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Liquid Crystal H-Bonded Polymer Networks under Mechanical Stress

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ABSTRACT: The orientation behavior of liquid crystal networks having the Sm C_A structure stabilized by H-bonds has been studied. The mesogenic groups formed by hydrogen bonds generate a layered structure of the polymer. The hydrogen bonds are responsible for the elastic properties of the liquid crystal polymer network and the mechanism of its plastic flow above the threshold strain. The mechanical response is interpreted in terms of the mechanism of breaking and reconnecting H-bonds under stress. The local sliding of layers is possible if H-bonds are temporarily disconnected and then reconnected again to restore the LC structure. The anisotropy of the mechanical properties of the H-bonded polymer materials is observed in the monodomain LC networks.

Introduction

The principle of molecular recognition, based on noncovalent interactions, such as electrostatic, van der Waals, and hydrogen bonding, became a very powerful tool in organic and polymer chemistry for designing new supramolecular materials. It is also useful for creating new liquid crystal (LC) systems in which H-bonding of various molecular moieties could generate mesogenic fragments.[1−4] These materials provide an easy way to control and manipulate their properties by simply adding different low molar mass agents, which can form stable rodlike mesogenic groups via H-bonding with monomeric units of the polymer backbone. Hydrogen bonds which generate a LC mesophase in side chain polymers also contribute to thermal and mechanical stabilization of a dense polymer network. The structure of the network and directionality of H-bonds should significantly affect the formation of monodomain LC structure under external forces, i.e., electric, magnetic, or mechanical field.

The main objective of this work is to study the structure and the orientation behavior of LC networks stabilized by H-bonds under mechanical stress. We here describe a LC polymer, poly[4-(6-acryloyloxyhexyloxy)-benzoic acid], and its blends with several low molecular weight additives, namely, 4-[*S*-(−)-2-octyloxy]benzoic acid (O*OBA), 3-fluoro-4-[*S*-(−)-3-methylbutoxy]benzoic acid (F*BA), and (*R*)-(+)-3-methyladipic acid (MAA). Figure 1 shows a schematic representation of the H-bonded LC polymer network with different additives.

Results and Discussion

Poly[4-(6-acryloyloxyhexyloxy)benzoic acid] (PA-6BA) is a mesogenic polymer which exhibits LC phase within a broad temperature range. It has the glass transition temperature (T_g) at 82 °C and the transition temperature from the LC phase to an isotropic state (T_{lc-i}) at 167 °C. The formation of cyclic dimers via hydrogen bonding of monomeric units (Figure 1) is believed to be the main reason for the mesogenic order. The presence of cyclic dimers stabilized by the H-bonding of carboxylic groups was proved by IR spectroscopy.[7] The LC structure of this polymer was found to be a smectic Sm C_A.[6,7]

Addition of up to 10 mol % of any low molecular weight benzoic acids and, as a result, the formation of mixed dimer do not influence the smectic structure. Two small-angle reflections with *d* spacings 28 and 14 Å (001 and 002) combined with the broad amorphous halo at wide angles indicate that the mesophase structure of the polymer/benzoic acids mixtures is identical to that of the original polymer (Figure 2). The LC−isotropic transition temperature also stays the same although T_g of mixtures slightly decreases in comparison with that of a pure polymer: polymer > polymer/F*BA > polymer/MAA > polymer/O*OBA. The latter is clearly seen in the DSC curves given in Figure 3.

The mechanical properties of these materials have been studied using thin films prepared under mechanical pressure above T_{lc-is} at 180 °C followed by cooling to room temperature. The X-ray patterns shown in Figure 4 characterize the structure of these films. There is only an amorphous halo in the wide-angle region when the X-ray beam is normal to the film plane (Figure 4a). If the X-ray beam is parallel to the film plane (Figure 4b), the small-angle equatorial reflection appears in the pattern. It means that films prepared under the mechanical pressure at the temperature above T_{lc-i} are polydomain with their smectic layers predominantly aligned parallel to the plane of the film. There is no preferable orientation of the LC director (or the mesogenic groups).

