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Shear induced molecular alignments of a side-chain liquid crystalline polyacetylene containing biphenyl mesogens

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Abstract

Mesomorphic properties of a side chain liquid crystalline polyacetylene, poly(11-{[(4′-heptyloxy-4-biphenylyl)carbonyl]oxy}-1-undecyne) (PA9EO7), are investigated using polarized optical microscope, X-ray diffraction, and transmission electron microscope. Polymer PA9EO7 forms enantiotropic smectic A and smectic B phases. It also exhibits an additional high order smectic phase, a sandwich structure consisting of different molecular packing of biphenyl mesogenic moieties from that of alkyl spacers and terminals, when it is prepared from its toluene solution. Shearing the polymer film at its smectic A phase generates banded texture with the alignment of the backbones parallel to the direction of shear force. While at its high order smectic phase, the mesogen pendants of the polymer are arranged parallel to the direction of shear. The different mesomorphic behaviors arise from different molecular alignments influenced by the fluidity.

Keywords: Liquid-crystalline polymer; Polyacetylenes; Shear orientation

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1. Introduction

Liquid crystalline polymers (LCPs), which are able to retain their molecular alignment in the solid state, have been found to exhibit remarkable mechanical properties, exceptional dimension stability, excellent thermal stability, and superior chemical resistance. The combination of these properties in one polymer makes it promising candidate in high mechanical strength fiber, aerospace application, bulletproof jackets, and so on. Attracted by the application perspective, many scientists have studied the orientation behaviors of LCPs. Most studies, however, are mainly focused on main chain liquid crystalline polymers (MCLCPs) and side chain liquid crystalline polymers (SCLCPs) with flexible backbones [1–3]. In these classes of polymers, the orientation of the backbones and the mesogens can be modulated by magnetic field, electric field, surface shearing, 'log-rolling' shearing and stretching in their liquid crystalline (LC) phases and the packing can be preserved by cooling the polymers to their glass states or crystalline states [2,4–8].

Recently, SCLCPs with stiff backbones have aroused much attention among scientists because of two reasons. First, the standard recipe for designing the molecular architecture of SCLCPs is 'flexible backbone + spacer + mesogenic group' [9,10]. Rigid polymer backbones are generally regarded as defects that distort the packing arrangement of mesogenic pendants. They, however, may be constructive in inducing novel molecular alignment in the SCLCP systems [11–14]. Second, polyacetylene is one of the simplest organic conjugated polymers. Attachment of mesogenic moieties to the conjugated polyacetylene backbone may lead to polymers possessing unique electrical, optical and LC properties. The alignment of the polymer backbone accompanied with the orientation of the mesogens induced by magnetic field may further enhance the conductivity and results in a remarkable electrical anisotropy [15].

Shear-induced and solidification-induced banded textures are usually observed in MCLCPs including aromatic

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polyamides, polyisocyanates, polypeptides, cellulosic derivatives, aromatic polyester or co-polyester [3,16–23]. They are also observed in SCLCPs with mesogens laterally attached on the backbones (side-on fixed) [24]. The backbone rigidity of these kinds of polymers is similar to those of MCLCPs. Thus, they exhibit similar orientation behaviors to those of MCLCPs.

The backbones of liquid crystalline polyacetylenes, in which the mesogens are attached longitudinally to the main chains (end-on fixed), also have high stiffness. In this paper, we investigated the orientation behavior of a side-chain liquid crystalline polyacetylene poly(11-{[(4′-heptyloxy-4-biphenylyl)carbonyl]oxy}-1-undecyne) (PA9EO7) at different LC phases using polarized optical microscope (POM), X-ray diffraction (XRD), and transmission electron microscope (TEM) and presented its novel mesomorphic properties.

The chemical structure of the liquid crystalline polyacetylene PA9EO7 is shown in Fig. 1. Its preparation can be found in our previous publication [25]. Polymer PA9EO7 shows enantiotropic smectic A (S_A) and smectic B (S_B) textures in the temperature ranges of 128.6–75.6 and 75.6 °C-room temperature (~23 °C), respectively. The alignment of the mesogenic pendants can be normal or parallel to the substrate in different liquid crystalline domain [26]. An additional high order smectic phase, a sandwich structure consisting of different molecular packing of biphenyl mesogenic moieties from that of alkyl spacers and terminals, is also found when the polymer sample is prepared by evaporation of its toluene solution. The packing of the mesogenic groups, however, is normal to the substrate only [27]. And the mesogenic pendants are normal to the polymer backbone in all the liquid crystalline phases. In this study, the effect of shearing on the mesomorphic properties of the polymer at S_A phase and the high order smectic phase is studied.

