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Reversible Crystal Deformation Observed in the Main-Chain Type of Liquid Crystalline Polyimide

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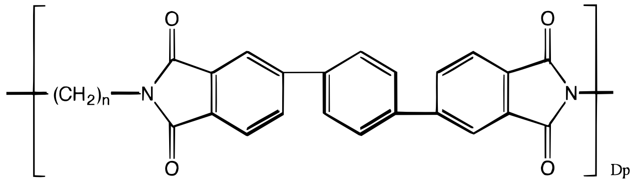
During a course of the studies to exploit the liquid crystalline polyimides, we have synthesized the simple main-chain type of polyimides in which the aromatic mesogen and alkylene spacer are linked in an alternate fashion through the imide linkage.[1,2] These polyimides were found to be prepared with high molecular weights by a high-pressure polycondensation of the nylon-salt-type monomers[2,3] derived from aliphatic diamines and aromatic tetracarboxylic acids. The polyimides having the terphenyltetracarboxdiimide groups, P-*n*TPE



(n= 8-12: the carbon number of spacer)

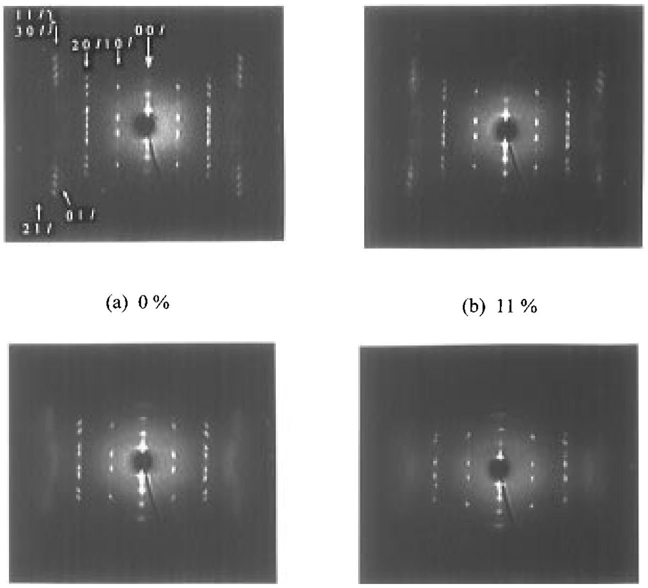
were found to show a thermotropic liquid crystalline phase.[2] As far as we know, this is the first example of a thermotropic liquid crystal which is formed from the simple polyimides.

One of most fantastic properties in the liquid crystalline polymers is easy processing. By drawing of a liquid crystal and annealing of the resulting fiber at an appropriate temperature, a highly oriented and crystalline fiber can be attained. This is also the case in the liquid crystalline P-*n*TPE polyimides, and its representative fiber has been prepared from P-11TPE as shown later.

More recently, we have found that such a crystalline fiber of P-11TPE shows successive extension and relaxation when it is subjected to mechanical tensile stress. The macroscopic mechanical deformation of the fiber is fairly large (22−25% of the unstretched length) and is connected directly to the microscopic molecular (or unit cell) deformation in the crystal. The aim in this study is to establish relationships between mechanical properties and X-ray crystallographic changes.

The P-11TPE polyimide used here was synthesized as described in detail in a previous paper.[2] The estimated inherent viscosity was 0.66 dL/g, this being determined by using a 0.5 g/dL solution in concentrated sulfuric acid. The P-11TPE polymer shows three mesomorphic transitions on cooling from isotropic melt: isotropic−nematic, nematic−smectic, and smectic−crystal at 210, 169 and 144 °C, respectively.[2]

The fiber which was spun from the nematic phase shows a high orientation, but its X-ray pattern is just similar to that of the smectic phase. This means that the nematic to smectic transition takes place immediately on cooling and the resulting smectic phase is glassified. The glass transition appears at around 90 °C on DSC thermogram. By annealing of the fiber at 125 °C for 10 min, a well-defined crystallization takes place and the glass transition disappears. These temperatures and times were enough to obtain the high crystallization. During this annealing process, the orientation is maintained, and so no additional drawing treatment is necessary. The X-ray pattern of the crystalline fiber is shown in Figure 1a. One can see the good orientation and crystallinity; the amorphous halo is nearly absent, and significant peaks with a narrow distribution are measurable up to $2\theta = 30°$ with about 50 peaks clearly detected. The crystal lattice is orthorhombic with a unit cell of $a = 12.5$ Å, $b = 4.56$ Å, and $c = 47.4$ Å.[4] The *c*-repeat distance is consistent with twice the repeat length of polymer, and the unit cell includes four repeat units.



(a) 0 %

(b) 11 %

(c) 17 %

(d) 22 %

Figure 1. Wide-angle X-ray diffraction patterns of P-11TPE crystal fiber taken under various strains of (a) 0%, (b) 11%, (c) 17%, and (d) 22%. The fiber axis (i.e., chain axis) is in the vertical direction.

