Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A triphenylene-containing side chain liquid crystalline ladder-like polysiloxane and its highly ordered superstructure

Chao-Yi Ba[a]; Zhong-Rong Shen[a]; Hai-Wen Gu[a]; Guang-Qing Guo[a]; Ping Xie[a]; Rong-Ben Zhang[a]; Chuan-Feng Zhu[b]; Li-Jun Wan[b]; Fu-You Li[c]; Chun-Hui Huang[c]
[a] State Key Laboratory of Polymer Physics and Chemistry, PCLCC, [b] CAS Key Laboratory of Molecule Nanostructure and Nanotechnology, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, PR China, [c] College of Chemistry and Molecular Engineering, Beijing University, Beijing, 100871, PR China,

To cite this Article Ba, Chao-Yi , Shen, Zhong-Rong , Gu, Hai-Wen , Guo, Guang-Qing , Xie, Ping , Zhang, Rong-Ben , Zhu, Chuan-Feng , Wan, Li-Jun , Li, Fu-You and Huang, Chun-Hui(2003) 'A triphenylene-containing side chain liquid crystalline ladder-like polysiloxane and its highly ordered superstructure', Liquid Crystals, 30: 3, 391 — 397

To link to this Article: DOI: 10.1080/0267829031000089924

URL: http://dx.doi.org/10.1080/0267829031000089924

LIQUID CRYSTALS, 2003, VOL. 30, NO. 3, 391–397

A triphenylene-containing side chain liquid crystalline ladder-like polysiloxane and its highly ordered superstructure

CHAO-YI BA, ZHONG-RONG SHEN, HAI-WEN GU, GUANG-QING GUO,
PING XIE, RONG-BEN ZHANG*
State Key Laboratory of Polymer Physics and Chemistry, PCLCC†,

CHUAN-FENG ZHU, LI-JUN WAN
CAS Key Laboratory of Molecule Nanostructure and Nanotechnology,
Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing, 100080, PR China

FU-YOU LI and CHUN-HUI HUANG
College of Chemistry and Molecular Engineering, Beijing University, Beijing,
100871, PR China

(*Received 17 April 2002; in final form 4 November 2002; accepted 21 November 2002*)

A liquid crystalline discotic triphenylene-containing side chain ladder-like polysiloxane (LPS) derivative was prepared by hydrosilylation. The superstructure was investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and isotherm surface pressure (π)–area (A) diagrams based on LB-film experiments. The XRD results suggest that the discotic triphenylene units in the side chains stack to form a columnar structure and the columns further align with each other to form a board-like superstructure because of the semi-rigidity of the ladder-like backbone. This suggestion has been confirmed by parallel nanowire-like stripes observed in the AFM image. Mixing small amounts of the corresponding low molar mass molecules with the polymer leads to a more ordered and denser columnar stacking, as shown by sharpened XRD patterns and a π–A curve with a steeper slope, higher collapse pressure and lower collapse area than those obtained either for the low molar mass molecules or the polymer individually.

1. Introduction

Hexakisalkoxytriphenylenes, are well known representatives of discotic liquid crystals, and have attracted much attention because of their unique photoconductive properties [1, 2]. Generally, the disc-like molecules self-assemble into a columnar mesophase through face-to-face stacking of the aromatic cores. The large π–π overlap between the electron-rich discotic units provides a pathway for transfer of charge or energy, while the peripheral hydrocarbon chains act as an insulating mantle [3]. A charge-carrier mobility of the order of $10^{-1}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ has been reported in the three-dimensionally ordered helical phase of hexahexylthiotriphenylene [4]. This is comparable to charge-carrier mobility in organic single crystals. These results promise future application as photo-electronic materials.

However, the poor stability and processibility of the low molar mass disc-like molecules are obstacles for their applications. Polymerization is a useful means to overcome these disadvantages [5]. The disc-like molecules either act as the repeat units in the main chain or are attached to the polymeric backbone as pendant side groups [6–8]. Discotic liquid crystalline polymer networks and elastomers have also been reported [9, 10]. Interestingly, rigid aromatic polyamides and polyesters with disc-like units in the main chain can form a board-like nematic phase with the boards stacked parallel to one another, as shown in figure 1 [11]. In general, because of their high viscosity, the macroscopic alignment of the columnar structure should be achievable through mechanical stretching or long term thermal treatment [12].