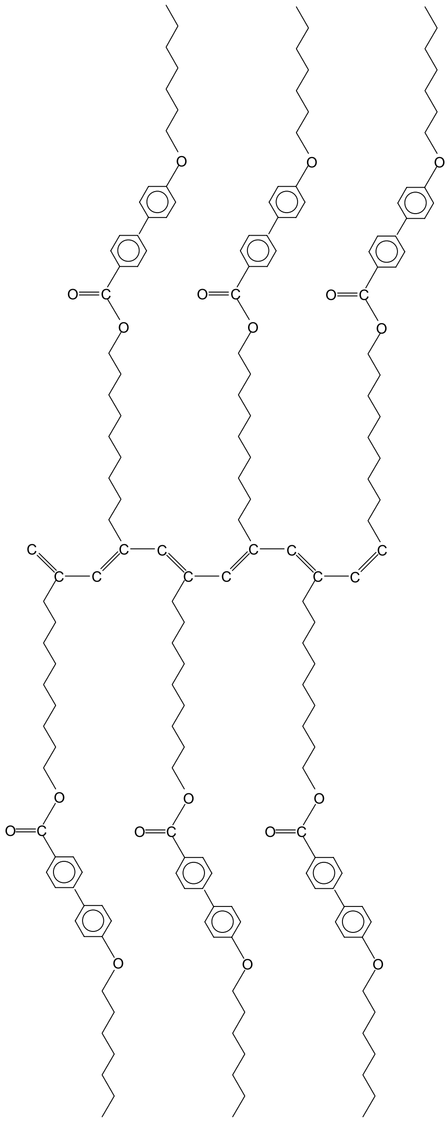

Fig. 1. Molecular structure of PA9EO7 with six repeating units.

2. Experiments

2.1. Instruments

Optical textures were obtained using a LEICA POM equipped with a hot stage in cross-polarized mode. XRD patterns were recorded on a Rigaku D/max 2500 PC diffractometer with a R-AXIS DS3 X-ray data collection system [28] using X-ray from Cu Kα radiation with a wavelength of 1.54056 Å. The camera length was 118 mm. The TEM experiments were performed on a JEOL2010 TEM operated at 200 KV. A field-limiting aperture of 50 μm in diameter was used to perform the selected area ED experiments. In case of damage of electron beam on the liquid nitrogen quenched specimens, a cold holder was used in observation. The low temperature experiment was performed at −54 °C obtained using liquid nitrogen. For measurement of thickness of film specimen, a QUESANT QScope and a Bio-Rad FPS315 Fourier transform infra-red spectrometer were used.

2.2. Specimen preparation

Film specimens sheared at S_A phase were prepared as follows: the polymer sample was melted at 170 °C on a glass slide and then annealed at the same temperature for 10 min. The isotropic liquid of PA9EO7 was cooled to 124 °C and held for 10 min. Afterwards, the sample film was sheared using another glass slide having the same temperature and then quenched by liquid nitrogen or air. The optical texture of the oriented film was observed using POM. For the TEM experiment, the preparation was similar to the above but NaCl single crystal slide was used instead of glass slide. The NaCl slide was removed by water and the oriented film was picked up using 400-mesh copper grids.

For the film specimens sheared at the high order smectic phase, toluene solution of PA9EO7 (0.05 wt%) was dropped on thin carbon films, which were deposited onto freshly cleaved mica surface. After the solvent was evaporated, the sample films obtained were annealed at 60 °C, which is below the phase transition temperature from high order smectic phase to S_A phase, for 12 h. The samples were then cooled to room temperature and sheared by another mica slides. The sheared samples were annealed again for 3, 6, and 12 h. The carbon films containing the film specimens were removed by water. The specimens were picked up on 400-mesh copper grids and sample observation and electron diffraction (ED) experiments were then performed on TEM.

To measure the thickness of sample film, CaF_2 slides were used to prepare shearing samples with the same experimental method and condition. In addition, a spin coating film was prepared using sample's toluene solution (1 wt%) at a spin speed 1000 rpm. The thickness of the spin coating film was measured using a QScope by scratching the film to the surface of substrate. Infrared spectra give characteristic stretching vibration band at 1713 cm^{-1} of carbonyl group with different absorption strength of different film specimen. Absorption strength linearly changes as a function of the thickness of film specimen. Hereby, the thickness of film specimen can be calculated from the thickness of spin coating film. And, the film specimen for POM experiment is about 3 μm in thickness, while the film specimen for TEM experiment is about 400 nm in thickness.