The uniaxial deformation of polydomain films at temperatures 20−40 °C above T_g is characterized by the stress−strain curves presented in Figures 5 and 6. The linear increase in the stress at low strain may be attributed to elastic deformation of the material. The tilt angle gives an estimation of the elasticity modulus *E*. The addition of monocarboxylic additives (benzoic acids) leads to a decrease in *E* value relative to that of

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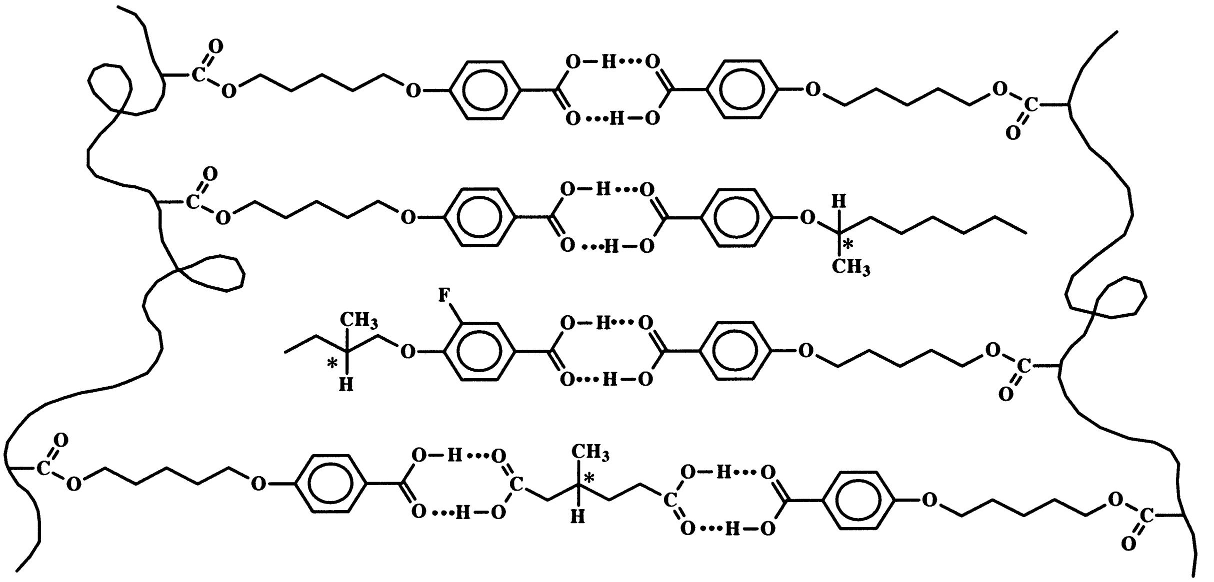

Figure 1. Four main types of structural elements within the polymer network: H-bonded rodlike dimers formed by carboxyl monomer units incorporated in the polymer backbone (shown schematically by the wavy line); mixed dimers containing H-bonded molecules of O*OBA, F*BA, and MAA.

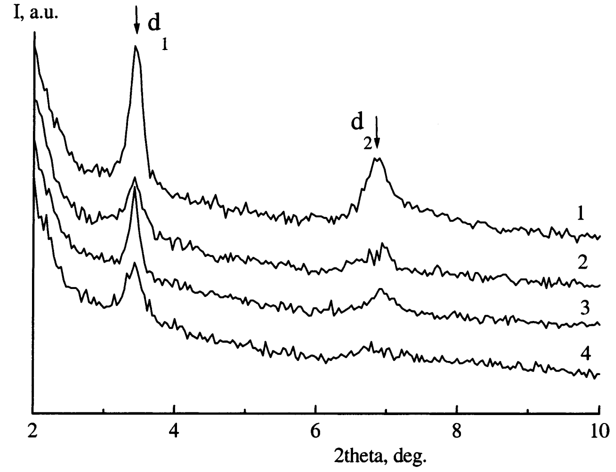

Figure 2. X-ray diffractograms of PA-6BA (1) and its blends with 10 mol % MAA (2), F*BA (3), and O*OBA (4).

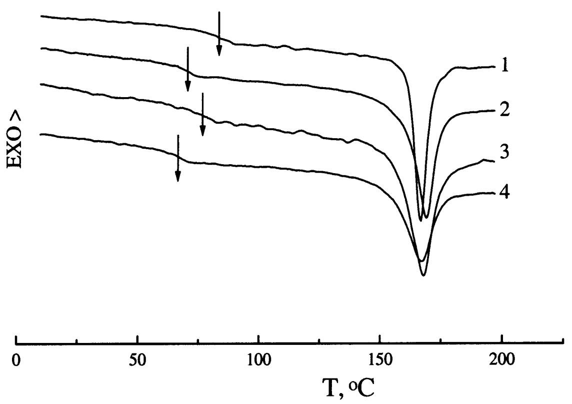

Figure 3. DSC scans of PA-6BA (1) and its blends with 10 mol % MAA (2), F*BA (3), and O*OBA (4).

