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Effect of Annealing on the Physical Properties of Biaxially Oriented Liquid Crystalline Copolyester Films

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ABSTRACT: Biaxially oriented liquid crystalline aromatic copolyester (LCP) films based on *p*-hydroxybenzoic acid (HBA), 4,4′-hydroxybiphenol (BP), terephthalic acid (TA), and isophthalic acid (IA) were studied in order to evaluate the effect of annealing on the thermal transitions, thermomechanical properties, microstructure, and dielectric relaxation behavior. By the analysis of DSC data, annealing near the liquid crystalline transition of the as-received films led to an increase in the degree of crystallinity as well as an increase in the transition temperature by 60–70 °C. This phenomenon appears to arise from the improved packing of the rodlike chains with a corresponding increase in dipole interactions. Thermomechanical analysis revealed that the coefficients of thermal expansion (CTE) of the as-received film A increased with increasing temperature: however, that of the as-received film B decreased with increasing temperature below 200 °C. Annealing appears to decrease the CTE of the two as-received films. A wide-angle X-ray diffraction (WAXD) study in the reflection mode was performed. The as-received films displayed a single X-ray peak characteristic of one-dimensional order. On the other hand, the annealed films showed two peaks with a new previously unreported peak. Dielectric measurements made from 10 kHz to 1 MHz and from −100 to +220 °C demonstrated that annealing near the liquid crystalline transition has little influence on the dielectric constant. The results obtained in this study are interpreted in terms of structural changes occurring during annealing.

Introduction

Thermotropic liquid crystalline aromatic copolyesters (LCP) exhibit excellent thermomechanical properties and high chemical stabilities.[1–3] Over the past 20 years these properties have been studied in detail, with emphasis on the liquid crystalline character of these polymers. An area of special interest has been the use of LCPs in microelectronic packaging.[4–8] However, the potential advantages of polymer thin films[9–13] in microelectronic packaging has not been fully exploited. For example, the potential exists to deposit metal circuitry lithographically onto biaxially oriented polyester films and then to consolidate a stack of these films by high-temperature sintering of the copolyester and of the interlayer metal interconnects.[14] The potential to consolidate LCP films in the solid state to form a strong adhesive bond at the interface has recently been shown to occur by interchain transesterification reactions.[15–19] Such structures could display greatly improved performance characteristics such as higher signal speed and reliability compared to current approaches to multichip, multilayer modules. Presumably, one could easily design a metal circuitry interconnect (via) technology using solders such as Pb–Sn which flow at the temperature of consolidation of the polymer films. The above-indicated processes require temperatures of 200–375 °C. Hence it is important to understand the dimensional stability of the films at elevated temperatures. In addition, one should be cognizant of possible structural or morphological changes in the polymer on annealing at high temperatures since the potential exists to greatly increase the use of temperature by ordering processes.[20,21] The effect of thermal treatments on the dielectric constant should be clarified, since there is some confusion in the literature concerning the correct values for these films.[7–13] Finally, it is surprising that there are practically no data published in the literature concerning the behavior of biaxially oriented LCP films at elevated temperatures. Hence we were fortunate to obtain two samples of such films from Superex Polymer, Inc. (affiliated with Foster Miller Co.).

In the present work we report on the effect of annealing of biaxially oriented LCP films on the liquid crystalline transitions, thermomechanical properties, microstructures, and dielectric relaxation behavior. The composition of the LCP consisted of *p*-hydroxybenzoic acid (HBA), 4,4′-hydroxybiphenol (BP), terephthalic acid (TA), and isophthalic acid (IA).

Experimental Section

The Xydar SRT-900 thermotropic liquid crystalline polymer was kindly supplied by Amoco Co. in the form of a powder, which is composed of 2 mol of HBA, 1 mol of BP, and 1 mol (60/40) of Ta and IA. Two types of biaxially oriented LCP films were prepared from this resin by Superex Polymer, Inc. The thickness of film A was 3 mil and that of film B 2 mil. The films were prepared as a single-layer material with biaxial orientation, utilizing a special circular die developed by Foster Miller. In order to compare the degree of orientation of the biaxially oriented films, the orientation angle (peak width at half-height) was determined from azimuthal scan through the strongest reflection of the samples by X-ray diffractometry. In the case of film A, the degree of orientation was higher in the machine direction (MD) ($\theta = 35°$) while in film B the degree of orientation was higher in the transverse direction (TD) ($\theta = 50°$). For an isotropic film $\theta = 45°$. In these blown films the degree of orientation is determined by throughput, die rotation, blow-up speed, and take-up speed.[22,23]

