Macromolecules **1999,** *32,* 7555−7561 **7555**

Comparison of Crystalline Phase Transitions in Fluorniated vs Nonfluorinated Parylene Thin Films

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Received June 29, 1999; Revised Manuscript Received September 10, 1999

ABSTRACT: Thermally induced morphological changes in thin (1−5 μm) films of poly(α,α,α′,α′-tetrafluoro-*p*-xylylene, $(C_6H_4CF_2)_n$) (Parylene-F or PPX-F) are characterized using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and thermal stress measurements. A reversible crystalline phase transition is observed between 360 and 400 °C, which to our knowledge has not been reported previously. The transition is accompanied by an increase of the in-plane tensile stress of the film, which is attributed to contraction of the in-plane polymer structure during the transition to the high-temperature crystalline form. The stress and thermal behavior are qualitatively similar to those occurring in the more extensively studied nonfluorinated material, poly(*p*-xylylene, $(C_6H_4CH_2)_n$) (Parylene-N or PPX-N), which undergoes a shift in stress during the $\beta_1-\beta_2$ transition (270−300 °C).

Introduction

The parylenes are semicrystalline organic polymers formed by chemical vapor deposition (CVD) techniques. Because of their low dielectric constant ($\kappa = 2.2-2.6$), these materials have been considered candidates for use as intra- or interlevel dielectrics (ILD) in microelectronic devices. Since signal propagation speeds in these devices are limited by RC delay, in recent years much effort has gone into the design and synthesis of such low dielectric constant ILDs. The advantage of CVD materials, in particular, is that they can be deposited using equipment and techniques similar to those currently used in the semiconductor industry. Additionally, CVD film deposition is generally conformal, exhibits good gap-fill properties, and minimizes precursor usage. The deposition process is also solventless, which minimizes chemical disposal costs.

For successful integration into devices, dielectric materials must satisfy a number of thermal, mechanical, chemical, and electrical performance requirements. Since changes in the crystallinity of the dielectric film can affect many of its important material properties, the reliability of semicrystalline polymers such as the parylenes needs to be assessed by carefully characterizing the structural transitions in thin films of these materials.

A number of studies concerning the crystallinity of PPX-N have been reported in the literature.[5,7−12] The material is known to undergo two crystalline phase transitions:[10]

$$\alpha \xrightarrow{231\ °\mathrm{C}} \beta_1 \xleftrightarrow{287\ °\mathrm{C}} \beta_2 \xrightarrow{427\ °\mathrm{C}} \text{melt}$$

The as-deposited films are normally composed of the monoclinic α crystalline phase. A β phase has been identified consisting of hexagonal unit cells, with $a = 20.52$ Å and $c = 6.58$ Å.[5,11,12] The difference between β_1 and β_2 phases is not well understood, although Miller et al. suggest a shortening of the *c* axis associated with the $\beta_1-\beta_2$ transition.[10] The $\alpha-\beta_1$ phase transition was reported to be irreversible by Niegish and co-workers,[11] but more recent work indicates that reversibility can be achieved by annealing for an extended period of time at sufficiently high temperature.[8,9] The $\beta_1-\beta_2$ transition is considered to be reversible. PPX-N has been reported to melt at approximately 427 °C.[10]

There are few reports in the literature addressing the crystalline phases or transformations in PPX-F. Recently, Blackwell et al. used three-dimensional WAXD to determine a crystal structure for 10−12 μm thick uniaxially drawn and undrawn PPX-F films that had been annealed at 450 °C.[1] Specifically, they proposed a triclinic structure with a unit cell having dimensions $a = 5.36$ Å, $b = 5.92$ Å, $c = 6.57$ Å, $\alpha = 97.0°$, $\beta = 63.1°$, and $\gamma = 73.1°$. WAXD data collected at room temperature by You[16] indicated an increase in crystallinity as the annealing temperature of the films was raised but gave no information about crystalline phase changes. A melting/decomposition temperature of 510 °C has been determined from DSC studies.[4]

Experimental Section

The PPX-F films used in the present study were deposited using the Gorham method.[3] In this process, the dimer is vaporized (∼100 °C) and then subjected to pyrolysis (∼650 °C) to give reactive monomers. The monomers enter a vacuum chamber where they polymerize on a substrate, which is held below room temperature. The PPX-F samples were supplied by Novellus Systems.

DSC data were collected using a Perkin-Elmer Pyris-1 DSC instrument. Measurements were performed on film samples of approximately 5−10 mg, which were prepared by scraping 1−5 μm thick films from Si wafers. The samples were taken through three cycles of heating and cooling. The heating rate in all experiments was 3 °C/min.

