degree of chain orientation studied here.

Xydar exhibits higher elastic modulus when stretched by the mechanical means than by the magnetic field, while Rodrun exhibits almost the same level irrespective of the method utilized. However, the mechanically stretched sample of Rodrun with the highest *OD* shows an extremely high value of the elastic modulus in comparison to the magnetically oriented sample with the almost same *OD*. Since a high aspect ratio of the elongated domain contribute to the increase in the elastic modulus[22], it is speculated that the domain in the mechanically aligned sample with the highest *OD* is highly elongated in comparison to the domains in the mechanically aligned samples with lower *OD*

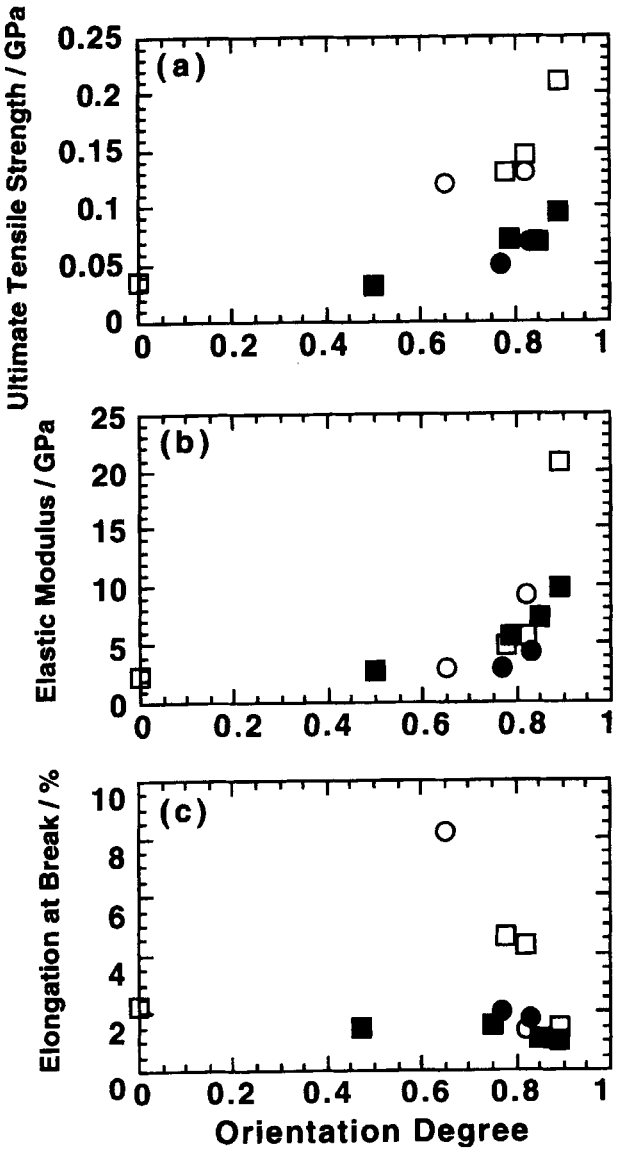

FIGURE 1 Orientation degree dependence of (a) ultimate tensile strength, (b) elastic modulus, and (c) elongation at break measured at room temperature for the magnetically oriented (●) and mechanically stretched (○) films of Xydar, magnetically oriented (■) and mechanically stretched (□) films of Rodrun.

or to the domains in the magnetically oriented samples.

Polarized Microscopy

Fig. 2 displays the micrographs of Xydar (left) and Rodrun (right) aligned by means of the magnetic field (a, b) and by the mechanical stretching (c, d). Both copolyesters oriented in the magnetic field exhibit texture patterns characteristic of nematic phase. In the case of Rodrun, dark spots are observed, which are due to segregated regions rich in poly(ethylene terephthalate) as evidenced by microscope FT-IR measurements[23]. The segregation could occur during a prolonged heat treatment necessary to attain the magnetic orientation.

Mechanically stretched samples exhibit band-like structures running parallel to the stretched direction. This structure is not the same as the banded structures of sheared liquid crystalline polymers[24].

X-ray Diffraction

Figures 3a and b show the equatorial scans of the magnetically and mechanically oriented samples of Xydar and Rodrun, respectively. A main peak around 2θ = 20° is observed for all samples. Less significant peaks around 2θ=22° and 28° (Xydar) and 2θ=23° and 28° (Rodrun) indicate low crystallinity for both materials.