The films were annealed in a hydraulic vacuum press under a nitrogen atmosphere after extracting the air for 10 min. Annealing of the as-received film was carried out at 320, 330, and 340 °C in order to further develop the crystalline order. Thermal properties were measured with a DuPont Model 10 thermal analyzer differential scanning calorimeter (DSC) in a nitrogen atmosphere. The heating rate was 20 °C/min, and the data obtained during the first and second heating stages are shown. The coefficients of thermal expansion (CTE) of both films were measured in the machine direction and

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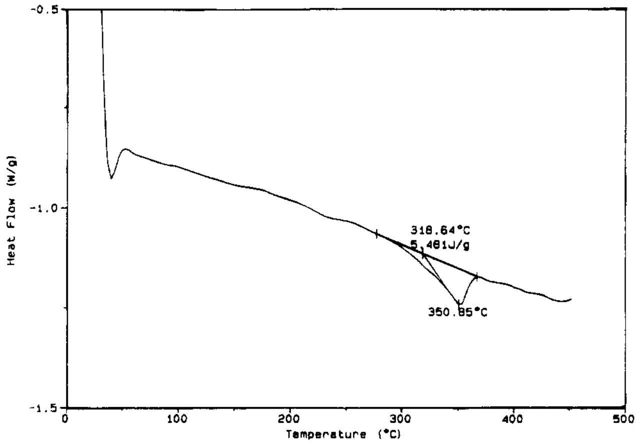

Figure 1. DSC thermograms of the as-received Xydar SRT-900 powder at a heating rate of 20 °C/min.

transverse direction with a DuPont Model 2940 thermal mechanical analyzer (TMA) equipped with a film fiber accessory, programmed at 5 °C/min over the range −100 to +300 °C, with 0.2 N film tension. Five test samples were prepared from each polymer, and the average values were taken.

Wide-angle X-ray diffraction (WAXD) experiments at room temperature were carried out using a Scintag Pad X diffractometer with a copper X-ray source at 42 kV and 5 mA. The scanning angle range ($2q$) was 10−35°, while the scanning rate was 2°/min with a step increment of 0.02.

Dielectric relaxation experiments were performed on both films using a Hewlett-Packard 4284A multifrequency LCR meter. A Delta design 9023 Hewlett-Packard 362 computer system was used to control the heating rate and frequencies at which the data were taken. The heating rate was 10 °C/min at temperatures ranging from −100 to +225 °C. A frequency range of 10 kHz to 1 MHz was examined. The gold-coated films were installed between polished rigid electrodes and placed on the hot stage. The dielectric constant (ϵ') and dielectric loss (ϵ'') were measured under an inert atmosphere.

Results and Discussion

Ordering during Annealing. Xydar copolyester has been commercially available for over 20 years; however, because of its relative intractability, little effort has been made to characterize it.[24,25] Part of the reason for the intractability is due to the blocky nature of the copolymer which arises from use of solid-state polymerization in the original synthesis.[15,16,26,27] Consequently, the thermal properties of the Xydar system have not been extensively studied. Hence one of our goals was to better characterize the potential for further ordering of the sequence distribution when exposed to a range of annealing temperatures and times.

Figure 1 shows an endothermic peak at 350 °C of the as-received Xydar 900 powder, which indicates a transition from a crystalline phase to a liquid crystalline mesophase. In order to minimize the effect of the previous thermal history, the as-received films A and B were subjected to second heatings. These results are shown in Figures 2 and 3. The DSC curves of both films at first heating exhibit a transition temperature at around 330 °C. This lower melting temperature suggests that the as-received films might be more random (possibly quenched) compared to the blocky structure of the as-received Xydar 900 powder.[15,16,26,27] However, DSC curves of the two films after the second heating exhibited a transition at 350 °C similar to the powder. It is noteworthy that in a separate study we have prepared this copolymer with a random sequence by melt polymerization, and such a system displays a transition at 300 °C.[14,15] Similarly, heating the as-received powder (Xydar 900) at temperatures in excess of 400 °C also produces the random phase $\approx$300 °C, presumably via interchain transesterification.[28−32] These results indicate that the random copolymer most likely melts at $\approx$300 °C and that the as-received powder and melt-blown film have a partial blocky structure.[15]