Stress−temperature profiles were obtained for on-wafer films using a custom-built bending beam apparatus detailed

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10.1021/ma991049w CCC: $18.00

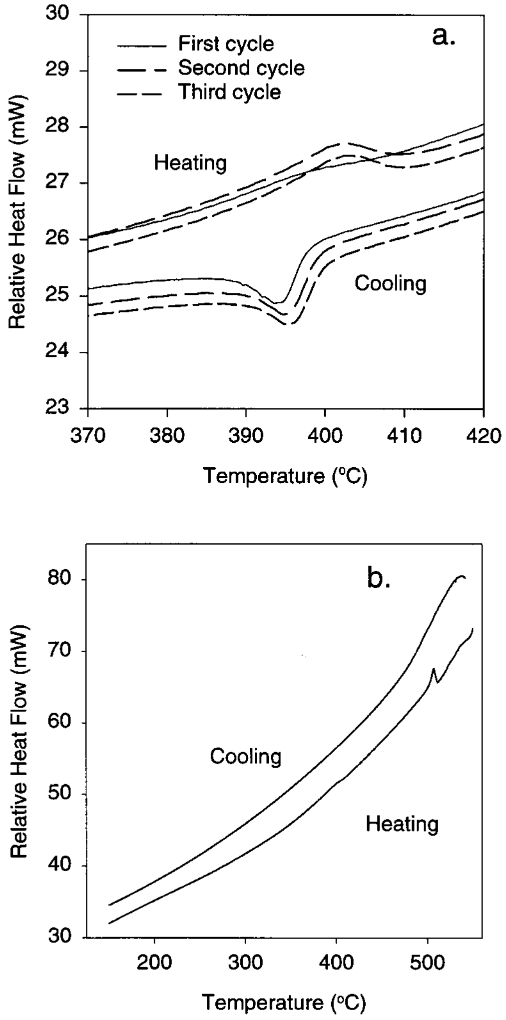

Figure 1. (a) Displayed is PPX-F DSC data for three temperature cycles in the region 375−425 °C. No thermal events were observed at lower temperatures. The peak is attributed to a reversible crystalline phase transition and occurs at slightly higher temperature in the heating curves (402−403 °C) than in the cooling curves (395 °C). (b) The peak at 507 °C, attributed to a melting, is followed by dissociation. The thermal event near 400 °C is not observed upon cooling from 550 °C.

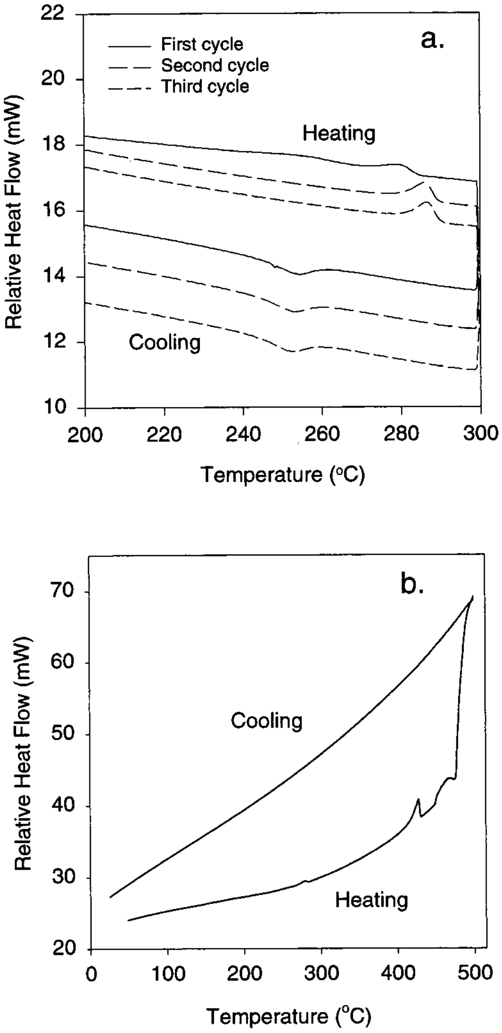

Figure 2. (a) Displayed is PPX-N DSC data for three temperature cycles in the region 200−300 °C. The peak is attributed to a reversible β_1−β_2 crystalline phase transition and occurs at significantly higher temperature in the heating curves (287 °C) than in the cooling curves (253−254 °C). No thermal events were observed under 200 °C. (b) The melting peak at 427 °C is followed by a sharp endotherm likely due to dissociation. The crystalline phase transition is not observed upon cooling from 500 °C.

elsewhere.[14,15] Beam samples consisted of 0.5−1 μm thick films of the polymer deposited on 125 μm thick Si substrates. Beam dimensions were 3 × 45 mm. The temperature ramp rate was 5 °C/min.