The position of the main equatorial peak can be attributed to the mean interchain spacing in nematic phases[25]. In the case of Xydar, the mean spacings for the magnetically oriented films (*OD*=0.83 and 0.77) is 4.51 Å and that for the uniaxially stretched film (*OD*=0.82) is 4.49 Å. Both are close to the value for the hot-pressed film (4.50 Å). However, the half width of the main equatorial peak is narrow for the magnetically oriented film (*OD*=0.83) than that for the uniaxially stretched film, which indicates more regular lateral packing in the former sample. The lateral correlation lengths determined by using the Scherrer equation were 99 Å for the magnetically oriented and 91 Å for the uniaxially stretched films. The difference between the structures on the chain level does not seem to explain the difference in the tensile properties between the magnetically oriented and the mechanically stretched films.

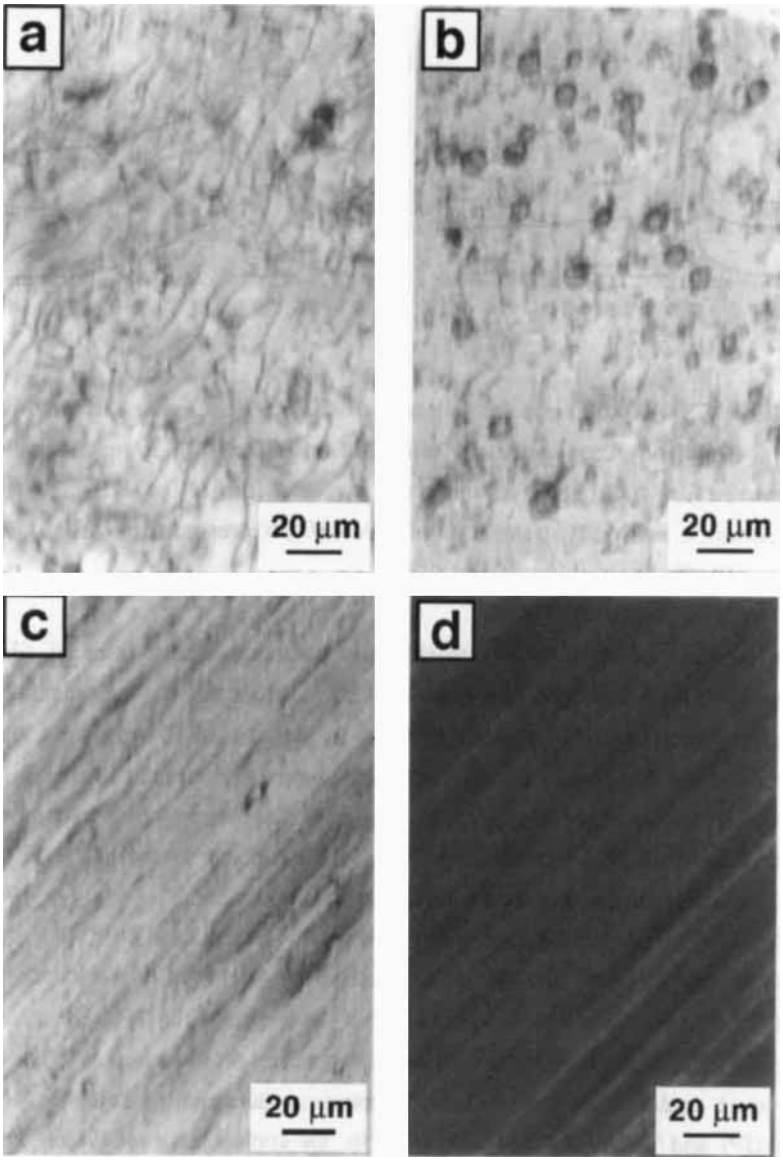

FIGURE 2 Polarizing micrographs of Xydar (left) and Rodrun (right) aligned by means of the magnetic field (a, b) and by the mechanical stretching (c, d).

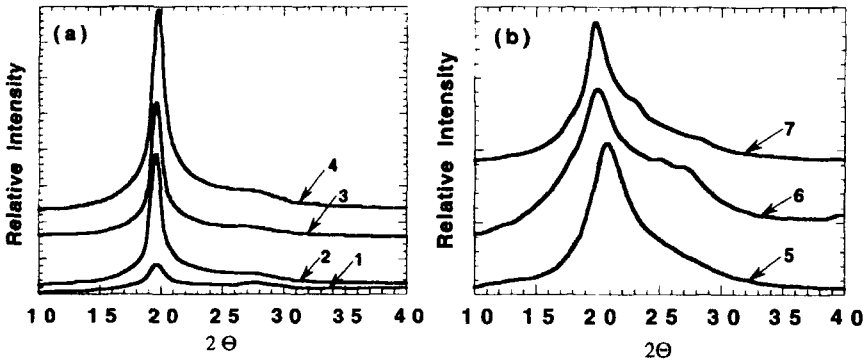

FIGURE 3 WAXD patterns (equatorial scans) of (a) Xydar, 1: pressed film (*OD*=0.65), 2: magnetically oriented film (*OD*=0.77), 3: magnetically oriented film (*OD*=0.83), 4: uniaxially stretched film (*OD*=0.82); and (b) Rodrun, 5: uniaxially stretched film (*OD*=0.89), 6: pressed film (*OD*=0), 7: magnetically oriented film (*OD*=0.88).