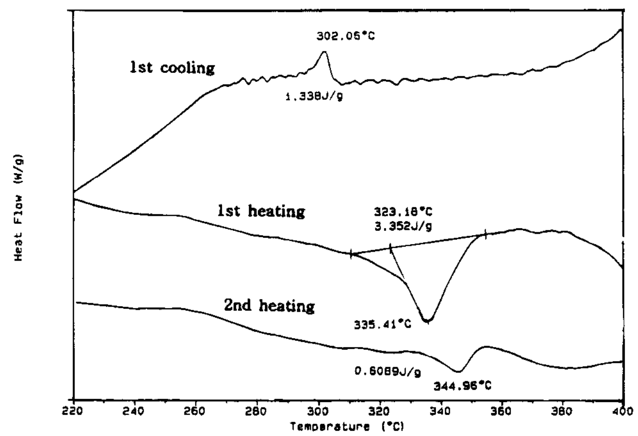

Figure 2. DSC thermograms of the as-received film A at a heating rate of 20 °C/min.

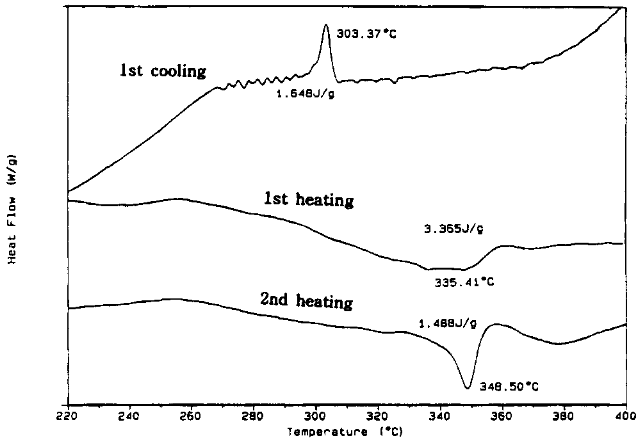

Figure 3. DSC thermograms of the as-received film B at a heating rate of 20 °C/min.

DSC curves showing the effect of annealing time at 320 °C for as-received film A are presented in Figure 4. With increasing annealing time, the transition of the as-received film continued to shift to a higher temperature (up to 400 °C) and the peak became narrower.[20,33,34] This implies further ordering in the sequence distribution of the polymer.[35] We feel that this ordering process occurs by ester interchange reactions within the existing crystallites near the melting point to produce more ordered sequences.[15−19] The driving forces for ordering arise from improved packing of the chains in the crystallites and a corresponding higher density and increased dipolar interactions between chains. Very likely, the degree of ordering is incomplete since the mobility of the chains within the crystallites decreases during annealing as the transition temperature increases to 400 °C.[32,34−37] Figure 5 shows the change in the liquid crystalline transition of film A at these different annealing temperatures with increasing time. Figure 6 shows the change in the transition enthalpy (ΔH_f) under the same annealing conditions. The slightly higher ΔH_f observed on annealing at 320 vs 340 °C may be due to several factors. For example, the potential for further polymerization at 340 °C could lead to a higher M_n with a modest decrease in the

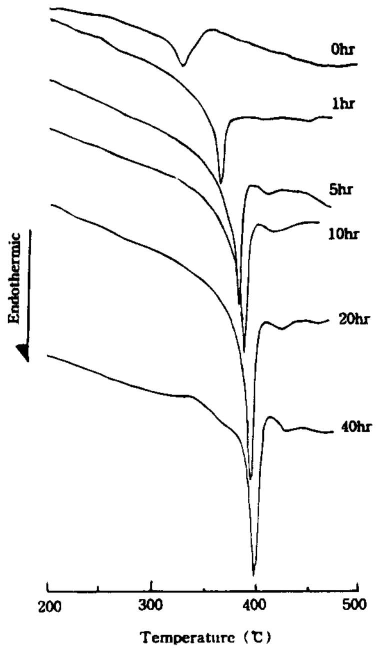

Figure 4. DSC thermograms showing the effect of annealing time at 320 °C on the crystal−nematic transition behavior for the as-received film A.