---

*Author for correspondence;
e-mail: zhangrb@infoc3.icas.ac.cn

† Polymer Chemistry laboratory, Chinese Academy of Sciences and China Petro-chemical Corporation

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000089924

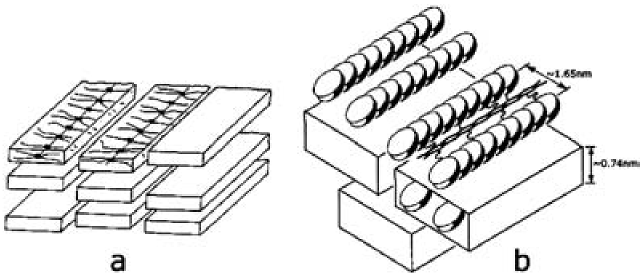


Figure 1. Schematic representation of two kinds of board-like superstructures based on (*a*) rigid discotic main chain polymer, (*b*) polymer **4**.

Ladder-like polysiloxanes (LPSs), which were first synthesized by this group via stepwise–coupling polymerization (SCP), are a new type of glass-like film-forming materials. Their inorganic semi-rigid backbone results in their excellent properties. In particular, various reactive LPSs containing vinyl, allyl and hydrogen side groups can be used to form functionalized polymers. Starting from the reactive LPSs, a series of fishbone-like or rowboat-like liquid crystalline polymers containing end-on or side-on fixed mesogens have been synthesized by hydrosilylation reactions [13]. Moreover, we have prepared several types of discotic compound, such as columnar bis(β-diketonate)copper(II) complexes with oligo(ethylene oxide) side chains [14], a metal chelate-bridged quasi-ladder main chain discotic liquid crystal polymer [15], and a trefoil-shaped liquid crystal based on 1,3,5-triazine with carbazole groups [16]. Their superstructures and conductive behaviour have been investigated in a preliminary manner.

In this paper, we use a reactive ladder-like co-poly-allyl-methyl-siloxane (AM-LPS) and a mono-functionalized triphenylene derivative as starting materials to synthesize triphenylene-containing side chain liquid crystalline LPS via hydrosilylation. We anticipated that the semi-rigid ladder-like backbone would assist the attached disc-like triphenylene units to stack into stable and highly ordered columnar structures.

2. Experimental

2.1. *Characterization*

FTIR spectra were recorded using a Bruker EQUINOX55 spectrometer. ^{1}H NMR spectra were obtained with a JNH-FX100 (JBOX) NMR (300 MHz) spectrometer using $CDCl_3$ as solvent. Elemental analysis was performed using a Heraeus CHN-RAPID, Datel Systems, Inc (Germany). X-ray diffraction (XRD) analysis was carried out using a Rigaku D/MAX 2400 X-ray diffractometer. The sample was annealed at 50°C and then quenched to room temperature. DSC measurements were made with a Mettler Toledo Star-822 differential scanning calorimeter. Atomic force microscopy imaging was done in contact mode with a Nanoscope III A AFM instrument (Digital Instruments, USA) at room temperature in air. To prepare the sample, the polymer was dissolved in THF and this dilute solution was coated onto a newly cleaved mica surface by dipping to obtain the quasi-monolayer thin film. π–A diagrams were determined using a 622 type single trough membrane-drawing instrument from the Nima Company using chloroform as solvent.

2.2. *Materials*

Reagents and solvents were used as purchased without further purification, unless otherwise stated. 1,1,3,3-Tetramethyldisiloxane of analytical grade was purchased from Acros Company. Methyltrichlorosilane and allyl bromide were distilled before use. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone. Dicyclopentadienylplatinum dichloride (Cp_2PtCl_2), used as the hydrosilylation catalyst, was prepared according to literature methods [17].