A Rigaku Rotaflex with high-intensity rotating anode Cu target ($\lambda = 1.542$ Å, weight-average of Kα_1 and Kα_2) was used for the X-ray source in the WAXD experiments. The Kβ radiation ($\lambda \cong 1.39$ Å) was not eliminated from the source, but peaks due to Kβ diffraction were well separated from, and were of much lower intensity than, those due to Kα radiation. The measurements were performed using a Huber goniometer equipped with a custom-built heating stage. Each axis was controlled by a motor unit having a precision of ±0.0025 deg. The source has high intensity (up to 18 kW), which was required due to the small diffraction volume and limited crystallinity of the thin-film samples. A heating and cooling rate of 2 °C/min was used for all samples. Multiple scans were performed for each temperature and summed in order to improve the signal-to-noise ratio.

Results and Discussion

Differential Scanning Calorimetry. The DSC data for as-deposited PPX-F (Figure 1a) show a reversible thermal event near 400 °C that is attributed to a crystalline phase transition. The heating curves show an endothermic peak just above 400 °C, the transition being less distinct and at slightly lower temperature in the first heating cycle than in later cycles. The peak is almost identical in the second and third heating cycles, occurring at 402−403 °C. The corresponding exothermic transition in the cooling cycles occurs at slightly lower temperature (~395 °C). The peak at 507 °C (Figure 1b), due to melting/decomposition of the material, is consistent with a previous report.[4] The reversible transition near 400 °C is not observed in the cooling cycle after heating above the melting temperature.

The thermal behavior is qualitatively similar to that accompanying the reversible β_1−β_2 phase transition in PPX-N (Figure 2). The temperature of this transition increases monotonically from the first (279 °C) through the third heating cycles (287 °C) and occurs at significantly lower temperature (253−254 °C) in the cooling cycles. The differing positions in the heating and cooling cycles suggest a kinetically slow transition. The small irreversible feature near 250 °C in the first heating cycle could be due to annealing of imperfect crystals[8] or could

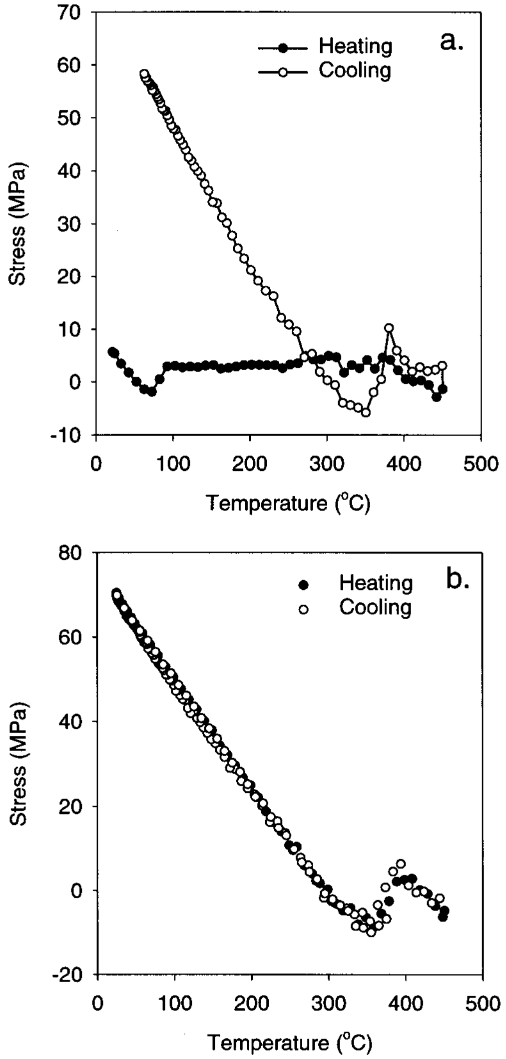

Figure 3. Shown is the first (a) and fifth (b) cycle bending beam stress measurement of a 1 μm thick film of PPX-F. The first cycle is similar to that for PPX-N, in that the stress shows a large hysteresis between the first heating and cooling cycles. In subsequent cycles the shift in the stress curve appears at nearly the same temperature in the heating (408 °C) and cooling (394 °C) cycles, in contrast to PPX-N. All temperature cycles after the first are similar.

indicate an α–β_1 phase transition. As in PPX-F, higher temperature data (Figure 1b) show an endothermic peak (428 °C) attributed to melting,[10] followed by dissociation of the material. The β_2–β_1 phase transition is not observed in the cooling cycle from 500 °C.