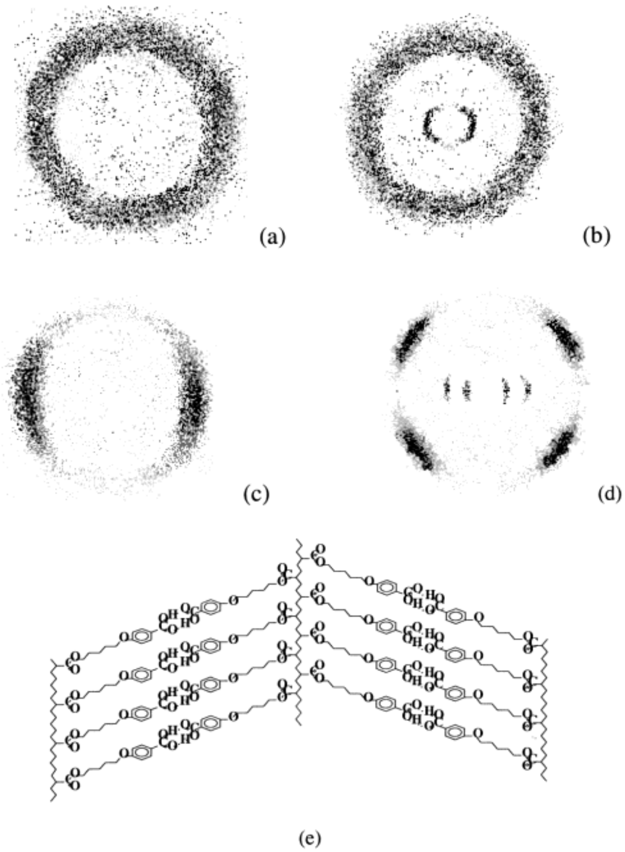

Figure 4. X-ray diffraction patterns of the film of PA-6BA: 10 mol % O*OBA blend prepared under pressure at 180 °C and then cooled to room temperature (a, b) and stretched at 100 °C above the threshold strain (c, d) measured in two different geometries: with the incident beam perpendicular (a, c) and parallel (b, d) to the film plane. The schema of the smectic C_A structure of the H-bonded PA-6BA polymer (e).

the pure polymer (Figure 5). If 2-methyladipic acid is used, the network stays stable, and there is no appreciable change in the *E* modulus of the system. The *E* values estimated are in the range 1.4−5.0 MPa, which is in good agreement with the reported elasticity modulus of the LC side chain elastomers.[8] Because both the LC polymer and its mixtures with benzoic acids are stabilized by H-bond network, we can assume that this network is responsible for the elasticity at low strains. The decrease in *E* with the insertion of monocarboxylic acids may result from the partial disruption of the

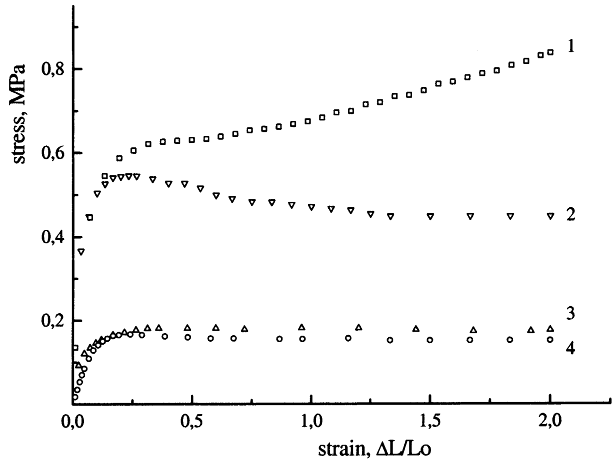

Figure 5. Stress−strain curves of PA-6BA (1) and its blend with 10 mol % MAA (2), F*BA (3), and O*OBA (4) at 100 °C with the deformation rate 2 mm/min.

H-bond network like it is schematically shown in Figure 1. As for the 2-methyladipic acid additive, it contains two carboxylic groups which can participate in interchain H-bonding, thus making the mixed H-bonded network as stable as it is in a pure polymer.

There is a certain threshold strain around 20%, at which point the slope of the stress−strain curves changes drastically (Figures 5 and 6). Above this threshold, the stress raises slightly with increasing the deformation of a pure polymer Figure 6a, whereas in composite polymer/benzoic acids films the stress stays nearly constant (Figure 6b,c). After the threshold strain is reached, the X-ray patterns, collected from the two orthogonal positions of the film with respect to the beam, change significantly. Two diffused equatorial arcs are now visible in the wide angles, as opposed to an isotropic amorphous halo prior to the deformation (Figure 4, c and a, respectively). At the same time, the set of small-angle reflections located at the equator become very obvious, and the amorphous halo is divided into four arcs (Figure 4d). The combination of these features implies that, after the process of elastic deformation is complete (small strains below 20%), a polydomain sample is transformed into a monodomain one. The well-ordered smectic layers, in which H-bonded mesogenic groups are tilted in an alternating fashion (Figure 4e), feature the structure of a monodomain film. This structure of stress-aligned H-bonded LC network is similar to that of a Sm C_A liquid crystal, where the direction of Sm C tilt is equally probable in both directions and alternates between the neighboring layers.