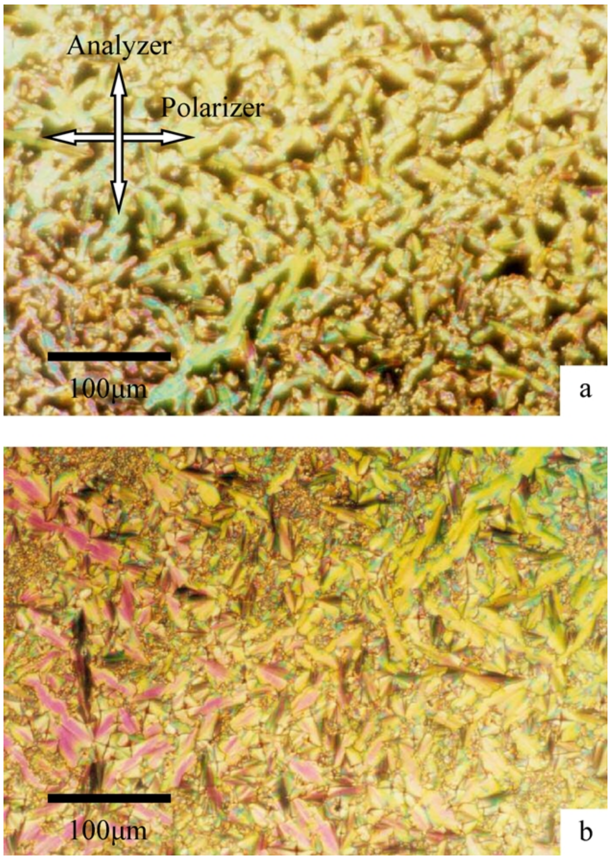

Fig. 2. Polarized optical micrographs of PA9EO7 observed on cooling at (a) 123 °C (focal-conic texture of S_A phase) and (b) 50 °C (broken focal-conic texture of S_B phase) from its isotropic melt.

3. Results and discussions

3.1. Shear induced banded texture

Fig. 2(a) shows a typical focal-conic texture of PA9EO7 observed on cooling its isotropic liquid to 123 °C. Alignment of the texture is completely irregular. The orientation of polarizer and analyzer is present in the image. The polarizer is in the horizontal direction and the analyzer is in the vertical direction. (The following POM images are obtained in the same orientation of polarizer and analyzer) Further lowering the temperature to the mesomorphic range of smectic B phase, a broken focal-conic texture is evolved (Fig. 2(b)). Because of lack of molecular fluidity in the process of phase transition from S_A to S_B phase, S_B phase thus exhibits a paramorphotic texture, broken focal-conic texture. And it also has no favorite orientation.

Fig. 3(a) shows the POM micrograph observed after a sheared PA9EO7 is cooled naturally to room temperature.

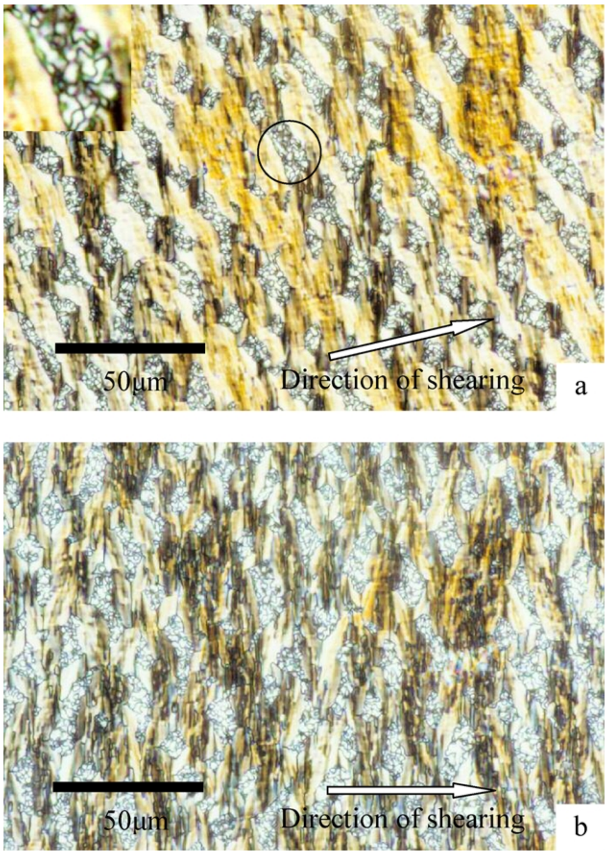

Fig. 3. (a) Texture observed after shearing PA9EO7 at 124 °C and then cooling the sample naturally to room temperature (b) change of brightness of the texture when the film specimen is rotated with respect to the polarizer and analyzer.