Figure 2a shows the stress−strain curve which was measured at room temperature for the crystalline fiber with a diameter of 30 μm by using an Instron TTDM-type tensile testor and tension Model UTM-4L with a strain rate of 5%/min. The stress was evaluated here by using the initial sectional area of a fiber. The apparent modulus (i.e., slope) determined at the initial stage of strain until 5% is around 2 GPa. The slope starts decreasing at above $\epsilon = 6-15\%$, followed by the second increase beyond $\epsilon = 15\%$. Finally, the fiber breaks down at around $\epsilon = 23\%$. Unloading at $\epsilon = 20\%$ before the fiber breaks recovers the fiber from the considerable strain (see Figure 2b), although some permanent strain around 6% remains. On successive loading and unloading cycles, the reversibility of the strain can be seen in the range 6−20%.

P-11TPE shows clear meridional reflections with indices of (00*l*). The appearance of the meridional reflections only with l = even is characteristic, and the detailed analysis of their intensities indicates that the molecule assumes a 2_1 helix and that the Bragg spacing of the first meridional reflection, d_{002}, corresponds to the monomer unit height measured along the chain axis.[4] The changes in the diffraction from these meridional reflections were determined at various strains; photographs taken at strains up to 22% are shown in

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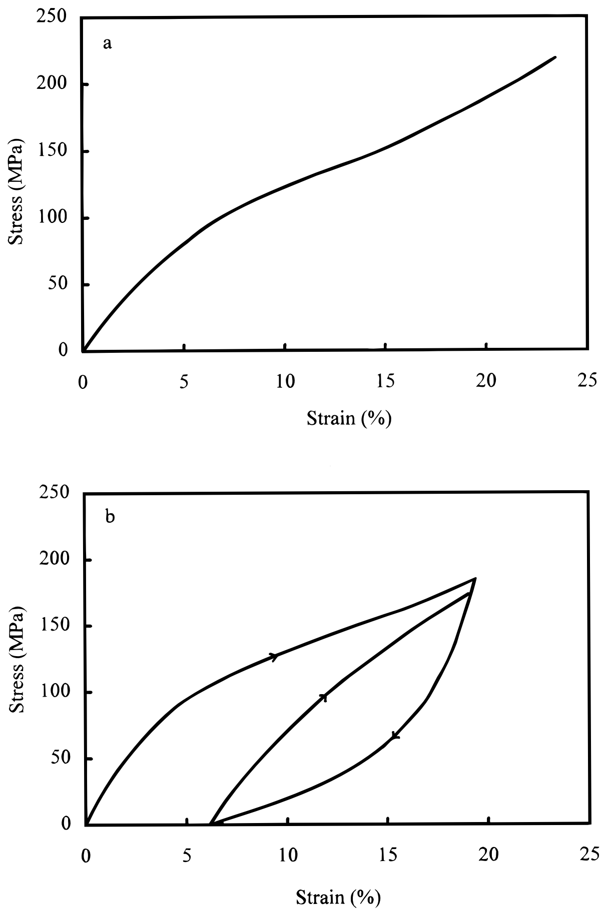

Figure 2. Stress−strain curves of P-11TPE crystal fibers: (a) the stress−strain curve observed up to the breaking point around 23%; (b) the extension and relaxation curves measured in a strain range of 0% to 20%. In part b, the arrows indicate whether the stress is increasing or decreasing.

Figure 1b−d where the stepwise strains were applied. Figure 3a shows the Bragg spacing (d_{002}) plotted against overall applied macroscopic strain. In Figure 3b, these results are plotted in terms of the lattice strain. It can be seen that there is a change in the Bragg spacing as soon as the fibers are strained, and moreover that the actual lattice strain is very close to the overall strain. The dashed line in Figure 3b represents the situation where the lattice strain is identical to the overall strain. It appears that a good approximation holds for the overall strains; for the overall strains as high as 20%, the lattice strains are at least 15%. The spacings of meridional reflections were also measured after unloading the fiber and given by the open marks in Figure 3a,b. The elongation is substantially reversible, although some lattice strain of 3% is retained as observed in the macroscopic strain.

The orthogonal nature of crystal lattice is invariably observed by applying the strain. This can be found in Figure 1b−d. From the average separation of $(h0l)$ and $(0kl)$ lines, respectively, the changes in *a* and *b* axes were determined in Figure 3b. As can be expected, the *a* and *b* axes gradually decrease with the increase of strain. This decrease of *a* and *b* axes can compensate the increase of *c* axis so that the density of crystal is remained constant.

The overall results thus show that the strains in the crystal are very similar if not identical to the overall strain. Taking into account the comparatively high crystallinity of the fiber, the most straightforward explanation of our results is that the deformation of the fiber is caused by the deformation of crystal.

