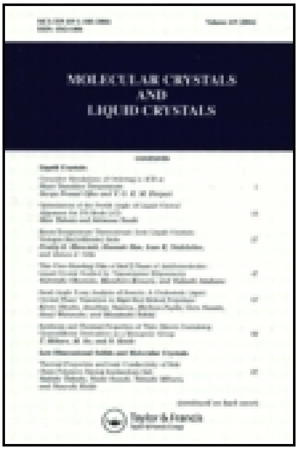

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

HIGH ORDER LIQUID CRYSTALLINE STRUCTURE OF POLY(11-{[(4′-HEPTYLOXY-4-BIPHENYLYL)CARBONYL]OXY}-1-UNDECYNE)

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Version of record first published: 18 Oct 2010

To cite this article: Jianxin Geng, Xiaoguang Zhao, Enle Zhou, Gao Li, Jacky Wing Yip Lam & Ben Zhong Tang (2003): HIGH ORDER LIQUID CRYSTALLINE STRUCTURE OF POLY(11-{[(4′-HEPTYLOXY-4-BIPHENYLYL)CARBONYL]OXY}-1-UNDECYNE), Molecular Crystals and Liquid Crystals, 399:1, 17-28

To link to this article: http://dx.doi.org/10.1080/15421400390223121

Mol. Cryst. Liq. Cryst., Vol. 399, pp. 17–28, 2003
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390223121

HIGH ORDER LIQUID CRYSTALLINE STRUCTURE OF POLY(11-{[(4′-HEPTYLOXY-4-BIPHENYLYL) CARBONYL]OXY}-1-UNDECYNE)

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Liquid crystalline properties of a mesomorphic polyacetylene {–[HC=C(CH$_2$)$_9$OOC-Biph-OC$_7$H$_{15}$]$_n$– (PA9EO7), Biph = 4-4′-biphenylyl} are investigated by X-ray diffraction, polarizing optical microscope, and transmission electron microscope. Polyacetylene PA9EO7 from solution adopts a sandwich structure, which is a high order smectic phase. The biphenylyl pendants pack in a hexagonal fashion and the distance between two appendages is 4.51 Å. The heptyloxy tails on one polymer backbone overlap with those on the neighboring chain. The nonyl spacer and the heptyloxy tail exhibit a hexagonal packing arrangement with intermolecular distance of 3.24 Å.

Keywords: liquid-crystalline polymers; morphology; polyacetylenes; structure; TEM

INTRODUCTION

In recent years, side-chain liquid crystalline (LC) polyacetylenes have attracted great interest among scientists in academic and industrial field owing to their unique light-emitting properties [1–3], photoconductivity [4], and mesomorphic properties [5–8].

We thank the National Natural Science Foundation of China (Project Nos. 29904008, 20174043, and 20023003) and the Research Grants Council of Hong Kong (Project Nos. HKUST6121/01P and 6085/02P) for financial support. This work was also subsidized by "The Special Funds for Major State Basic Research Projects."

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The standard recipe for designing side-chain liquid crystalline polymers (SCLCPs) is "flexible backbone+spacer+mesogenic moiety" [9,10]. While SCLCPs with flexible backbones have received much attention, those with rigid backbones are often prepared to demonstrate the destructive role of the stiff main chains on the packing of the mesogenic pendants. One advantage of stiff macromolecules over their flexible-chain counterparts is their orientability by external fields and/or flow processes. In our previous paper [11], we found that poly(10-{4-[(4-methoxy) phenoxycarbonyl] phenoxycarbonyl}-1-decyne) displays unusual schlieren texture with disclinations of 3/2 and 2 after it is rotationally agitated at 136°C. The translational shear creates the inversion wall, solidification of which produces the well-ordered parallel bands. The long relaxation time of the stiff polyacetylene backbone plays an important role in stabilizing the shearing-induced orientation textures.

While the rigid backbone imparts novel properties to the polymer, it, however, distorts the packing of the polymer into three-dimensional lattice [12]. In this article, the LC phase structure of PA9EO7 from toluene solution is studied using transmission electron microscope (TEM), X-ray diffraction (XRD), and polarized optical microscope (POM).