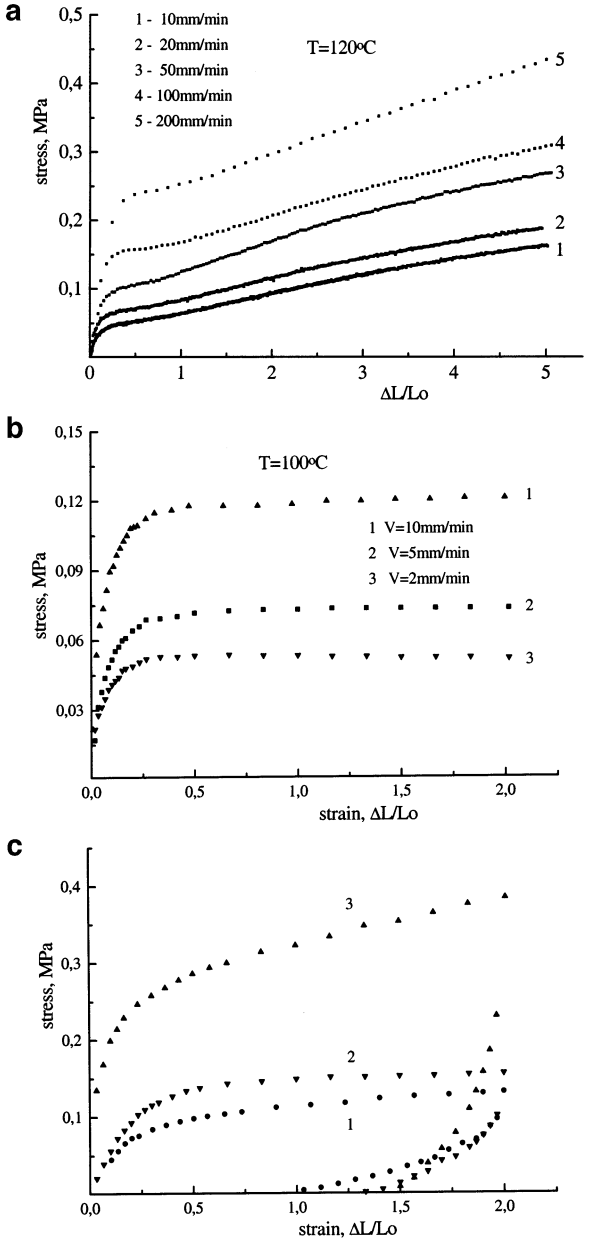

Figure 6. Stress−strain curves of PA-6BA (a) and its blend with 10 mol % F*BA (b, c) measured and at different temperatures (b) with different deformation rates (a, c). c: 1, 1 mm/min; 2, 2 mm/min; 3, 3 mm/min. T = 90 °C.

The shape of the stress−strain curves (Figures 5 and 6) is reminiscent of the flow developing in the polymer materials when the stress exceeds the threshold. However, after the deformation stops and the stress decreases, we can observe the strain relaxation (Figure 6c). The stress−strain curves obtained at various strain rates and the following relaxation curves demonstrate a considerable hysteresis. After the sample is stretched up to 200−300% followed by complete removal of the external mechanical field, a residual strain in the sample still remains high (100−125%). However, annealing of the material at elevated temperature (20−30 °C above T_g) results in complete recovery of the sample's size and shape. This observation is indicative of the H-bonded network with relaxation times much longer than those of typical elastomers. It is worth noting that in the contrast to covalent polymer networks the H-bonded network is very labile. Although the lifetime of a single hydrogen bond (a single physical cross-link) is about several milliseconds, the cooperative H-bonding in a LC network creates the conditions when relaxation processes occur within the real time scale.