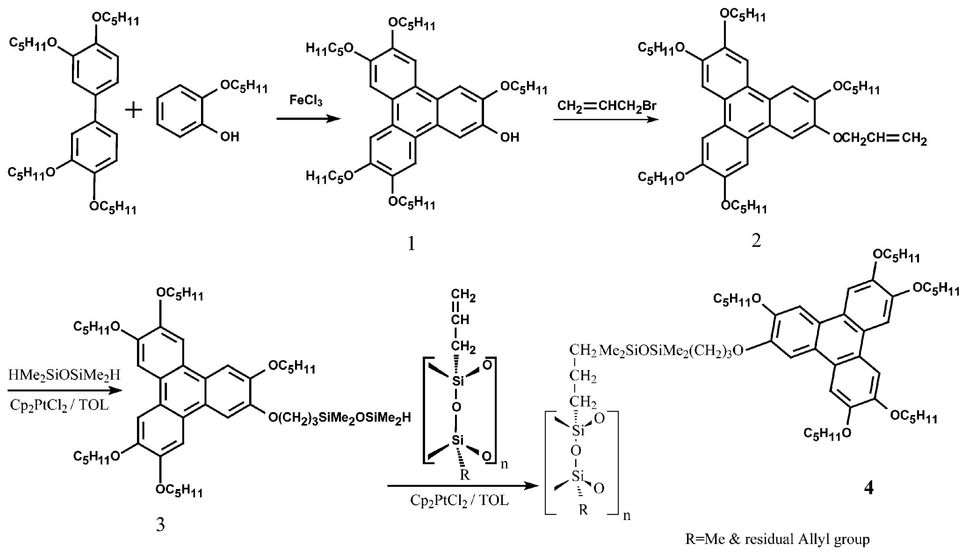
The synthetic route and chemical structures of the target polymer and the intermediates are shown in the scheme.

2.2.1. *Synthesis of 2-hydroxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene (**1**)*

Monomer **1** was prepared by directly coupling 3,3′,4,4′-tetrapentoxybiphenyl and excess *o*-pentoxy phenol following a similar procedure to that described in [18] instead of the selective cleavage of the ether as described in most literature reports [19]. Methanol and dichloromethane were removed and the crude product separated by silica gel column chromatography, eluting with benzene to give the product as a pale yellow solid. This was recrystallized from ethanol to give a white solid, yield 65%. IR (KBr): 3549 (OH), 3079, 2955, 2931, 2860 cm^{-1} (CH, aromatic and aliphatic). ^{1}H NMR (200 MHz $CDCl_3$): $\delta = 7.96, 7.83, 7.77$ ($3 \times$ s, Ar–$\underline{H}$, 6H), 5.91 (s, O$\underline{H}$, 1H), 4.31–4.19 (m, $OC\underline{H}_2$, 10H), 1.97–1.90 (m, $OCH_2C\underline{H}_2$, 10H), 1.58–1.39 (m, $O(CH_2)_2(C\underline{H}_2)_2$, 20H), 0.97 (t, $C\underline{H}_3$, 15H).

2.2.2. *Synthesis of 2-allyloxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene (**2**).*

Monomer **1** (0.7 g, 1.0 mmol) was stirred with allyl bromide (0.2 ml, 2.3 mmol) and anhydrous potassium carbonate (11 g) in ethanol (50 ml) and heated at reflux for 30 h. The solution was decanted carefully into water (70 ml) and extracted with dichloromethane (4×25 ml). The organic layer was dried and evaporated, and the crude product recrystallized from ethanol to give a white crystalline compound, yield 85%. IR (KBr): 3079, 2955, 2931, 2860 (CH, aromatic and aliphatic), 1648 cm^{-1} ($CH{=}CH_2$). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.92$–7.77 (m, Ar–$\underline{H}$, 6H), 6.32–6.12 (m, OCH_2, $C\underline{H}{=}CH_2$1H),



Scheme. Synthetic route and chemical structure of the triphenylene-containing side chain LPS **4**.