EXPERIMENTS

Molecular structure of PA9EO7 is shown in Figure 1. Its synthetic procedure was reported in our previous paper [13]. It is gray solid powder in appearance. The samples for TEM measurements were prepared as follows: PA9EO7 was dissolved in toluene to make 0.05% (wt%) solution. The solution was dropped on thin carbon film, which was evaporated on the surface of freshly cleaved mica. After the solvent evaporated, thin film of PA9EO7 was obtained. Further treatments have been done on the sample films. The first one was annealing the sample film at 60°C for 12 h in order to improve the molecular packing arrangement. The second treatment was rubbing the sample film and then annealing it at 60°C for a further 12 h. The films were removed by water and picked up on 400-mesh Cu grids. The samples on Cu grids were obliquely shadowed with Pt/C at an angle of tg = 1:4 with the substrates in a vacuum evaporator to improve the contrast during morphology observation. The calibration substance Au was occasionally evaporated after carbon coating.

Thermograms were obtained using Perkin-Elmer DSC at a scanning rate of 5°C/min under nitrogen. Optical textures were obtained using a LEICA POM in cross-polarized mode. XRD patterns were recorded on a Rigaku D/max 2500 PC diffractometer at room temperature using X-ray from Cu Kα

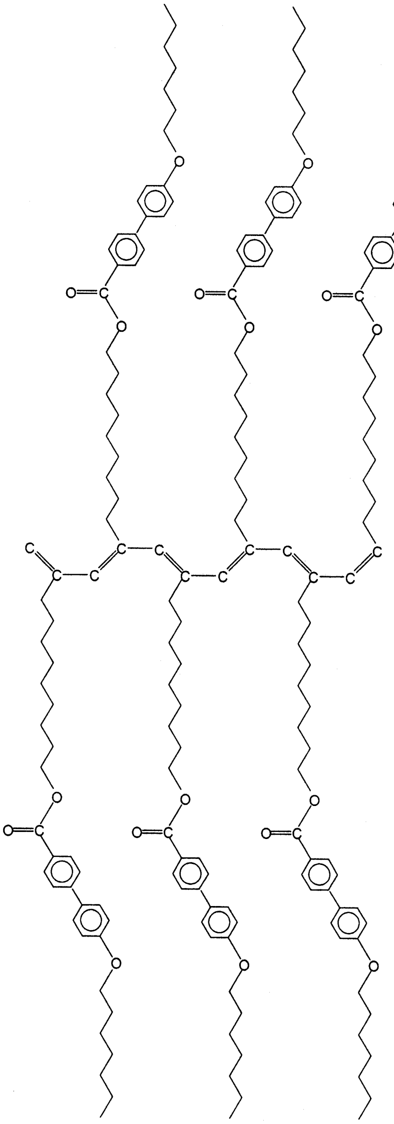


FIGURE 1 Molecular structure of PA9EO7.

radiation with a wavelength of 1.54056 Å. The TEM samples were investigated using a JEOL2010 TEM operated at 200 kV. A field-limiting aperture of 50 μm in diameter was used to perform the selected area electron diffraction (ED) experiments.

RESULTS AND DISCUSSION

We synthesized a liquid crystalline polyacetylene by incorporation of biphenyl pendants into the polyacetylene structure through a long spacer length. The DSC thermogram recorded on the first heating scan is shown in Figure 2. Two peaks corresponding to S_B–S_A and S_A–i are observed at 77.4 and 129.0°C, respectively. When a polymer thin film is prepared by evaporation of its 1%toluene, sanded texture is observed (Fig. 3). In order to obtain more information about crystallographic structure, XRD experiment is carried out. Figure 4 shows the XRD curve of the polymer. Derived from Bragg law, $2d\sin\theta = n\lambda$, d-spacings of the reflection peaks at low angles have integral multiple relationship, i.e., $d_1 = 2d_2 = 3d_3 = 34.62\,\text{Å}$ (subscript represents the sequence of reflection peak appeared in the XRD pattern from low angle to wide angle). Long distance regularity of 34.62 Å is detected in the structure.