In the case of Rodrun, the spacing for the magnetically oriented film (*OD*=0.88) and the pressed film is about 4.50 Å, while that for the uniaxially stretched film (*OD*=0.89) is about 4.44 Å. In the case of Rodrun we could expect that the denser packing observed in the uniaxially stretched film could be related to its higher elastic modulus. Probably, a smoother and more uniform mechanical alignment is possible in Rodrun due to the presence of ethylene units than the case for the wholly aromatic Xydar.

The meridional profiles are shown in Fig. 4. In the case of Xydar, the peaks around $2\theta = 44^\circ$ and 46° correspond to the one third of the length of the HBA repeating unit and the one eighth of the length of the TPA-BP dimer unit [26]. The peak positions are different depending on the samples. These difference could be attributed to the difference in the repeating unit (HBA or TPA-BP) and / or also to the difference in the conformation of these units. The peak intensity maxima seem to depend on the orientation degree: the peak intensity at $2\theta = 46^\circ$ is dominant for the samples with higher orientation degree (*OD* = 0.93 for the magnetically oriented film, and *OD* =0.95 for the fiber),

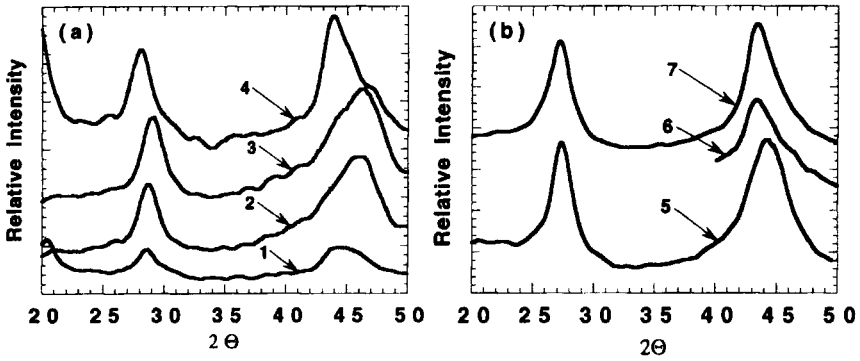

FIGURE 4 WAXD patterns (meridional scans) of (a) Xydar, 1: magnetically oriented (*OD*=0.83), 2: magnetically oriented (*OD*=0.93), 3: fiber (*OD*=0.95), 4: uniaxially stretched (*OD*=0.82) films; and (b) Rodrun, 5: uniaxially stretched (*OD*=0.89) films, 6: pressed (*OD*=0), 7: magnetically oriented (*OD*=0.88).

while the intensity at 2θ=44° is dominant for the samples with lower orientation degree (*OD*=0.83 for magnetically and *OD*=0.82 for mechanically stretched films).

In the case of Rodrun, the peak around 2θ=44° is also attributed to the HBA repeating unit, and a slight difference in peak position could be attributed to the conformation of the HBA sequence[23]. In this case, the orientation degrees for the uniaxially and magnetically oriented films are close to each other (0.89 and 0.88, respectively), but the 2θ value of the peak position for the former is larger than for the latter.

CONCLUSIONS

The tensile properties and the structures of magnetically oriented commercially available liquid crystalline copolyesters, Xydar and Rodrun, were investigated. The results were compared with those obtained for the mechanically stretched samples in order to assess the "intrinsic" tensile properties attained by means of the magnetic field. Since the mechanically stretched films studied

in this work are thin, they are almost free from skin-core structures usually unavoidable in thick sheets and molds. Considering the ability of the magnetic field to penetrate into the material, the orientations in the interior and on the surface would not differ for the film samples prepared in the magnet.

Therefore, the samples used in this study possess the orientation degree which is uniform throughout the samples, and hence enable the comparison of the "intrinsic" tensile properties between magnetically and mechanically stretched samples. Though the "intrinsic" tensile properties for the samples prepared in the magnet are slightly inferior to those for the mechanically stretched samples, the magnetic field would have an advantage over the mechanical means when it is applied to oriented thick sheets or mold of these copolyesters because the magnetic field can penetrate irrespective of the thickness of products.

Structure analyses of the oriented samples prepared by means of magnetic and mechanical orientation revealed that the structures ranging from the microscopic level (WAXD) to the microscope observation level are highly dependent on the orientation method. The difference is attributed not only solely to the orientation means but also associated with the prolonged thermal history required for the magnetic orientation.

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