5.59–5.32 (m, $OCH_2CH{=}C\underline{H}_2$, 2H), 4.82 (d, $OC\underline{H}_2CH{=}CH_2$, 2H), 4.22 (t, $OC\underline{H}_2$, 10H), 1.98 (m, $OCH_2C\underline{H}_2$, 10H), 1.66–1.36 (m, $O(CH_2)_2(C\underline{H}_2)_2$, 20H), 0.97 (t, $C\underline{H}_3$, 15H). Elemental analysis: calc. for $C_{46}H_{66}O_6$ C 77.31, H 9.24; found C 77.20, H 9.21%.

2.2.3. *Synthesis of 2-(1′,1′,3′,3′-tetramethyldisiloxane)-propoxy-3,6,7,10,11-pentakis(pentyloxy)-triphenylene (**3**).*

Monomer **2** (0.4 g, 0.56 mmol) was stirred vigorously under argon with 1,1,3,3-tetramethyldisiloxane (1 ml, 5.6 mmol) at 70°C for 48 h, using Cp_2PtCl_2 as the catalyst and methylthiophene-free dry toluene (50 ml) as solvent. The solvent and the remaining 1,1,3,3-tetramethyldisiloxane were removed under vacuum. The product was obtained as a viscous solid, yield 90%. IR (KBr): 2961, 2934, 2861 (CH, aromatic and aliphatic), 2123 (Si–H), 1089, 1033 cm^{-1} (Si–O–Si). ^{1}H NMR (300 HMz, $CDCl_3$): $\delta = 7.82$ (s, Ar–$\underline{H}$, 6H), 4.23 (m, $OC\underline{H}_2$, 12H), 1.96 (m, $OCH_2C\underline{H}_2$, 12H), 1.51 (m, $O(CH_2)_2(C\underline{H}_2)_2$, 20H), 0.98 (t, $O(CH_2)_4C\underline{H}_3$, 15H), 0.21–0.07 (m, $(C\underline{H}_3)_2SiOSi(C\underline{H}_3)_2$ & $C\underline{H}_2Si$, 14H).

2.2.4. *Synthesis of the triphenylene-containing side chain-grafted LPS (**4**)*

Reactive AM-LPS was synthesized through stepwise coupling and polymerization as described elsewhere [20]. An allyl to methyl molar ratio of 3 : 2 was calculated from the peak areas in the ^{1}H NMR spectrum. The characterization data for the AM-LPS is summarized in table 1. The grafted polymer was synthesized by a hydrosilylation reaction using excess of compound **3** (424 mg, 0.5 mmol) and MA-LPS (36 mg, containing 0.25 mmol allyl group), with Cp_2PtCl_2 as the catalyst and thiophene-free dry toluene (50 ml) as the solvent. The mixture was stirred under an argon atmosphere at 90°C for 72 h. The solvent was evaporated to give a solid product, which was dissolved in toluene and reprecipitated with methanol five times to remove low molar mass impurities. Finally a solid, film-forming product was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): all peaks were broad and no peak splitting could be detected. $\delta = 7.80$ (Ar–$\underline{H}$), 5.78, 5.0 (residual vinyl group), 4.22 ($OC\underline{H}_2$), 1.93 ($OCH_2C\underline{H}_2$), 1.54–1.45 ($O(CH_2)_2(C\underline{H}_2)_2$ & $C\underline{H}_2Si$), 0.98 ($O(CH_2)_4C\underline{H}_3$), 0.76–0.73 ($C\underline{H}_2Si$), 0.2–0.1 ($(C\underline{H}_3)_2SiOSi(C\underline{H}_3)_2$). From the ratio of relative intensities of the two peaks representing hydrogen atoms on the aromatic core and on the residual vinyl group,

Table 1. Characterization of AM-LPS.