Figure 5a shows the morphology of PA9EO7 obtained by evaporation of its toluene solution on thin carbon film and then annealing the sample at 60°C for 12 h. It gives a hexagonal form with a dimension of about 2 μm. Its in situ ED pattern is shown in Figure 5b. It forms a hexagonal two-dimensional lattice. The d-spacing of the strong ED spots calculated by the calibration

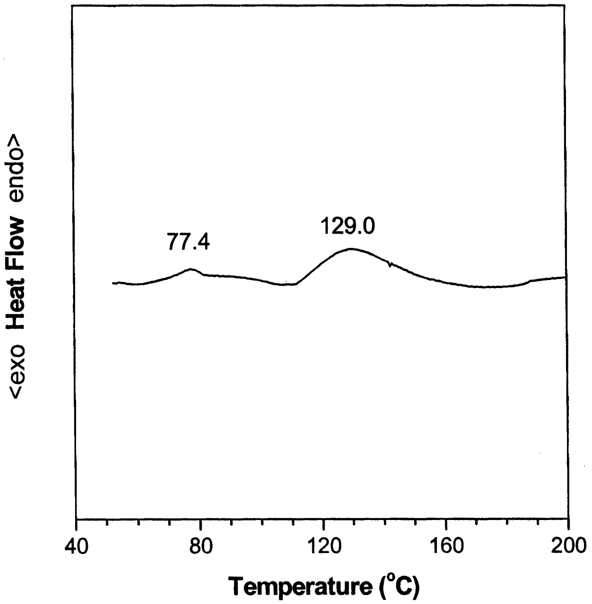


FIGURE 2 DSC heating curve of PA9EO7 from toluene solution at scanning rate of 5°C/min under nitrogen atmosphere.

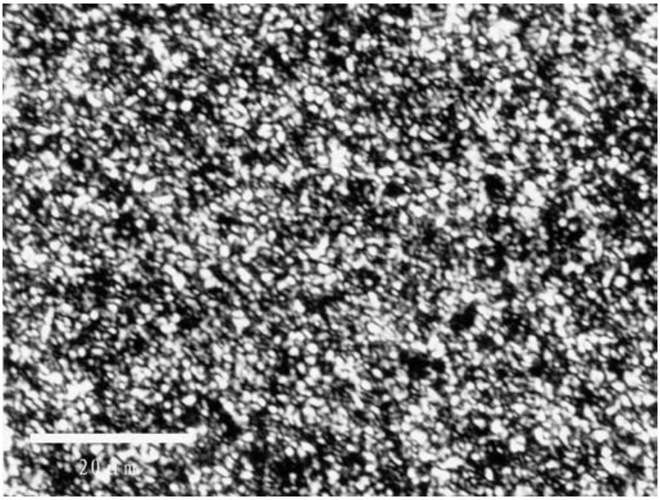


FIGURE 3 Sanded texture of PA9EO7.

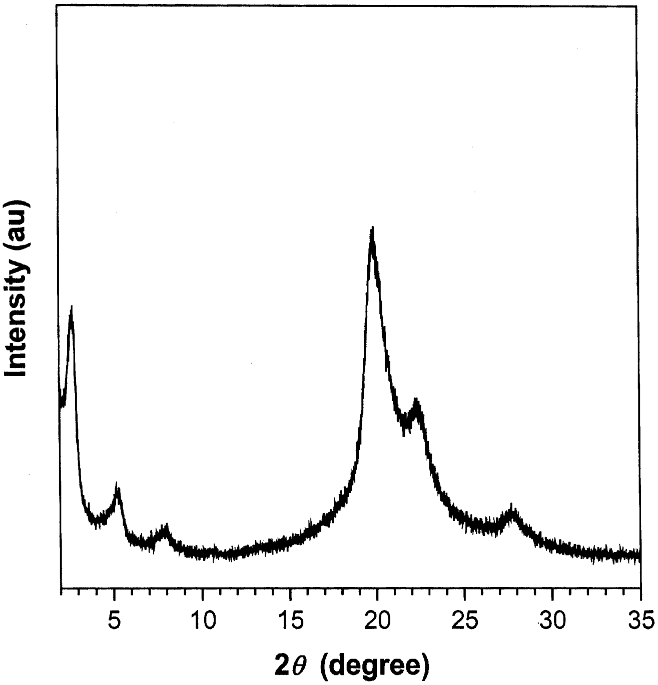
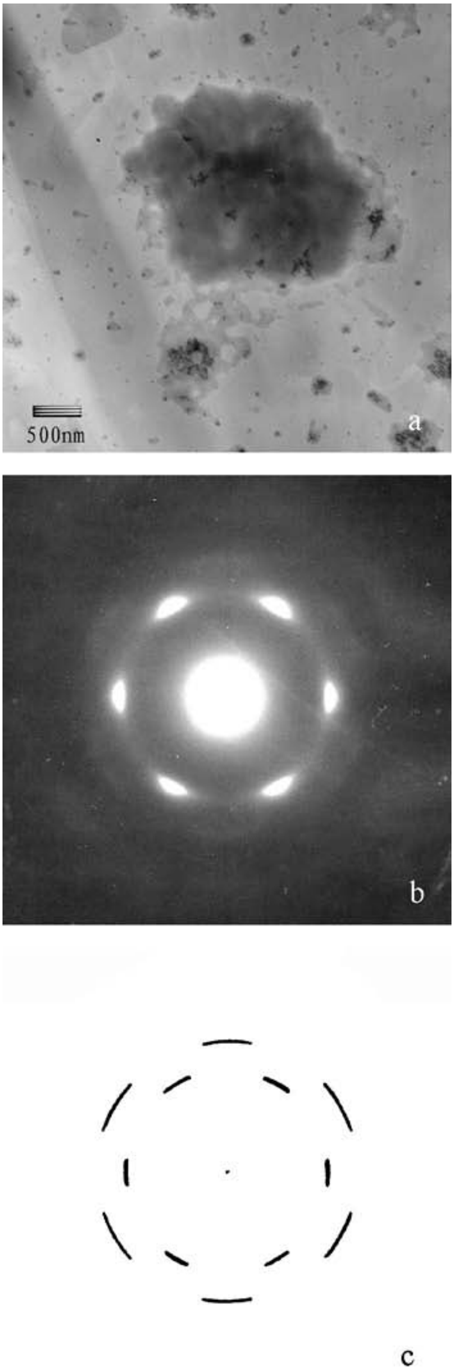