Stress Measurement by Bending Beam. The stress of PPX-F was measured through three temperature cycles from room temperature to 450 °C (Figure 3). The as-deposited film is shown to have very low stress, which increases upon thermal cycling. The large hysteresis between the first heating and later temperature cycles indicates an irreversible structural change, which could be due to a phase transition or to an annealing of the amorphous regions of the polymer. All thermal cycles after the first are similar and show a local maximum resulting from a shift in the stress curve between 360 and 400 °C. The shift in stress apparently is due to the crystalline phase transition observed in the DSC data.

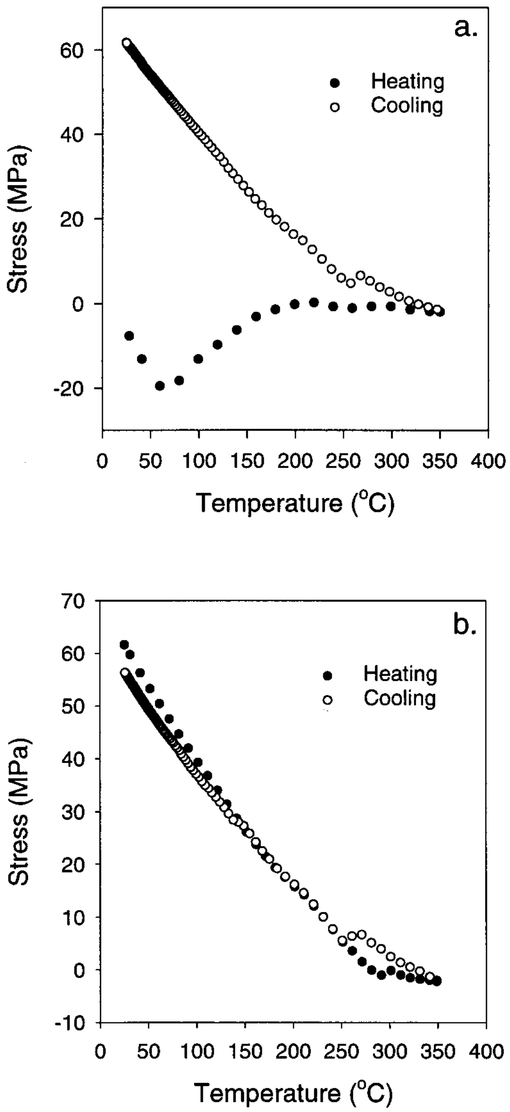

Figure 4. Shown is the first (a) and second (b) temperature cycles of the bending beam stress measurement for a 0.5 μm thick PPX-N film. The first cycle shows a change from compressive to tensile stress upon heating of the as-deposited material. The second cycle shows a shift in the stress at higher temperatures due to the β_1–β_2 phase transition. The transition occurs at higher temperature in the heating part of the cycle (300 °C) than in cooling (270 °C). Third and later cycles appear similar to the second cycle.

The stress data for PPX-N (Figure 4) is qualitatively similar to that for PPX-F and is consistent with previous measurements.[2] Specifically, there is hysteresis between the first and later cycles, and a shift in stress accompanying the reversible (β_1–β_2) phase transition, which was reported previously by Ryan and co-workers.[13] For PPX-N there is a small inflection in the slope of the stress curve at 215–220 °C in all cycles after the first heating cycle, possibly due to partial reversibility of the α–β_1 crystalline phase transition.

The upward shift in stress in the heating curve for PPX-N at the phase transition is likely caused by contraction of the crystal structure along the polymer chain (*c*-axis) that occurs upon passing from the β_1 to β_2 crystalline form.[5,10] It has been speculated that this contraction is due to a kinked or helical chain conformation in the higher temperature crystalline form.[10] Since the polymer chains in PPX-N thin films align preferentially parallel to the substrate,[6,12,17] such a chain contraction should result in an increase in the in-plane tensile stress. If this is the case, then the similar shift in PPX-F, which is more pronounced than that in PPX-

N, may also be due to chain contraction accompanying a phase transition. Note that the size and location of the stress shift in PPX-F are about the same in the heating and cooling cycles, whereas in PPX-N the peak in the cooling cycles occurs ~30 °C lower in temperature and is significantly larger than in the heating cycles. The larger separation of the heating and cooling stress shift in PPX-N compared to that inPPX-F is in agreement with the transitions observed in the DSC results.