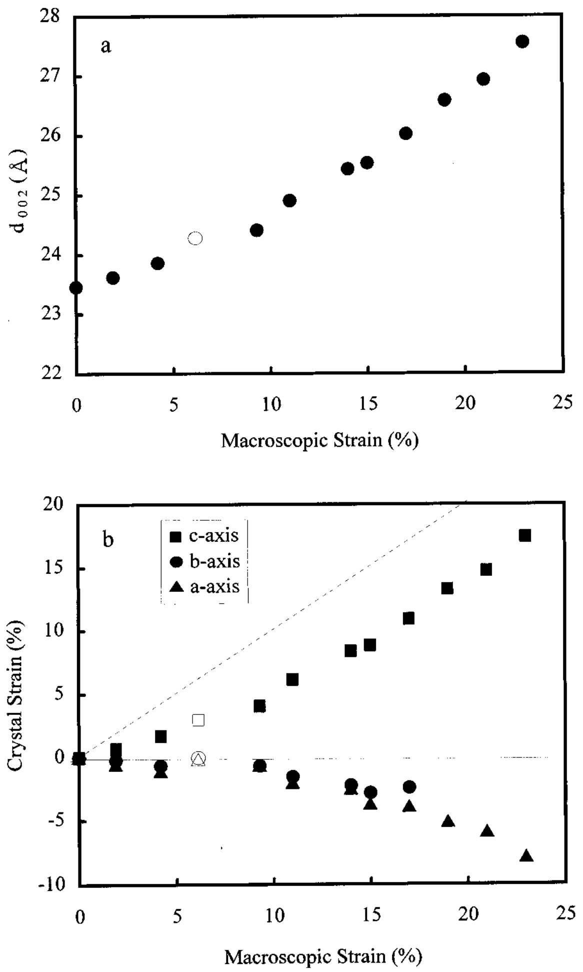

Figure 3. Plots of (a) the value of d_{002} and (b) the crystal strain against the applied macroscopic strain. In part b, the triangles, circles, and squares represent the crystal strain along *a*-, *b*-, and *c* axes, respectively. The open marks show the values measured after unloading the fibers.

A very large deformation of crystal lattice and a reversibility of lattice strain can be understood from our knowledge for the chain conformation characteristic to the main-chain type of liquid crystalline polymers.[5−9] It is well-known that in the main-chain polymers the chain conformation appears different depending on the odd−even parity of the carbon number of the flexible spacer. The chain in the odd-membered polymers takes up a zigzag form with the mesogenic groups tilted alternately, whereas the chain in the even-membered ones assumes an extended form with the mesogenic groups parallel to each other.[7] This difference in chain conformation reflects in the chain length; the chain length oscillates depending on the odd−even character of the flexible spacer since the chain length in the zigzag form should be fairly smaller than that of the extended one.[9] The present P-11TPE belongs to the odd-membered homologue. In fact, the observed chain length of 23.4 Å as well as the 2_1 helical conformation is explained only by a zigzag arrangement of mesogenic groups as illustrated in Figure 4a. The characteristic X-ray pattern including the intense layer reflections along the direction tilted by 30° from the equatorial line (see Figure 1a) also suggests the tilted association of the mesogenic groups which have the relatively high electron density. The longitudinal extension and relaxation,

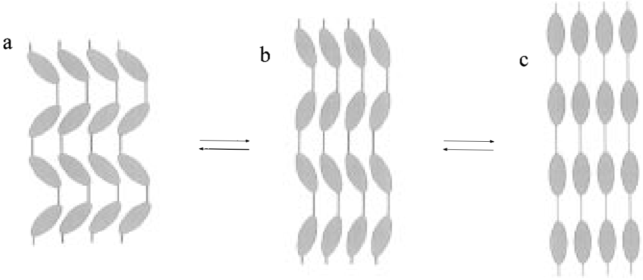

Figure 4. Tentative illustration of molecular conformation of P-11TPE. In relaxed state the mesogenic groups are tilted in an alternate fashion to the fiber axis as shown in part a, their tilt angle gets small under some stress as in part b, and finally in the most stretched state they tend to lie parallel to each other as in part c.

thus, can be attributed to the conformation change from the zigzag form to the extended form (compare Figure 4c with Figures 4a,b). This speculation can be supported by the fact that the repeat length in the highest extension, 27.5 Å, is approximate to the value (29 Å) of the most extended form. It is further justified from the observation that the P-9TPE in the odd-membered homologue shows a similar crystal deformation while the even-membered polyimides such as P-8TPE and P-10TPE show only a small elongation up to 6−8%.

The reversible extension and relaxation have been reported in the crystals of polyesters and polyethers such as PBT and PEO.[10−15] In these polymeric systems, the reversible solid state transition between the two crystal forms has been attributed to the reversible deformation.[12−16] In this system, however, such a solid state transition may be ruled out since we have no evidence for the coexistence of the two crystal forms. The meridional reflection was remained sharp and its spacing gradually changed over the whole strain range, showing the gradual change in the conformation. The study is proceeding to clarify the mechanism for the reversible lattice deformation.

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