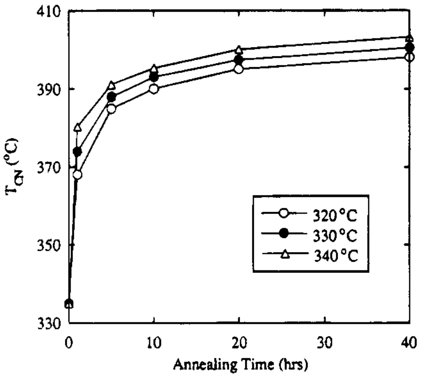

Figure 5. Effect of annealing time on the crystal−nematic transition temperature for the as-received film A.

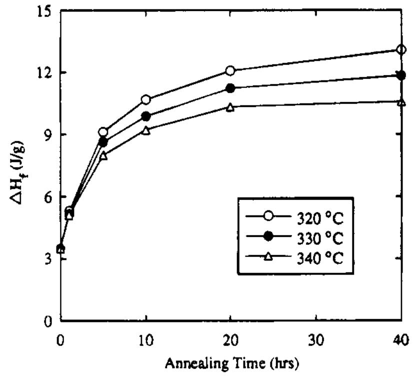

Figure 6. Effect of annealing time on the crystal−nematic transition enthalpy for the as-received film A.

temperature of crystallization.[26,38] Alternatively, the potential for incipient degradation reactions at 340 °C cannot be ruled out.[14] Film B gave almost identical results on annealing to those of film A; hence, these data are not included.

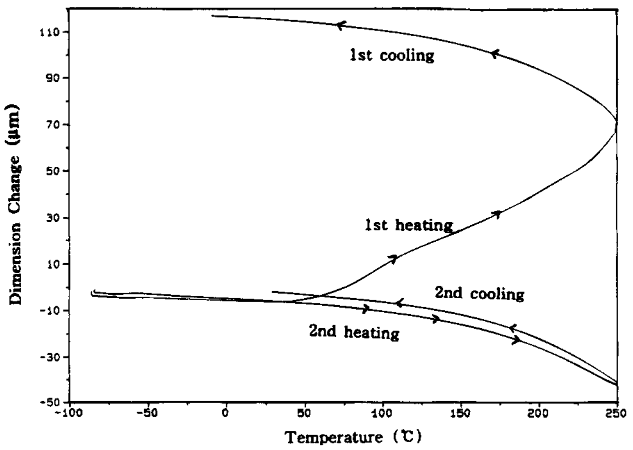

Figure 7. Thermal expansion behavior for the as-received film A in MD.

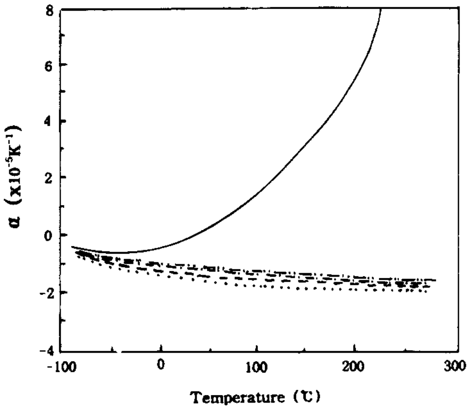

Figure 8. Thermal expansion behavior of film A in MD: (—) as received; (— — —) annealed at 330 °C for 10 h; (– • •) annealed at 320 °C for 10 h; (– • –) annealed at 320 °C for 20 h; (• • •) annealed at 320 °C for 40 h.