An obvious texture orientation is observed and the orientation is almost normal to the direction of shear force. The micrograph is still focal conic texture in character. In addition, as shown in the magnified area, the polymer also displays a schlieren texture, which results from break-up of smectic arrangement. When the film is rotated with respect to the direction of the polarizer–analyzer, the brightness of different domains interchange (Fig. 3(b)), indicative of different molecular orientation in the adjacent sections. Through these observations, an angle of approximate 13° exists between different director orientations.

Fig. 4(a) shows the texture observed by quenching the sheared polymer film by liquid nitrogen. Banded texture with an average width of 8.5 μm normal to the shear direction is observed. When the film specimen is rotated with respect to the orientation of polarizer–analyzer, the brightness of the dark lines becomes brighter, revealing that different director exist in the dark lines from the bright bands. The focal conic texture is difficult to evolve because the sheared texture is frozen rapidly by liquid nitrogen. In fact, the mesogenic pendants are more likely to arrange laterally when the polymer sample is quenched using liquid nitrogen. The LC domains will contract normal to the direction of the main chain, which results in the formation of banded texture [18]. When the film specimen is heated, the dark lines in the banded texture disappear (Fig. 4(b)) owing to adjustment of the packing of the pendant groups.

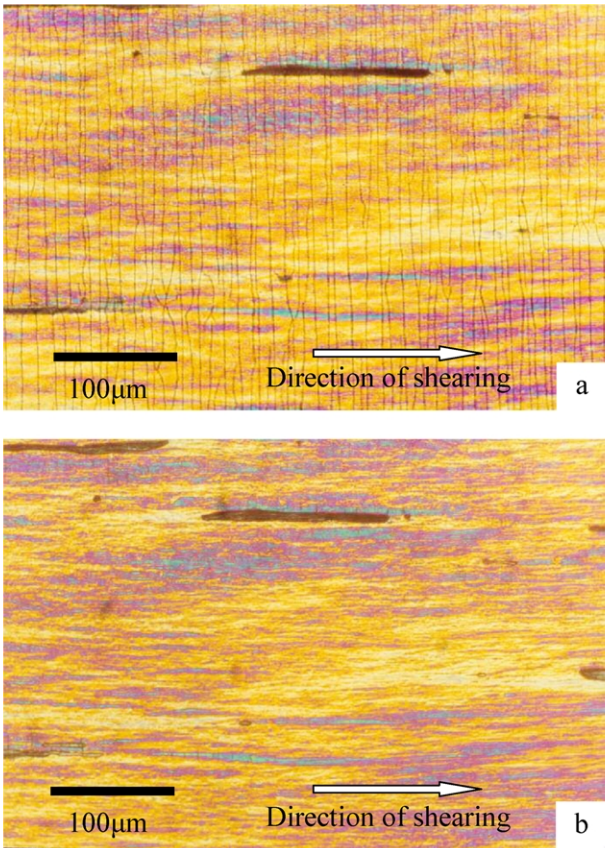

Fig. 4. (a) Banded texture observed after shearing PA9EO7 at 124 °C and then quenching the sample by liquid nitrogen (b) texture observed after heating the sample film to 50 °C.

3.2. Shear induced orientation in S_A phase

To investigate how shearing affects the packing of the mesogenic pendant groups, we carried out XRD analysis of the film specimen sheared at 124 °C, and then naturally cooled to room temperature. Fig. 5 shows the XRD diffractogram of the sheared polymer film. It is a typical XRD pattern of smectic phase. The diffraction arcs, indexed as 001 diffraction, at low angle correspond to the distance between layer planes of smectic phase. Since its direction is normal to the direction of shearing, the orientation of the mesogenic pendants is also perpendicular to the shear direction. In another words, the backbones of the polymer are aligned parallel to the direction of shear. Applying the molecular orientation information to the aligned focal-conic texture in Fig. 3, we conclude that biphenyl mesogenic moieties pack with their long molecular axis parallel to the radial direction of focal-conic texture.

To further study the morphology and the orientation behavior of the sheared film, we analyzed the sample by TEM. Fig. 6(a) gives the morphology of sheared PA9EO7. The morphology of the sheared film is preserved at the original state when it is quenched using liquid nitrogen.