FIGURE 4 XRD pattern of PA9EO7.


500nm
a
b
c

substance Au is 4.51 Å, which corresponds to the XRD peak at $2\theta = 19.67°$ (Fig. 4). In addition, there are six hexagonal weak diffraction arcs outside the circle defined by the strong hexagonal reflection spots. Besides, each diffraction arc locates on the perpendicular bisector of its two neighboring strong diffraction spots, as shown clearly in the model pattern in Figure 5c. The strong ED spots and the weak ED arcs are, however, two different sets of ED patterns, suggesting that there are two kinds of different hexagonal molecular packing arrangements in this direction.

In order to obtain the ED patterns of different zones, we rubbed the sample film after it was annealed at 60°C for 12 h. Figure 6a shows the resultant morphology. Clearly, the rubbing trace still remains in the image. Figure 6b is its in situ ED pattern, which is a classical ED pattern of smectic phase. The strong ED arcs, whose direction are parallel to the rubbing direction and are close to the incident electron beam direction, correspond to a long distance regularity of 34.62 Å. Those weak ED arcs, in which their direction is normal to that of the strong ED arcs and located far from the incident electron beam, correspond to the lateral distance between the mesogens.

The ED arcs close to the incident electron beam suggest that the orientation of long distance regularity is not perfectly uniform in the selected area. In order to improve the orientation, the rubbed sample was annealed at 60°C for 12 h. The morphology is shown in Figure 7a. The rubbing trace disappeared. Compare this to the ED pattern in Figure 6b, where the ED arcs close to the incident electron beam turn to spots, which indicates uniform orientation of long distance regularity in the selected area (Fig. 7b). Along the direction of the ED spots, two weak diffraction arcs located almost outside the ED ring of calibration substance Au are observed (Fig. 7c). It shows a much shorter regular packing arrangement (2.15 Å) than the long distance regularity of 34.62 Å. In the direction normal to that of long distance regularity, two sets of ED arcs are found which correspond to the X-ray reflection peaks at $2\theta = 19.67$ and 27.50° in Figure 4 and suggest that there are two different kinds of lateral distance. It is worth mentioning that the ED arcs near to the incident electron beam correspond to the strong ED spots in Figure 5b and the ED arcs far from incident electron beam correspond to the weak ED arcs in Figure 5b.

Two kinds of packing arrangements exist in PA9EO7 from its toluene solution. The first is a hexagonal phase, in which the long distance regularity is 34.62 Å and the lateral distance between mesogenic pendants is

FIGURE 5 (a) Morphology of PA9EO7 by evaporation of its toluene solution on carbon film and then annealing for 12 h at 60°C, (b) in situ ED pattern of the morphology, and (c) model of the ED pattern.