Stress−strain curves depend on both temperature and the strain rate. As an example, the deformation curves obtained at different temperatures (a) with different strain rates (b, c) are shown in Figure 6. The threshold stress drops dramatically when the deformation rate is decreasing. An example of a stress−strain curve obtained in a close to equilibrium regime is given in Figure 7a. It was obtained by taking a small step increment of strain and allowing 20 min of stress relaxation, thus making the effective deformation rate about 0.02 mm/

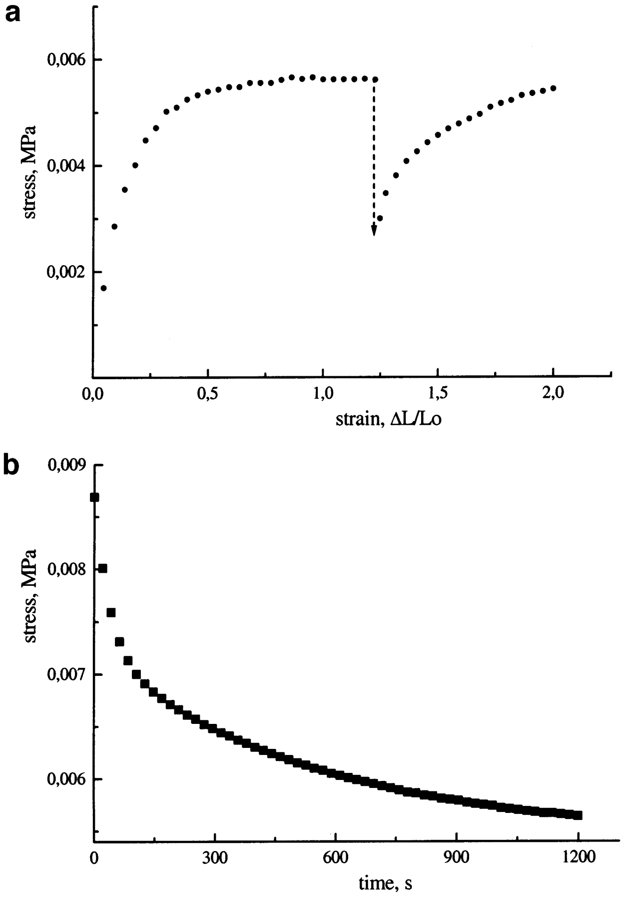

Figure 7. Stress−strain curve of PA-6BA blended with 10 mol % of MAA measured at quasi-equilibrium conditions (a) and the kinetics of the stress relaxation to the threshold stress (b). Both are measured at 90 °C.

min. The stress value falls by 1−1.5 orders of magnitude under these conditions.

After a certain threshold level is exceeded, the system behaves as a solid in which the stress remains constant upon increasing the deformation. It is reasonable to assume that the threshold stress can break a certain amount of hydrogen-bonded dimers present in the system, which would be just enough to ensure the macroscopic flow of the sample. In other words, at this particular stress level the external mechanical field becomes energetically comparable to the energy of hydrogen bonds responsible for the structural integrity of the physical network. This would explain the fact that the deformation can proceed without further increase in the average stress. Therefore, if one keeps the deformation constant for a certain period of time, the system will equilibrate in the new configuration and will eventually undergo a complete stress relaxation by reconnecting the broken H-bonds (Figure 7b). The complete "resetting of stress" must take a very long time, being a dynamic process with self-retardation. However, we see a clear signature of such a behavior, when the strain was kept constant at 125% for 24 h, after which the initial deformation rate has been reapplied. If we now try to follow the strain relaxation, then contrary to the previously discussed relaxation of the strain, we have not observed any visible strain relaxation after the sample deformation under quasi-equilibrium conditions.

These data imply that the H-bonded networks are very sensitive to the deformation rate and the stress relaxation. If stretching is done at a high deformation rate with no long-term stress relaxation allowed, one can envision a nonequilibrium system with some H-bonds broken for as long as the mechanical field is applied. In such a case the number of carboxyl groups that stay "free" may be fairly high, and their reconnection after annealing the sample at elevated temperature may lead to the complete strain relaxation. If the stretching is done in a slow (equilibrium) regime, it is enough time for the reconnection, and we do not observe more than 1% of the strain relaxation during the same period of time.

Thus, the results may be interpreted in terms of the mechanism of breaking and reconnecting of H-bonds under stress (Figure 8). In the case of LC H-bonded materials, one has to consider the mesogenic groups formed by hydrogen bonds. This means that the local sliding of layers is possible if H-bonds are temporarily disconnected and then reconnected again to preserve the LC structure.

The LC structure of the H-bonded network causes the anisotropy of its physical properties. In particular, mechanical properties of the material depend on the correlation between the LC director and the strain direction. The scheme describing the preparation of the oriented films for stress−strain measurements is shown in Figure 9a. The external mechanical pressure applied to a polymer or polymer/benzoic acid composites below $T_{\mathrm{lc-i}}$ at 160 °C induces the radial spreading of the LC material, and it results in the alignment of the LC director. The Sm C_A layers in the oriented samples are aligned parallel to the Z^0X^0 plane with the preferable *c*-director orientation along the X^0 axes in sample 1 (Figure 9b) and along the Z^0 axes in sample 2 (Figure 9c).