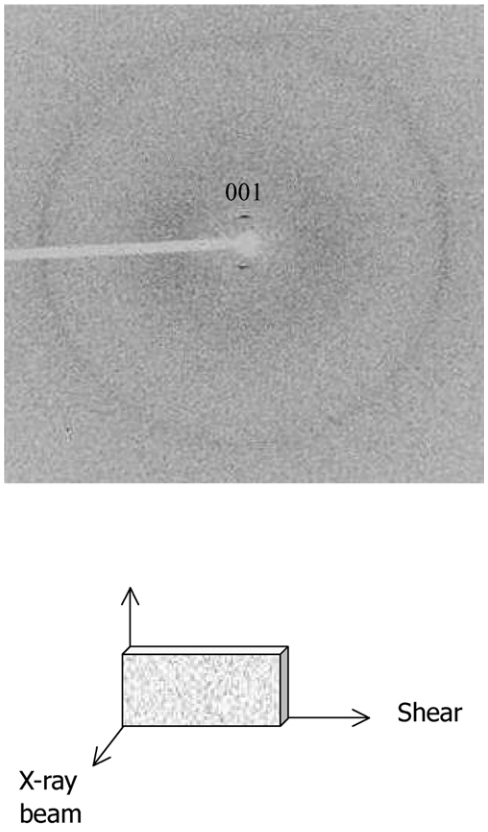

Fig. 5. XRD pattern of sheared PA9EO7 film specimen.

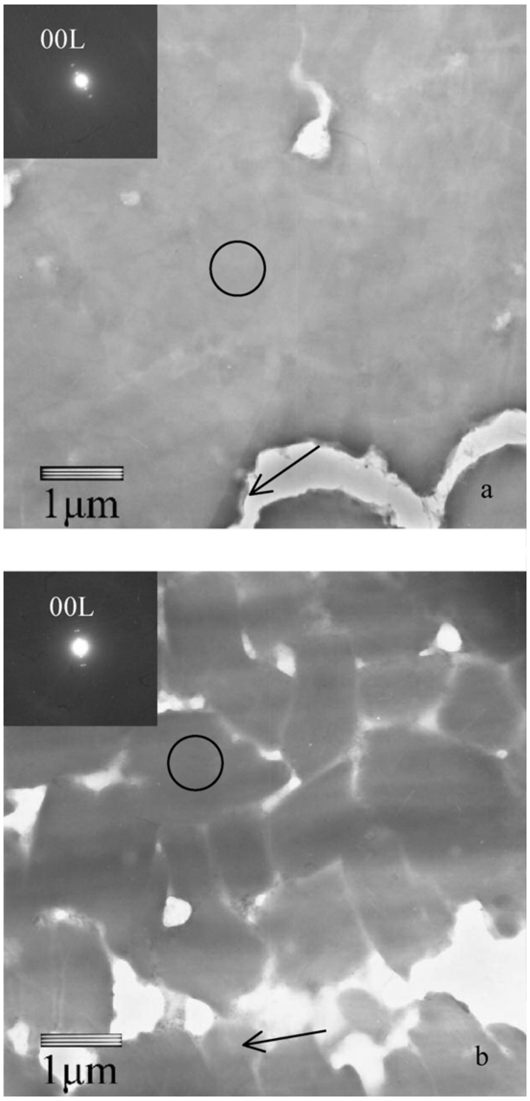

Fig. 6. TEM morphologies of the film specimen after it is sheared at 124 °C and then quenched by (a) liquid nitrogen and (b) air. The arrow in the image shows the direction of shearing.

Some cracks, probably due to film shrinkage by rapid cooling in liquid nitrogen, are also observed. Deduced from the in situ ED pattern obtained from the circle selected area, the main chains of the polymer are aligned parallel to the direction of shear force. The ED spots close to the incident beam correspond to the distance between layers of smectic phase and also the direction of mesogenic pendants. Because the quenching process by air is slow, the pendant groups have time to adjust their conformation and direction to form different LC domains, as shown in Fig. 6(b). The mesogens in different domains have different orientation. On the other hand, the main chains of the polymer still have a favorite orientation along the shear direction because the conformation relaxation and molecular rearrangement are limited in the quenching process owing to molecular stiffness.