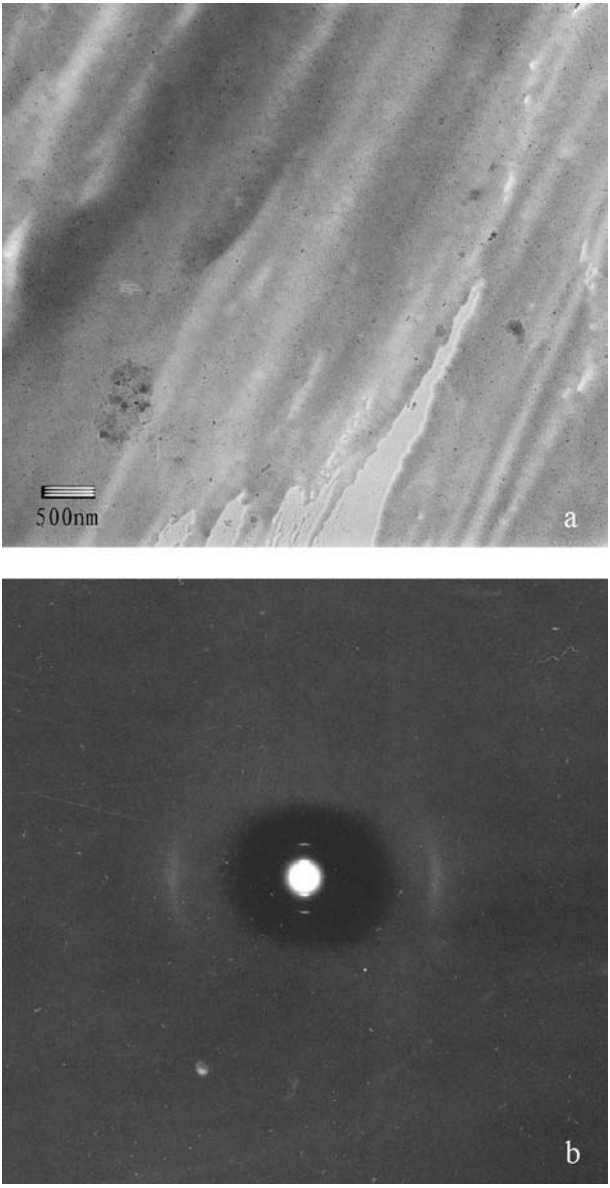


FIGURE 6 (a) Morphology of rubbed PA9EO7 and (b) in situ ED pattern of rubbed sample.

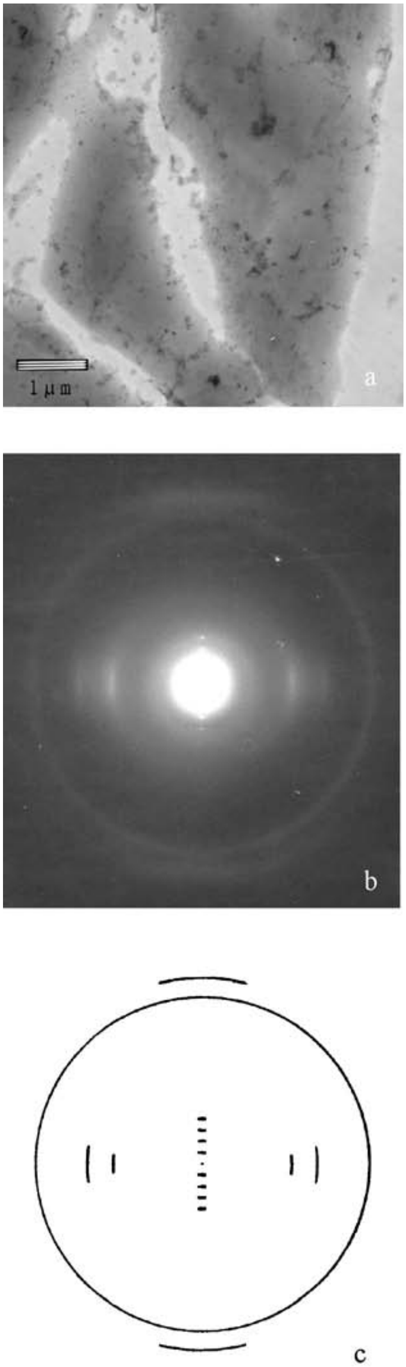


FIGURE 7 (a) TEM morphology of PA9EO7 annealed for 12 h at 60°C after rubbed, (b) in situ ED pattern of morphology, and (c) model of the ED pattern in (b).