It is interesting that the stress shift in the bending beam heating curve for PPX-F begins around 350 °C, which is much lower than the temperature at which the transition is seen in the DSC (~400 °C). Additionally, the shift in the stress occurs over a much broader temperature range than does the thermal event in the DSC. It is possible that confinement of the film by the substrate in the bending beam experiment is responsible for these differences from the DSC result. If a high-temperature structure of PPX-F has a more compact chain axis than the low-temperature form (as has been reported for PPX-N), then the compressive thermal stress in the plane of the substrate-confined film would increase the stability of the high-temperature relative to the low-temperature phase. This driving force of the thermal stress in the confined film could cause conversion to the higher temperature phase at a lower transition temperature than observed for the free-standing film studied by DSC. Likewise, confinement of the film by the substrate would be expected to hinder molecular motions accompanying the phase transition, thereby slowing the transition in the bending beam study, so that the transition appears over a broader temperature range than in the DSC experiment. The bending beam results are consistent with X-ray measurements of substrate-confined PPX-F films (vide infra).

In contrast to PPX-F, PPX-N does not transform from the low- to high-temperature phase much earlier in the bending beam experiment than in the DSC. This could be because the molecular chains of PPX-N do not contract as much during the phase transition, and therefore the substrate does not provide as much of a driving force to lower the temperature of the transition in confined films. This argument is supported by the smaller size of the vertical shift for PPX-N compared to that for PPX-F, which suggests there is a less drastic change in the size of the crystal structure in the in-plane direction for PPX-N.

According to the work of Miller et al.,[10] the *c*-axis contraction accompanying the $\beta_1-\beta_2$ transition may be as high as 1−2% for PPX-N. An estimate of the contraction can be calculated from the shift in the stress data:

$$\Delta\sigma = \frac{E}{1-\nu}\Delta\epsilon \tag{1}$$

where $\Delta\sigma$ is the shift in stress, E is the Young's modulus, ν is the Poisson ratio, and $\Delta\epsilon$ is the change in strain (i.e., contraction) of the film. Using the room-temperature value of $E = 2$ GPa[13] and assuming a Poisson ratio of 0.33, the ~5 MPa shift in stress suggests a contraction of only 0.1−0.2%. A similar calculation for PPX-F ($E = 4.9$ GPa) for the ~20 MPa stress shift gives a 0.3% contraction. Since the modulus typically decreases substantially with temperature, using the room-temperature modulus gives a lower limit to the contraction observed at high temperature.

Note that the slope of the stress vs temperature curves is larger before the stress shift than after. This change in slope indicates that the material has different thermomechanical properties above the transition than below. The nonzero slope at temperatures above the transition indicates that the material retains some mechanical strength at these higher temperatures and precludes assignment of the discontinuity in the stress to a melting or T_g event. The T_g of PPX-N and PPX-F is reported to be 13[10] and 16 °C,[4] respectively.

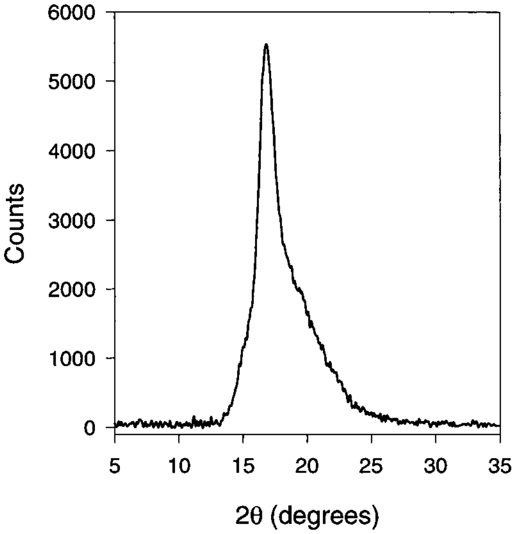

Figure 5. Displayed is the WAXD data for a 1 μm thick film of as-deposited PPX-N taken at 40 °C. The peak at 16.8° is assigned to the (020) plane of the α phase.

Wide-Angle X-ray Diffraction. **(a) PPX-N**. The WAXD results for PPX-N at 40 °C (Figure 5) show a peak at $2\theta = 16.8°$, corresponding to planes having a $d = 5.28$ Å. The peak is assigned to the (020) plane of the α phase.[7,9] The WAXD results taken at 200 °C show some interesting dynamics. As shown in Figure 6a, there is a strong time-dependent behavior in the diffraction pattern at 200 °C, and the film morphology does not stabilize with annealing times of up to 13 h. The data taken immediately upon reaching 200 °C show a second peak growing in at $2\theta = 19.35°$. As the annealing time increases, this peak becomes more intense, while the peak at 16.8° decreases in intensity. The two smaller peaks in the 200 °C spectra are due to diffraction of the Kβ radiation.