Effect of Annealing on the Coefficients of Thermal Expansion. Polymers with a low CTE could be particularly useful as substrates in printed circuit boards and as dielectric insulation layers for semiconductor devices. Thus it is important to learn to control the CTE of the polymer in order to minimize thermal stresses due to a mismatch of the CTE's between two different materials.[39−45] As noted earlier, the thermal expansion behavior of biaxially oriented LCP films based on the PHBA/BPT system has not been examined in any detail. This system is of particular interest since it can be designed to display good dimensional stability from room temperature to as high as 375 °C, which would make it compatible with most processes for manufacture of microelectronic devices. Thermal expansion behavior for as-received film A is shown in Figure 7. Thermal expansion measurements were performed in the course of first heating/cooling and second heating/cooling in order to minimize the thermal history of the as-received and annealed samples. With the as-received sample an irreversible elongation occurs on first heating. However, with the second heating the film shows a negative CTE. The elongation on first heating can be interpreted as an increase in chain orientation in the noncrystalline part induced by the externally applied tensile force.[46] Unlike the as-received samples, annealed samples show a reversible thermal contraction. The influence of the drawing process in MD and TD on the coefficients of thermal expansion for both film specimens is described along with the effect of annealing in Figures 8−11. Figure 8 shows the thermal expansion behavior of film A in MD as a function of annealing temperature. The CTE of the as-received film A increases with increasing temperature. This phenomenon is more prominent above the glass transition

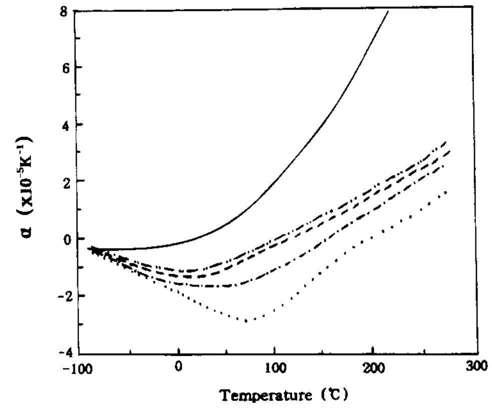

Figure 9. Thermal expansion behavior of film A in TD: (—) as received; (– – –) annealed at 330 °C for 10 h; (– • •) annealed at 320 °C for 10 h; (– • –) annealed at 320 °C for 20 h; (• • •) annealed at 320 °C for 40 h.

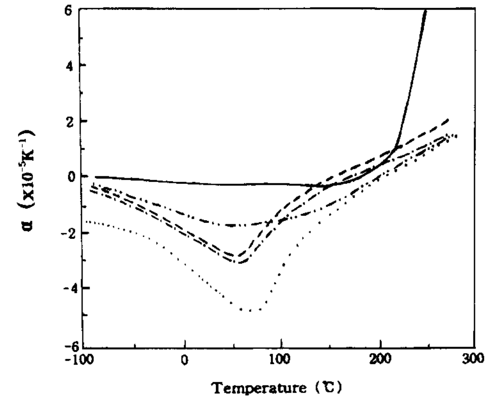

Figure 10. Thermal expansion behavior of film B in MD: (—) as received; (– – –) annealed at 330 °C for 10 h; (– • •) annealed at 320 °C for 10 h; (– • –) annealed at 320 °C for 20 h; (• • •) annealed at 320 °C for 40 h.

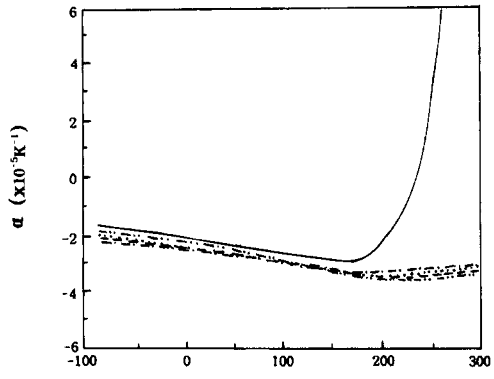

Figure 11. Thermal expansion behavior of film B in TD: (—) as received; (– – –) annealed at 330 °C for 10 h; (– • •) annealed at 320 °C for 10 h; (– • –) annealed at 320 °C for 20 h; (• • •) annealed at 320 °C for 40 h.

temperature (T_g) due to an increase of chain orientation in the noncrystalline regions. However, thermal expansions of the annealed films in the MD are decreased with increasing temperature and degree of annealing. Thermal contractions may be due to the thermal fluctuation motions perpendicular to the chain direction, that is, segmental vibrational/torsional motions of the oriented main chains.[47] Similar results have been reported for the uniaxially oriented liquid crystalline polyamides[46] and liquid crystalline PET/POB.[48] Thermal expansion behavior of film A in TD is shown in Figure 9. Thermal expansion of the as-received film increases with increasing temperature and shows a similar tendency to that of the MD. These results suggest that the as-received film A has modestly balanced thermomechanical properties in MD and TD,[44] consistent with the experimental data obtained from Superex Polymer, Inc. On the other hand, the coefficients of thermal expansion in TD of film A annealed at 320 or 330 °C decrease with increasing temperature and a lower degree of annealing. The CTE's of the annealed films show relaxation transitions at around 100 °C. This may be due to the relaxation of the oriented LCP chains.