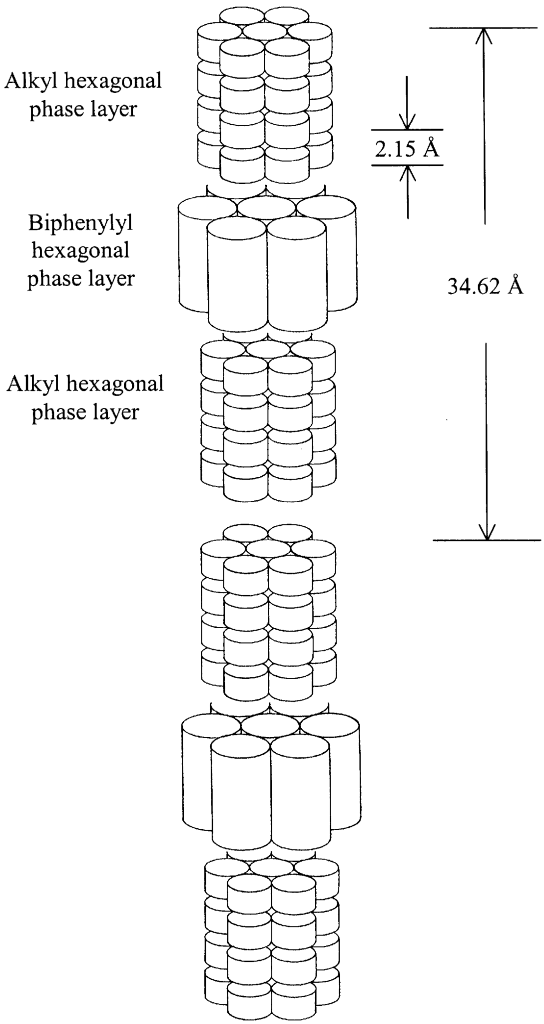


FIGURE 8 Two repeat unit of the sandwich structure adopted by PA9EO7 from toluene solution.

4.51 Å. The XRD peak at $2\theta = 22.57°$ (in Figure 4) is one of the (014) plane. Therefore, the first kind of molecular packing arrangement is a high order smectic phase. The second is also a hexagonal phase but the repeat distance of layer is 2.15 Å. The lateral intermolecular distance is 3.24 Å.

As shown in Figure 1, the side-chains on the same side of one backbone are separated by two single bonds and two double bonds, corresponding to a length of 4.2 Å. Such distance clearly cannot accommodate the side-chain from the neighboring polymer backbone. Therefore, the side chains on one polymer backbone tend to overlap with those on the other side of the neighboring polymer chain. This results in an arrangement in an anti-parallel overlapping manner when viewing parallel to the smectic layers. The biphenyl pendants are thus packed as in a hexagonal fashion. The packing of the nonyl spacer and the heptyloxy tail is affected by two factors. First, since they are connected at the two ends of the biphenyl pendant, they are also induced to form into a hexagonal phase. Second, because of the influence of the rigid polyacetylene backbone, it is hard for the nonyl spacer and the heptyloxy tail to adopt an orthorhombic unit cell similar to that of polyethylene [14,15]. The repeat unit is 2.15 Å in length, which is a little shorter than the unit cell constant (2.53 Å) of polyethylene because the alkyl chains do not adapt a well extensive conformation. As a conclusion, PA9EO7 obtained from toluene is a sandwich structure with an arrangement of alkyl hexagonal phase layer+biphenylyl hexagonal phase layer+alkyl hexagonal phase layer (Fig. 8). The total thickness of the sandwich is 34.62 Å and the alkyl hexagonal phase layer has an intrinsic repeat distance of 2.15 Å.

CONCLUSIONS

PA9EO7 from toluene solution exhibits a high order smectic phase, which is a sandwich structure. The thickness of the structure is 34.62 Å. The nonyl spacer and the heptyloxy tail arrange in a hexagonal manner because of the inducing effect of the biphenyl pendant and the rigid polymer backbone. The distance between two methylenes is 2.15 Å.

PA9EO7 gives a hexagonal morphology, and the layers of smectic phase are parallel to the substrate. Rubbing can direct the arrangement normal to the substrate, but the orientation of the long distance regularity is not perfectly uniform. Annealing at 60°C can adjust the conformation and the position and gives a uniform orientation.

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