Parameter	Observations
Solubility	Soluble in toluene, THF, chloroform, acetone
FTIR (KBr, cm^{-1})	3431 (OH); 3082 (=C–H); 2977 (CH_3); 1635 (>C=C<); 1118 (Si–O–Si); 770 (Si–C)
^{1}H NMR ($CDCl_3$, ppm)	0.20 ($-CH_3$); 1.66 ($-C\underline{H}_2CH{=}CH_2$); 4.96 ($-CH_2CH{=}C\underline{H}_2$); 5.78 ($-CH_2C\underline{H}{=}CH_2$)
M_n by VPO	1.6×10^4
Distance [d(nm)/2θ(°)] by XRD	1.07/8.22 and 0.40/22
T_g (°C)	28.25

the grafting ratio of triphenylene-containing side chains was calculated as 51% of the total side groups. The ^{1}H NMR spectrum is shown in figure 2.

3. Results and discussion

Three key points for the synthesis of the target polymer should be noted. First, the molar ratio of allyl to methyl in the AM-LPS could be controlled by adjusting the feed ratio of the original materials, allyltrichlorosilane and methyltrichlorosilane, and is almost the same as the feed ratio. Secondly, the Si–H terminated triphenylene derivative **3** can be prepared by a hydrosilylation reaction using the vinyl-terminated monomer **2** and excess 1,1,3,3-tetramethyldisiloxane (molar ratio = 1 : 10) in order to reduce the vinyl-termination of 1,1,3,3-tetramethyldisiloxane. The excess 1,1,3,3-tetramethyldisiloxane can be easily removed under vacuum. Finally, the low molar mass impurity mixed with the target polymer can be completely removed by repeated precipitation with methanol.

Following the same route, we have synthesized a series of AM-LPSs with different molar ratios of allyl to methyl, such as 100 : 0, 60 : 40, and 50 : 50. They were used to react with the triphenylene derivative **3**. As a result, the molar ratio of triphenylene side groups to the total side groups was about 50% independent of the amount of allyl groups. This result means that each repeat unit ($2SiO_{3/2}$) on the ladder-like backbone can support only one triphenylene side group.

The DSC trace of polymer **4** (figure 3) shows two transitions, at 20.6 and 62.1°C, which are assigned to the glass transition and transition from columnar to isotropic phase, respectively. After annealing at 50°C, the columnar structure can be frozen to room temperature.

In general, XRD patterns of discotic liquid crystalline main chain and side chain polymers show an intense peak in the small angle region and a diffuse peak in the wide angle region, which can be assigned to column–column spacing and disc–disc spacing in a column, respectively [12]. In polymer **4**, there are three diffraction peaks corresponding to spacings of 1.65 nm ($2\theta = 5.4°$), 0.74 nm ($2\theta = 11.9°$) and 0.40 nm ($2\theta = 22°$), respectively, as shown in figure 4(*b*). Similar XRD patterns have been found for a few special discotic liquid crystalline main chain polymers, in which disc-shaped units are linked together by amide or ester groups to form a board-like

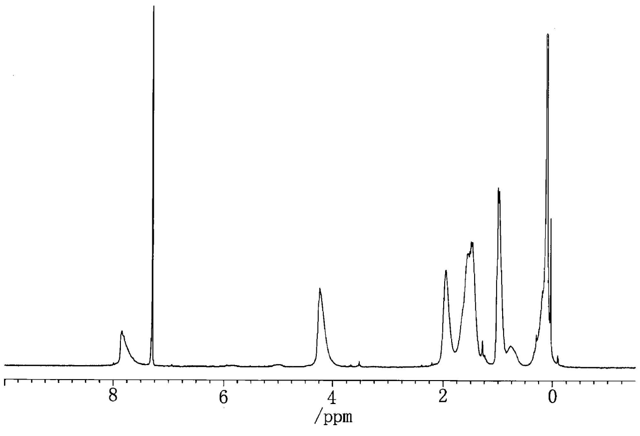


Figure 2. ^{1}H NMR spectrum of polymer **4**.