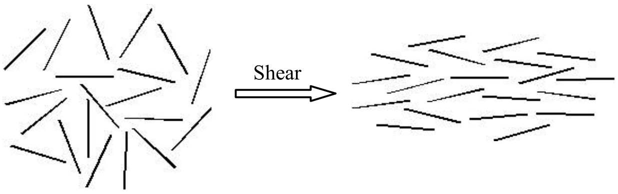

Fig. 7. Schematic diagram of PA9EO7 sheared at 124 °C. The sticks represent the backbones of the polymer.

^{1}H NMR analysis shows that PA9EO7 possess high stereoregularity with a predominant *trans* conformation. Thus, the LC side chains are alternatively located on both sides of the polyene chain, giving rise to a stereoregular sequence such as head–tail–head–tail linkage [26]. The side chains on one polymer backbone tend to overlap with those on the other side of the neighboring polymer chain. The backbones, however, have no favorite alignment in the two-dimensional layer planes of smectic phase. Under the shear, two mechanisms of polymer molecules responding to the shear flow can be imagined. Polymer backbone is parallel or normal to the direction of shear flow. It is obvious that the flow resistance is smaller in the former case than in the latter. Thus the stiff backbones tend to align along the direction of shear flow, as shown in Fig. 7. In another words, the mesogenic pendants are normal to the direction of shear flow. The sticks in the model represent the stiff backbones of the polymer.

3.3. Shear induced orientation at high order smectic phase

Fig. 8 shows the LC domain of PA9EO7 at its high order smectic phase. It gives a hexagonal morphology. The in situ ED pattern of one of the LC domains is shown in the same figure. It is a two-dimensional hexagonal pattern, suggestive a hexagonal packing of biphenyl mesogenic moieties. The mesogenic pendants of the polymer sample, which is prepared by evaporation of its toluene solution, are always

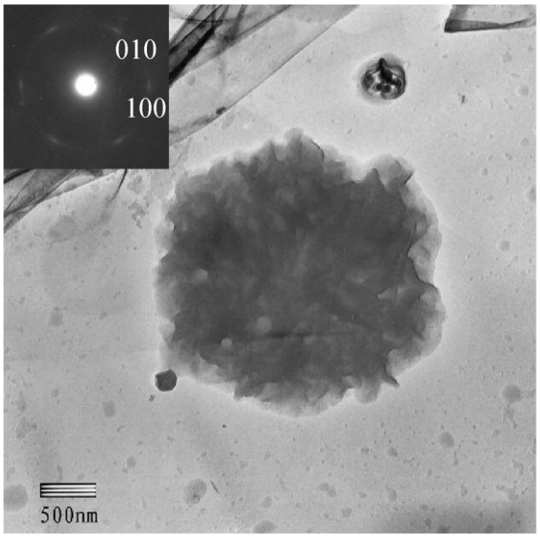

Fig. 8. Morphology and in situ ED pattern of PA9EO7 prepared by evaporation of its toluene solution.