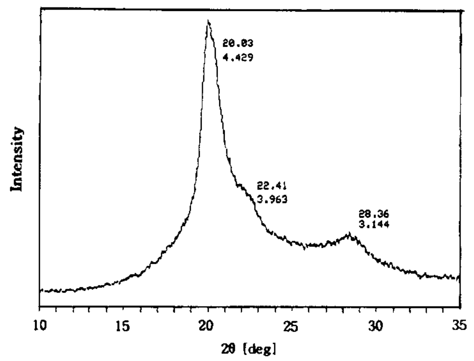

Figure 12. WAXD patterns of the as-received Xydar SRT-900 powder in reflection runs.

Thermal expansion behaviors of film B in MD and TD are presented in Figures 10 and 11. Thermal expansion coefficients of the as-received film in MD and TD decrease slightly with increasing temperature below 200 °C. However, the CTE of the as-received film in TD is lower than that of the as-received film in MD. This indicates that film B has slightly unbalanced thermomechanical properties in MD and TD.

It is well established that in the case of films based on rigid rod structures, an increase with draw ratio[2,3] leads to an increase in the degree of orientation and modulus, and hence the CTE is decreased.[49] Although the degree of orientation of as-received film B in MD is slightlly lower than that of film A, the CTE of the as-received film B is lower than that of film A. This may be ascribed to the fact that thinner films generally show a lower CTE than thicker films.[12] Also, annealing appears to decrease the CTE of the two as-received films (see Figures 8–11).

Changes in Microstructure with Annealing. WAXD was used to observe the effect of annealing on the microstructure of LCP films. Figure 12 describes the WAXD pattern for the as-received Xydar 900 powder. As shown in this figure, the as-received powder at room temperature exhibits one sharp peak at 20.03° and two diffuse peaks at 22.41 and 28.36° (2θ) [d spacing: 4.43, 3.96, 3.14 Å].[8,14] The three peaks can be indexed as the 110, 200, and 211 reflections of an orthorhombic cell. Figure 13 presents the WAXD patterns showing the effect of annealing on the microstructure of the biaxially oriented film A. Compared with the X-ray diffraction results of the as-received powder, as-received biaxially stretched film A displays a broad asymmetrc peak with maximum at $2\theta = 20.03°$ and a shoulder at around 21° (2θ). No additional peaks or weak reflections were observed at approximately 28° (211 reflection). This suggest a pseudohexagonal interchain packing order associated with a more random sequence distribution.[27] This may be ascribed to the fact that the films were quenched after extrusion. This is in good agreement with Blackwell's[27] results that melt-spun fibers show a random sequence based on

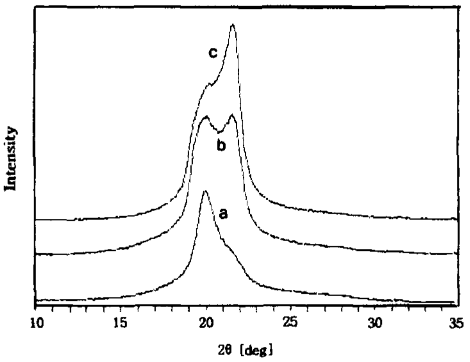

Figure 13. WAXD patterns of film A in reflection runs: (a) as received; (b) annealed at 330 °C for 10 h; (c) annealed at 320 °C for 40 h.