The analysis of the final structure after the stretching shows that *c*-director does not change its direction if the strain is applied along the X^0 axis (Figure 9b). If the stress applied in the layer plane perpendicular to the *c*-director, it rotates by 90° upon the deformation. The final orientation of the *c*-director in sample 2 after stretching is similar to that of sample 1. As for the stretching process itself, there is a strong difference in the stress response if strain is applied in different directions with respect to *c*-director axis. In Figure 10 the stress−strain curves are given (1, 2) in comparison with that of the polydomain sample (3). In all three samples the stress axis lies within the film plane parallel to the smectic layers. Curve 1 indicates a strong increase in the stress as the strain increases. Contrary to sample 1, the sample 2 shows a clear "yield" stress behavior (curve 2) which is very similar to that of a polydomain sample during the polydomain−monodomain transition (curve 3).

To find an explanation to the observed phenomenon, we have to consider the polymer chain structure of the LC material under investigation. The smectic ordering in side chain polymers is known to create an anisotropic distribution of polymer segments.[9] Polymer backbones should be localized in planes separated by ordered mesogenic groups. The polymeric coils are anisotropic entities having a shape of rotational ellipsoids. There is a solid correlation between the long axis of such an ellipsoid and the LC director. The ellipsoids of smectic

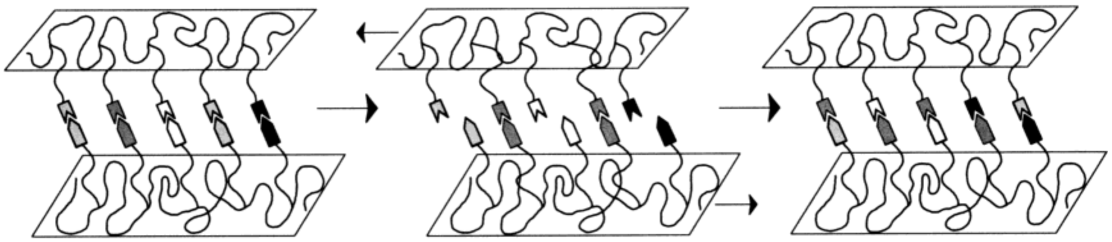

Figure 8. Scheme for the mechanism of breaking and reconnecting of H-bonds under stress.