The peak at $2\theta = 19.35°$ corresponds to $d = 4.59$ Å, which can be extrapolated back to a room-temperature value of 4.43 Å, assuming expansion of the β_1 phase similar to that observed for the α phase. This spacing suggests assignment of the peak to the (400) plane of the β_1 phase[5,11,12] of PPX-N. For example, Niegisch[11] determined $d = 4.443$ Å for this plane at room temperature. Thus, we have evidence of the α−β_1 crystalline phase transition occurring at temperatures significantly *below* the reported transition temperature of 220−240 °C.[8,10]

There has been some discrepancy in the literature as to the reversibility of the α−β_1 phase transition in PPX-N. Niegisch's original observations suggested that it was irreversible,[11] while more recently reversible behavior has been seen under certain circumstances.[8,9] As mentioned above, the bending beam and DSC experiments showed little evidence of reversibility in this transition. However, the X-ray data in Figure 6b show that when the sample is cooled to 40 °C after the 200 °C thermal cycle, the β phase peak decreases, while the intensity

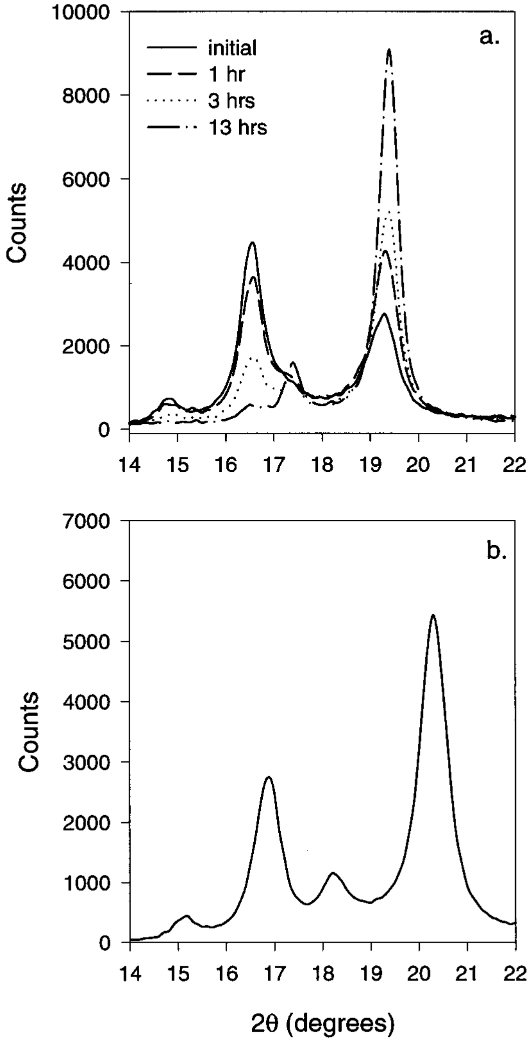

Figure 6. (a) Displayed is the time dependence of the WAXD data for a 1 μm thick film of PPX-N at 200 °C, showing the dynamics of the α to β_1 phase transition. The peak near 16.8° from the α phase (020) plane decreases in intensity, as the peak from the β_1 phase (400) plane at 19.35° increases in intensity as a function of time. (b) Upon cooling to 40 °C after the anneal at 200 °C, the size of the α peak increases relative to the β_1 peak, indicating significant reversibility of the transition.

of the α phase peak increases. Thus, the WAXD results clearly indicate some degree of reversibility.

The reversibility noted in the WAXD could have resulted from the fact that the α$-\beta_1$ phase transition was not completed in our study, since we were limited to a maximum temperature of ~200 °C due to rapid oxidation of the film at temperatures as low as 230 °C. Since the reversibility is known to be affected by the sample's thermal history,[8,9] different behavior might have been observed had it been possible to study the film above the transition temperature. Because of film decomposition at elevated temperatures, we were not able to investigate the higher temperature $\beta_1-\beta_2$ phase transition. To do so would require performing the experiment in an inert atmospheric environment.