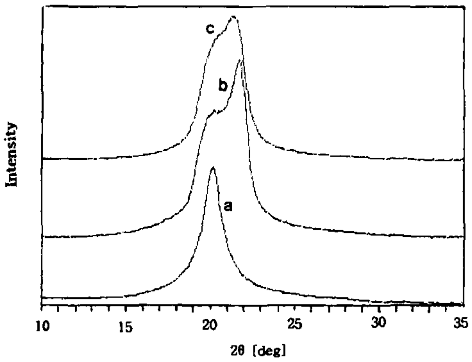

Figure 14. WAXD patterns of film B in reflection runs: (a) as received; (b) annealed at 330 °C for 10 h; (c) annealed at 320 °C for 40 h.

simulations of the WAXD patterns. X-ray diffraction results recorded for the as-received film A show a high sensitivity to annealing similar to that of the powder.[7,8] Annealing was carried out near the melting point of the as-received films at 320 and 330 °C. These annealing conditions were selected based on the transition enthalpy data shown in Figure 6. Thus at 320 °C for 40 h the highest ΔH_f values were obtained, while at 330 °C for 10 h the value was significantly lower. In the case of annealed film A at 330 °C for 10 h, a highly ordered pattern evolves, with reflections at 20.09° (4.42 Å) and 21.61° (4.11 Å). Annealing at 320 °C for 40 h led to a sharpening of the peak at $2\theta = 21.61°$ with a considerable increase in intensity. Therefore the ratio of the intensity of the two peaks at $2\theta = 20.2$ and 21.61° is increased and the d spacing at $2\theta = 20.03°$ (4.43 Å) tends to shift to lower values (4.33 Å) with increasing degree of annealing.

The effect of annealing on the WAXD pattern for film B is shown in Figure 14. The as-received film B showed one symmetric peak at $2\theta = 20.14°$, characteristic of hexagonal interchain packing order. Annealed films B displayed a similar diffraction pattern to the annealed films A with a new peak present at $2\theta = 21.44-21.71°$. This peak, which is only observed in biaxially oriented film, may be related to the spacings between the biaxial layers.

Change in Dielectric Properties with Annealing. Dielectric constant relaxation measurements for the as-received and annealed films were performed over the temperature range of −100 to +220 °C. Figures 15 and 17 show the dielectric constant (ϵ') and dielectric loss (ϵ'') behavior for the as-received A and B films at different frequencies. In both cases the dielectric constants increased with increasing temperatures and decreasing frequencies. Compared with published data for films based on similar compositions,[4-8] the measured values of dielectric constants (ϵ') for the as-received biaxially oriented A films tend to be somewhat higher than those predicted from the literature. This may be due to the fact that oriented films generally show a higher dielectric constant than that of the isotropic phase.[4,50] In the glassy state, long-range, long-axis orientational ordering is retained at very low temperatures.[51] The sharp increase in dielectric constant obtained for the as-received film over the range of 50−100 °C reflects the relaxation transition.[51] This indicates that some correlation exists between the dipoles in the LCP. At this temperature range the benzene rings in the chain begin to flip based on deuterium NMR studies.[16] Also, X-ray diffraction studies indicate a crystallographic transition for the related Xydar 300 at ≈100 °C.[26] The ester units presumably would not begin to spin or orient until one approaches the liquid crystalline transition.[16] From DSC measurements it is difficult to detect any transitions in this lower temperature range (see Figures 1−4). The dielectric loss (ϵ'') curves show a single distinct maximum for each case, and the positions of the peak in these curves are frequency dependent and increase with increasing frequency. Ionic conduction phenomena are not observed over the range −100 to +220 °C. The effect of annealing on the dielectric constant behavior of both films shown in

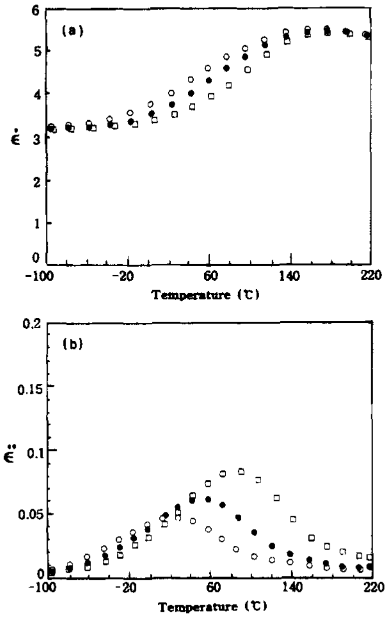

Figure 15. (a) Dielectric constant (ϵ') and (b) dielectric loss (ϵ'') behavior of the as-received film A at a heating rate of 10 °C/min: (○) 10 kHz; (●) 100 kHz; (□) 1 MHz.