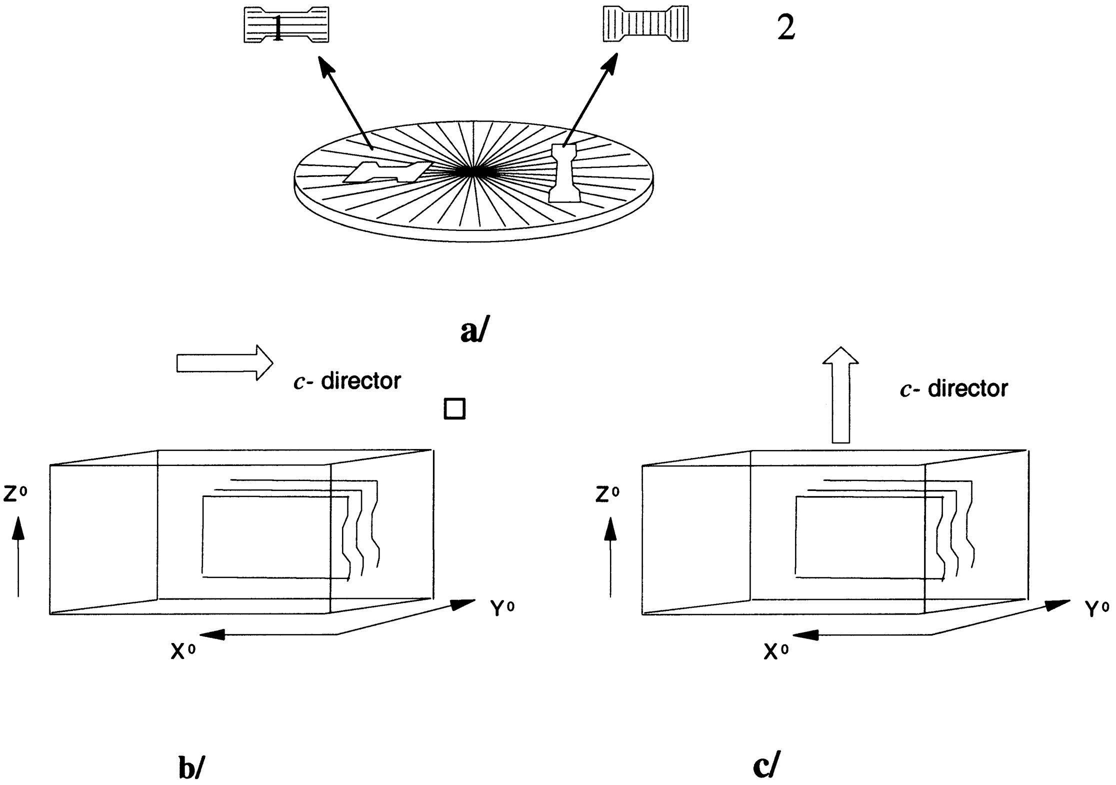

Figure 9. Schematic presentations of the preparation of single domain preoriented samples 1 and 2 (a) and the *c*-director alignment in samples 1 (b) and 2 (c).

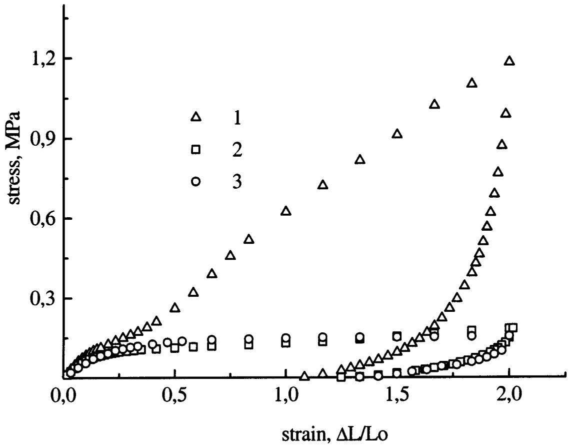

Figure 10. Stress–strain curves of preoriented films of polymer:10% O*OBA blend related to samples 1 and 2 in Figure 9 (1, 2) given in comparison with that of the initially polydomain sample (3) measured at 90 °C with the deformation rate of 2 mm/min.

LC polymers have the oblate shape relative to the LC director axis. Taking into account that in our case the oblate coils should be connected to each other via H-bonds, which produce the tilted rodlike mesogens (Figure 11), the difference in the stress–strain behavior of samples 1 and 2 may be schematically explained as follows.

If the strain is normal to the *c*-director, the elongation of the H-bonded network proceeds due to the reorientation of the *c*-director which should be accompanied by the realignment of the oblate coils (Figure 11, route Y). At the yield stress this process is followed by the plastic flow which may proceed via the reconnection of H-bonds. Polymer backbones do not seem to change their distribution. From this viewpoint there is no difference between the behavior of the backbones upon the deformation of polydomain and monodomain samples accompanied by either orientation or reorientation of the *c*-director. That is why the mechanical response of the monodomain sample (Figure 10, curve 2) is very similar to that of the polydomain one (Figure 10, curve 3). As for the deformation along the *X* axis (Figure 11), one may expect that instead of the “soft” mechanical response associated with the *c*-director rotation, the polymeric backbones become involved in the stretching process, providing the “hard” response as the stress raises upon the increase in deformation (Figure 10, curve 1).