(b) PPX-F. Figure 7 shows on-wafer WAXD measurements of an as-deposited PPX-F (5 μm thick) film at 40 °C and the same sample after heating to 200 °C. Both data sets were fitted and deconvoluted into Kα and Kβ peaks in order to calculate the peak locations. At 40 °C, the Kα radiation results in a peak at $2\theta = 18.35°$ (4.84 Å), which shifts to $2\theta = 18.9°$ (4.70 Å) at 200 °C. These results are qualitatively consistent with those of You,[16] whose room-temperature measurements showed a shifting of the peak to higher angle as the annealing temperature was increased. Our experiments do not indicate any shifting of the peak back to lower angle upon cooling.

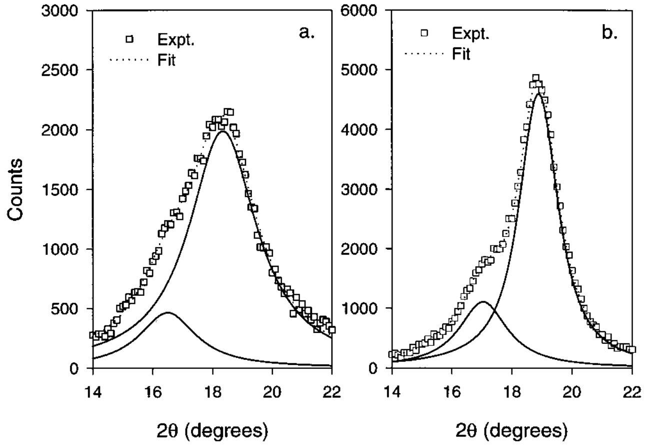

Figure 7. Shown is WAXD data for PPX-F taken at (a) 40 and (b) 200 °C. Measured data were fitted using a Voigt profile, for Kα and Kβ radiation. The Kβ radiation leads to the smaller peaks. The data indicate both an increase in crystallinity and a shift in peak position accompanying the change in temperature.

The present measurements show an increase in crystallinity with annealing temperature that is in agreement with You's results. In addition to becoming sharper and more intense, the diffraction peak observed at 40 °C after a 400 °C anneal shifts to $2\theta = 20.5°$. The corresponding d spacing (4.33 Å) is in good agreement with the value of 4.4 Å obtained by Blackwell et al. on thicker films annealed at 450 °C.[1] Those workers assigned this peak to (100) planes lying parallel to the film surface. This interpretation is consistent with our measurement, which is most sensitive to reflections from planes that are parallel to the surface of the film.

WAXD data were taken at a series of temperatures between 300 and 450 °C in order to directly observe the morphological changes observed in the DSC and stress measurements. Figure 8a shows that starting around 360 °C there is a dramatic increase in the intensity of the diffraction peak, accompanied by a substantial shift in peak position to lower angle, which is believed to be due to a crystalline phase transition. By 380 °C the transition is largely complete, as there is relatively little change in the peak position as the temperature is increased above 380 °C. The size of the peak, and therefore the degree of crystallinity, continues to increase with temperature to 450 °C.

The temperature of the phase transition in the WAXD experiment is similar to that observed in the stress measurement but lower than that seen in DSC. This is consistent with the argument given above concerning confined vs unconfined films. Specifically, the transition is observed at ~360 °C for confined films and at ~400 °C for unconfined films.

Upon cooling from 450 °C (Figure 8b) two different peaks can clearly be distinguished, with the high-temperature peak near $2\theta = 17.3°$ decreasing as the low-temperature peak near $2\theta = 18.7°$ increases. The two peaks are apparently due to two different crystalline phases. At 360 °C in the cooling cycle the d spacings