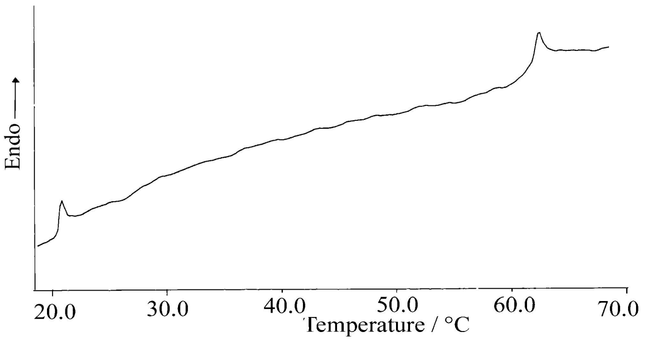


Figure 3. DSC trace of polymer **4**.

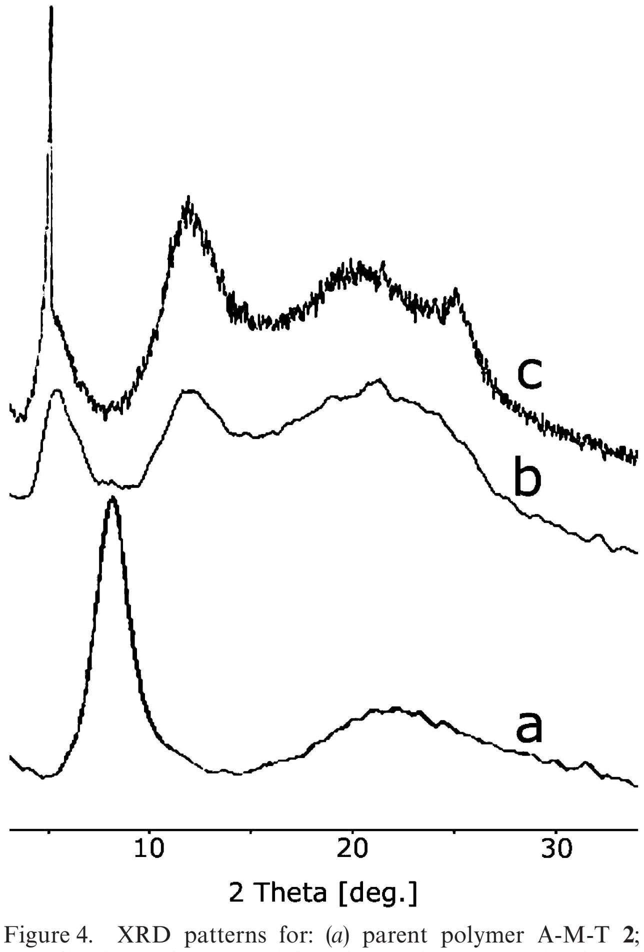


Figure 4. XRD patterns for: (*a*) parent polymer A-M-T **2**; (*b*) triphenylene-containing side chain LPS **4**; (*c*) mixture of polymer **4** with 10 mol% of **5**.

nematic, represented as figure 1 (*a*) [11]. Thus we suggest that a board-like superstructure can also be formed via the parallel alignment of the ladder-like main chain with discotic side groups, figure 1 (*b*). The peak at $2\theta = 11.9^\circ$ ($d = 0.74$ nm) can be assigned to the board thickness which is approximately equal to the diameter of the column. A diffuse peak ($2\theta = 22^\circ$) covering the wide angle region can be related to the flexible aliphatic chains and spacers. In order to interpret the semi-rigid character of the ladder-like backbone, the XRD pattern of the parent polymer A-M-T is also shown, figure 4 (*a*). In this there are two diffraction peaks corresponding to spacing of 1.07 nm ($2\theta = 8.22^\circ$) and 0.40 nm ($2\theta = 22^\circ$) respectively, which can be assigned to the width and thickness of the ladder-like backbone [20]. It is obviously different from those of flexible chain polymers.

Interestingly, when mixing the polymer with only 10% molar ratio of low molar mass hexapentoxytriphenylene (**5**) molecules, a new peak appears at $2\theta = 25.04^\circ$ ($d = 0.36$ nm) which corresponds to disc–disc spacing, see figure 4 (*c*) [12]. The other two peaks at $2\theta = 8.22^\circ$ and 22° are also sharpened. This means that intercalated low molar mass discotic molecules can obviously improve the columnar stacking.