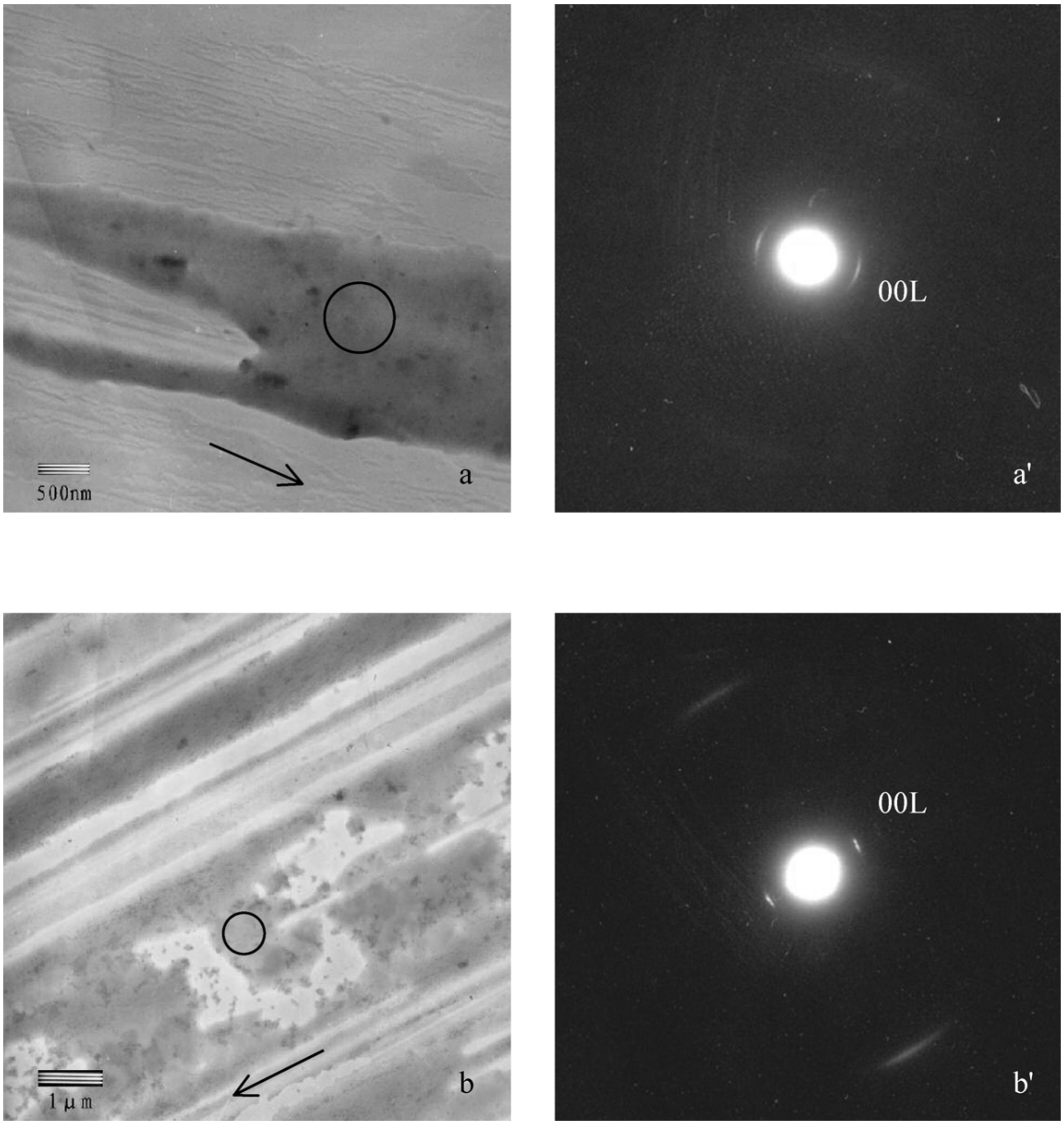

Fig. 9. TEM morphologies of the polymer film after it is sheared at its high order smectic phase and annealed at 60 °C for (a) 0 h, (b) 3 h, (c) 6 h, and (d) 12 h. The corresponding in situ ED patterns are shown in 9(a′)–(d′). The arrow in the image shows the direction of shear force.

normal to the substrate. In other words, the backbones of the polymer are parallel to the substrate but they have no favorite orientation [27].

Unlike at S_A phase, shearing at the high order smectic phase can align the pendant groups parallel to the direction of shear (Fig. 9(a) and (a′)). The shearing trace is also observed. The ED arcs close to the incident electron beam, indexed as 00L diffraction, in the in situ ED pattern suggest that the orientation of the mesogens is not uniform in the selected area. In order to improve their alignment, the sheared film specimens were annealed at 60 °C for 3, 6 and 12 h. The resultant morphologies and in situ ED patterns are shown in Fig. 9(b)–(d′). The shearing traces disappear for longer annealing and the ED arcs of 00L diffraction transform into diffraction spots, revealing that the LC side chains realign in a uniform direction.

The different orientation behavior of the polymer at the high order smectic phase from that at S_A phase may be due to the low fluidity. Individual polymer chain cannot respond to shearing but layer planes of smectic phase can glide along the shear direction, as schematic model in Fig. 10. In a LC domain, shearing clearly affects the packing of the mesogenic pendants. After subsequent annealing, the pendant groups can adjust their conformation and position to realign in a uniform direction in the scope of a LC domain.