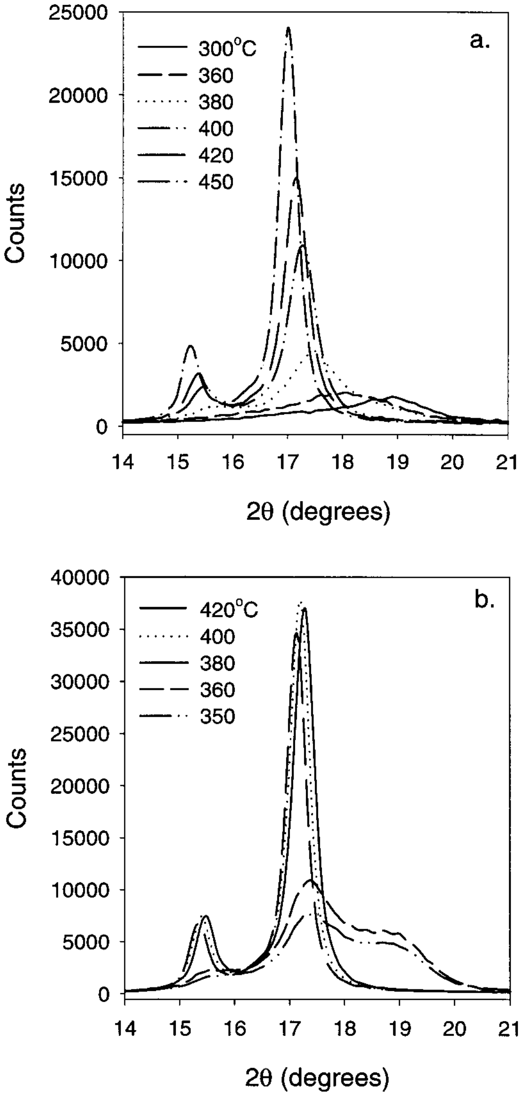

Figure 8. (a) Shown is WAXD data for PPX-F from 300 to 450 °C for the initial heating of the as-deposited film, indicating a change in crystalline structure. (b) The cooling cycle shows the crystalline phase transition more clearly, as the peak from the low-temperature phase near 18.7° grows at the expense of the peak from the high-temperature phase (near 17.3°). The third peak at lowest angle is due to diffraction of Kβ radiation.

are 4.74 and 5.10 Å for the peaks at 18.7° and 17.4°, respectively. Detailed peak profiles at 360 °C in the cooling cycle are presented in Figure 9 with deconvoluted peak locations. Although the identity of the two crystal structures cannot be determined from the present work, the d spacing associated with the one diffraction peak observed for the low-temperature phase is similar to one that has been assigned to a triclinic structure by Blackwell et al.[1] The qualitative similarity in stress behavior between PPX-N and PPX-F at the phase transition, however, seems to suggest a correspondence in the crystal structures of the fluorinated vs unfluorinated polymers. The phase transition was not seen in the WAXD work of You[16] because the transition is reversible, and those experiments were only done at room temperature after annealing, rather than in situ as a function of temperature.

Note that the peak at low angle near $2\theta = 15.4°$ is due to diffraction of Kβ radiation from the same high-temperature crystalline plane that gives rise to the main Kα peak. Likewise, there should be a small peak due to Kβ diffraction from the low-temperature phase buried under the other features in the spectrum. Deconvolution of the data at 360 °C into these four peaks is shown in Figure 9.

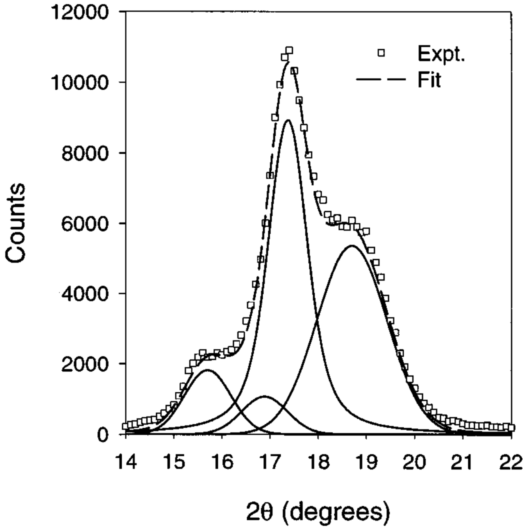

Figure 9. WAXD data for PPX-F at 360 °C during the first cooling cycle of Figure 8 are fit using four peaks having a Voigt profile, one peak from each crystalline phase for Kα and Kβ radiation. The Kβ radiation leads to the smaller peaks.

Conclusion

The crystallinity of PPX-F and PPX-N was studied using a variety of techniques. The α–β_1 phase transition in PPX-N was kinetically slow, which results in an observed transition temperature that is technique-dependent, occurring anywhere between 200 and 250 °C. This transition is partially reversible; the degree of reversibility may depend on such variables as ramp rate, annealing time, and maximum temperature achieved.[8,9]

The reversible β_1–β_2 phase transition also occurred over a broad temperature range between 270 and 300 °C.

The as-deposited PPX-F films were observed to undergo a reversible transition, which occurs at 360 °C in the thermal stress and WAXD measurements, and at a higher temperature of 400 °C in the DSC experiment. The lower transition temperature using the first two techniques may be related to the fact that the film is confined in those experiments, whereas it is free-standing in the DSC experiment.

In both materials the reversible transition is accompanied by a sudden shift in stress, which is attributed to contraction of the molecular chains. The much larger size of the shift in PPX-F compared to PPX-N is partly due to a higher elastic modulus for PPX-F and partly to a more significant in-plane morphological change for PPX-F during the transition. This result may have important implications for integration of these materials as ILDs, as crystalline transitions during thermal processing could affect structural reliability.

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