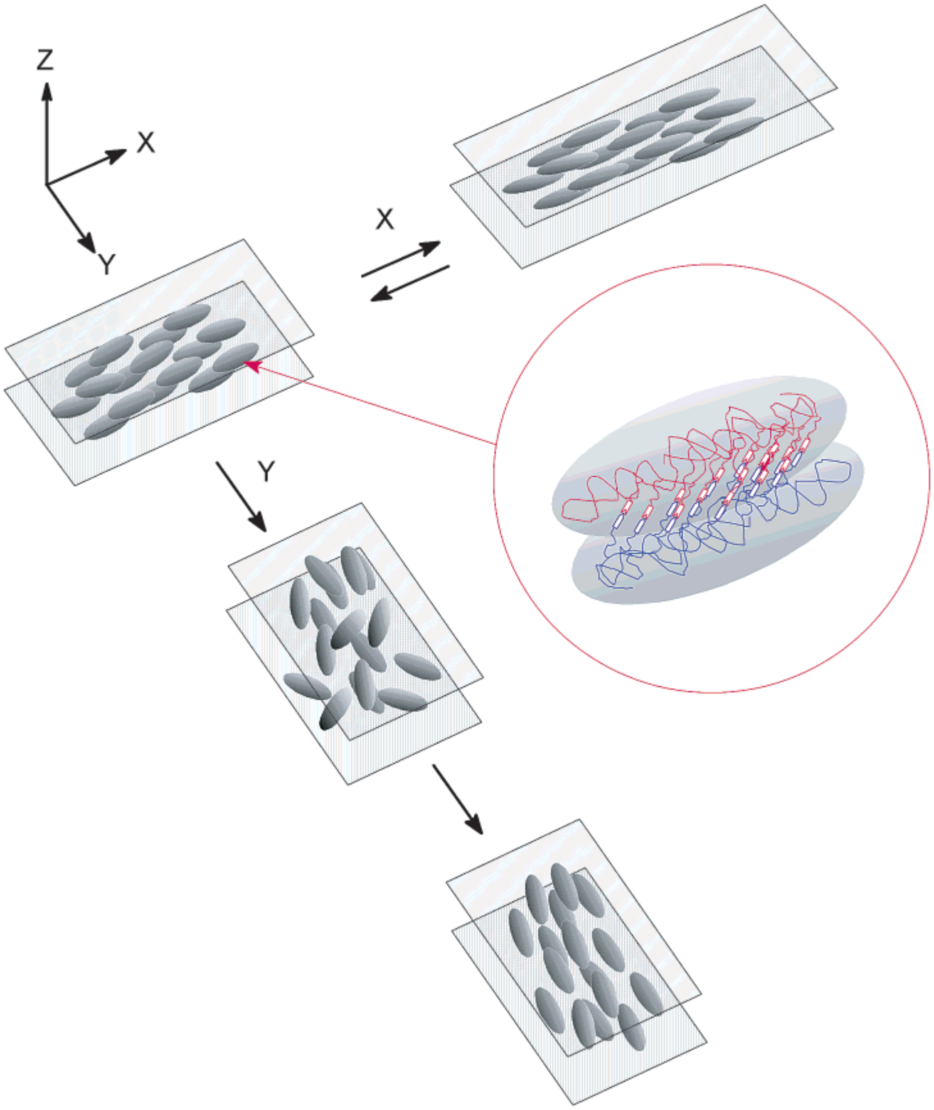

Figure 11. Schematic presentation of the molecular alignment and realignment in the single domain H-bonded Sm C_A polymer under stretching.

Conclusions

We have studied H-bonded polymer networks with the smectic C_A structure where the layered structure and the molecular tilt are stabilized by the H-bonding between the side groups. The application of the mechanical stress results in a two-stage process. The first stage is associated with the elastic behavior of H-bonded network which proceeds up to 20% of strain with the alignment or realignment of the LC *c*-director. The plastic flow of the polymer induced above the threshold strain is believed to proceed in accordance with the mechanism of reconnecting of hydrogen bonds. The H-bonds provide the yield-stress behavior of the systems in which they stabilize both the LC phase and the polymer network. The anisotropic mechanical response of the monodomain networks is related to the difference of their *c*-director alignment. There is no complete evidence for the role of the backbones in the plastic flow behavior of the monodomain samples if it proceeds along the *c*-director axis. One of the most challenging approaches to find such evidence is the direct study of the polymer backbone conformation during the flow process, which could be measured by small-angle neutron scattering in deuterated materials.

Experimental Section

The monomer, 4-(6-acryloyloxyhexyloxy)benzoic acid, was synthesized as previously described. The polymer was produced by radical polymerization of the above monomer in benzene at 65 °C for 35 h. 2,2′-Azoisobutyronitrile (0.1% of the total weight of the monomer) was used as initiator. The polymer was precipitated from the benzene solution after the polymerization was complete. It was separated, dissolved in THF, reprecipitated in benzene, and dried under vacuum. The polymer yield was 60%.

Films of poly[4-(6-acryloyloxyhexyloxy)benzoic acid] and its blends with additives were prepared under mechanical pressure above the glass transition temperature in the LC state (at 160 °C) and in the isotropic melt (at 180 °C). The thickness of the layer was determined by the thickness of a metal ring, which did not restrict the radial flow of the material during the sample preparation.

The thermal behavior of different samples was studied by DSC (Mettler TA-4000) with the heating/cooling rate equal 5

K/min. The stress–strain curves were obtained on an "Instron-1122" instrument at 10^{-2}–1 N. The stress was uniaxially applied to LC films of 6 × 9 mm size. The deformation rate was varied from 0.1 to 500 mm/min.

Wide- and small-angle X-ray scattering patterns were collected on DRON-3.0 and IRIS-3.0 instruments (Cu Kα radiation, Ni-filtered, transmission mode). The incident beam was normal to the surface or directed toward the edge of the polymer film.

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