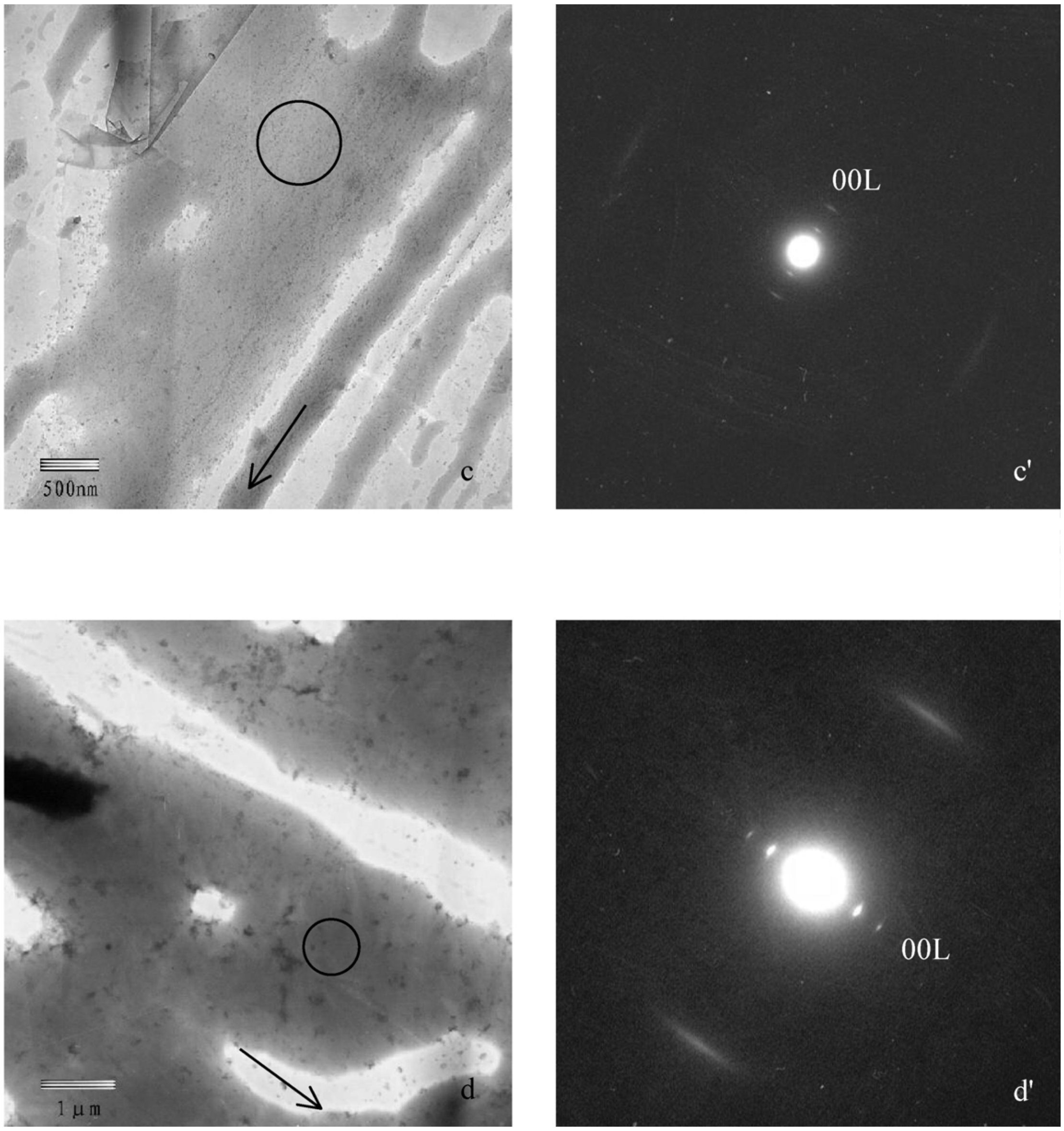

Fig. 9 (*continued*)

4. Conclusions

Banded texture, which is common observed in oriented films of MCLCPs and side-on fixed SCLCPs, can also be observed in oriented liquid crystalline polyacetylene with mesogenic pendants longitudinally attached to the main chains. This implies that the rigid conjugated backbones play an important role in modulating the chain conformation when the polymer film is sheared.

In respond to shearing, the polymer backbones align parallel to the shear direction at S_A phase. Because the high order smectic phase of PA9EO7 resembles to solid state, it is difficult or impossible for a single polymer backbone to align. The layers of smectic phase, however, can glide parallel to the direction of shear, leading to an orientation of the mesogens parallel to the shear direction.

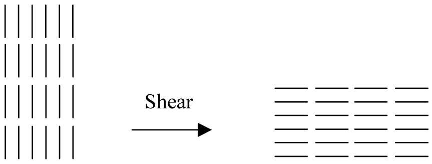

Fig. 10. Schematic model of PA9EO7 sheared at room temperature. The sticks represent mesogenic moieties of the polymers.

Acknowledgements

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[28] The R-AXIS DS3 is an X-ray data collection system that uses the Imaging Plate (IP). It reads an X-ray diffraction pattern imaged over the IP surface and loads it into the host computer as digital data. The IP is a storage radiation detector. It stores incident radiation energy and allows you to read the stored energy later.