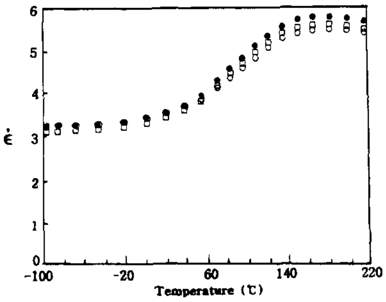

Figure 16. Dielectric constant (ϵ') behavior of film A showing the effect of annealing at a heating rate of 10 ° C/min and 1 MHz: (○) as received; (●) annealed at 330 °C for 10 h; (□) annealed at 320 °C for 40 h.

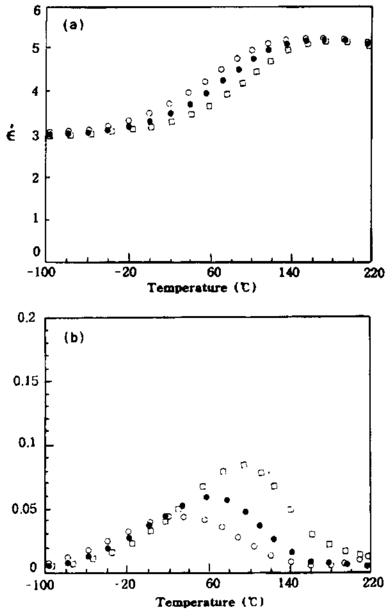

Figure 17. (a) Dielectric constant (ε') and (b) dielectric loss (ε'') behavior of the as-received film B at a heating rate of 10 °C/min: (○) 10 kHz; (●) 100 kHz; (□) 1 MHz.

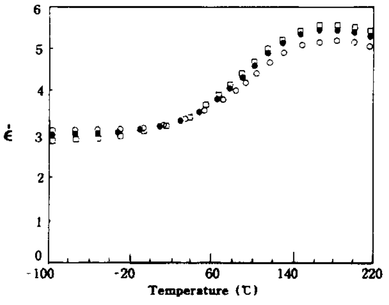

Figure 18. Dielectric constant (ε') behavior of film B showing the effect of annealing at a heating rate of 10 °C/min: (○) as received; (●) annealed at 330 °C for 10 h; (□) annealed at 320 °C for 40 h.

Figures 16 and 18 indicates little change in the measured dielectric constants of the as-received film and annealed film at −100 to +220 °C. Hence the changes in the interchain packing order with annealing that are indicated by the DSC thermograms and X-ray diffraction patterns have little influence on the dielectric constant behavior. This may be due to the fact that rotational segmental mobilities of the as-received films are as active as those of annealed films. For a polymer comprising HBA/HQ/CB/BP/TA, similar results were reported by Bechtoldt et al.[52]

Conclusions

(i) Attempts to increase the high-temperature dimensional stability of the LCP films through annealing near the crystal−nematic transitions were successfully demonstrated, resulting in films with highly ordered crystallites and a much higher melting point. These results confirm that these aromatic copolyesters can be melt processed at lower temperatures into films and then annealed to achieve dimensional stabilities at higher temperatures.

(ii) In the thermal mechanical analysis, as-received film showed irreversible and positive thermal expansion behaviors, but annealed film displayed reversible thermal contractions due to the thermal vibrational motion perpendicular to the chain direction.

(iii) The WAXD pattern of the as-received Xydar 900 powder exhibits three-dimensional order, while the as-received films showed pseudohexagonal interchain packing order. The annealed films showed two-dimensional order, as would be expected for biaxially oriented films.

(iv) In the dielectric relaxation measurements long-range, long-axis orientational order is retained in the glassy state. The increase in dielectric constant at 50−100 °C is highly related to the onset of rotational motions of benzene rings about the chain axis. Microstructural changes in the interchain packing order with annealing has little influence on the dielectric constant and presumably the rotational motions of the rings in the main chain of the oriented film. The increase in dielectric constant from room temperature values of 3.0 to as high as 4.5 at 100 °C suggests limitations in the operating temperatures of microelectronic devices.

In summary, annealing strongly influences the thermal behavior and thermomechanical properties as well as inducing increased order in the microstructure. On the other hand, little change is observed in the dielectric properties with annealing. The overall conclusions from the evaluation of the two films, A and B, where film A had a higher degree of orientation in MD and film B in TD, showed practically little difference in the properties examined in this study.

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