LB-membrane experiments provide further data in support of this suggestion. Previously there have been some reports of the spreading behavior of discotic liquid crystalline compounds to form mono- and multi-layers at the air–water interface [21, 22]. Unconventional low collapse areas of the triphenylene derivatives have been explained by an 'edge on' model for the arrangement of the aromatic cores, which can be attributed to the strong π–π interaction between the cores. In this case the isotherm surface pressure (π)–area (A) diagrams of four samples are given in Figure 5. All parametric data characterizing the ability to form monolayers are listed in table 2. There are some differences in the monolayer behaviour of the 2,3,6,7,10,11-hexakispentyloxytriphenylene **5** and the monohydroxy compound **1**. Compound **1** has a plateau region, which is similar to the coexistence region in conventional amphiphiles, and the low collapse area corresponds to tight packing. Unfortunately, the monolayer of polymer **4** is less stable, in the sense that collapse takes place at a lower spreading pressure. This may be attributed to the limited grafting ratio of triphenylene-containing side chains on the ladder-like main chain. However, it is interesting to note that, the mixture **5** + **4** [molar ratio **5**:**4** = 1:10] shows good ability to form a monolayer. This has been demonstrated by the lowest collapse area, higher collapse pressure and steep solid phase slope. It should be noted, that the surface area per molecule of the mixture is significantly smaller than the specific area for sample **5**, and even less than that of hydrophilic hydroxy-containing sample **1**. This significant effect, may be explained by the intercalation of low molar mass hexapentoxytriphenylene molecules between the homologous side chains which allows a more dense packing to be obtained. This is in accord with the interpretation of the XRD results.

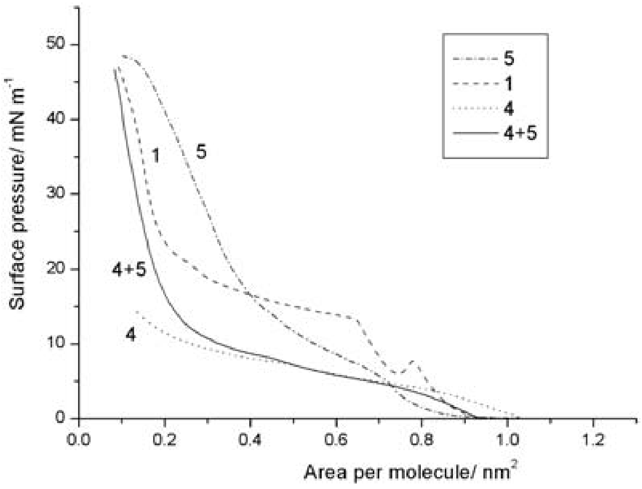


Figure 5. Isotherm surface pressure (π)–area (A) diagrams.

The highly ordered superstructure of polymer **4** was further imaged by AFM in contact mode. Figure 6 (*a*) shows its fine structure, which consists of alternate dark and bright stripes. The average distance between two neighbouring bright stripes is about 1.7 nm, which is in agreement with the inter-columnar distance obtained by XRD. This result provides further evidence demonstrating that the highly ordered columnar phase can easily be formed. The bright stripes in the image represent the columnar structure. This image also indicates that the columns are aligned almost parallel to the substrate surface like nanowires and shown schematically in Figure 6 (*b*). By contrast, columns of low molar weight discotic molecules tend to lie perpendicular to the substrate surface.

4. Conclusions

A mono-functionalized triphenylene derivative was grafted onto the LPS main chain by a hydrosilylation reaction. A board-like columnar structure was formed

Table 2. Characterization of the ability to form a monolayer.

Compound	Collapse area /nm^2	Collapse pressure /mN m^{-1}	Solid phase slope /mN m^{-1} nm^{-2}
5	0.50	48	143
1	0.26	47	375
4	0.49	14	—
5 + **4**	0.22	46	375

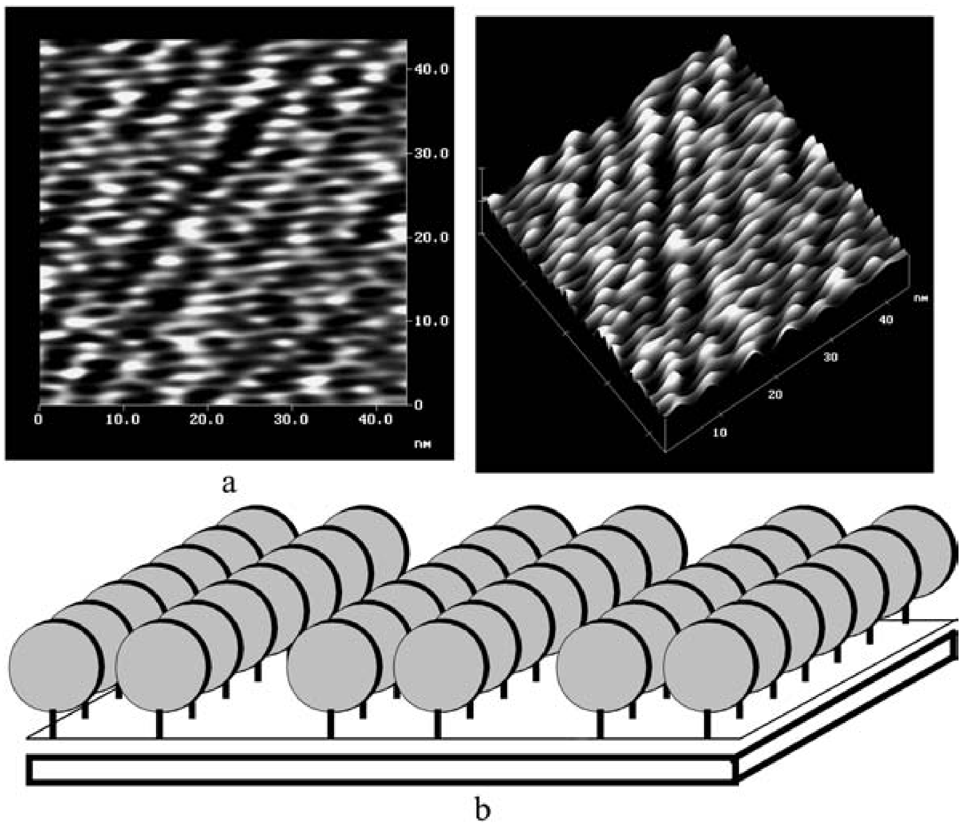


Figure 6. (*a*) AFM image of the triphenylene-containing side chain LPS; (*b*) schematic model for columns aligned on the mica sheet surface.

as shown by the XRD results. Its formation is attributed to the parallel alignment of the columns attached on the semi-rigid ladder-like main chains. Furthermore, a well aligned nanowire structure was imaged by AFM, in agreement with the interpretation of the XRD results. Interestingly, the mixing of a small amount of low molar mass discotic homologue with the polymer can improve the ordering of the superstructure, as demonstrated by the sharpened XRD patterns, high collapse pressure and low collapse area in the LB-membrane process.

This project was supported by NSFC (29974036, 50073028).

References

[1] Bengs, H., Closs, F., Frey, T., Funhoff, D., Ringsdorf, H., and Siemensmeyer, K., 1993, *Liq. Cryst.*, **15,** 565.

[2] Simmerer, J., Glusen, B., Paulus, W., Kettner, A., Schuhmacher, P., Adam, D., Etzbach, K. H., Siemensmeyer, K., Wendorf, J. H., Ringsdorf, H., and Haarer, D., 1996, *Adv. Mater.*, **8,** 815.

[3] Van Nostrum, C. F., 1996, *Adv. Mater.*, **8,** 1027.

[4] Adam, D., Schuhmacher, P., Simmerer, J., Häussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., and Haarer, D., 1994, *Nature*, **371,** 141.

[5] Chandrasekhar, S., 1993, *Liq. Cryst.*, **14,** 3.

[6] (*a*) Wang, T., Yan, D. H., Zhou, E. L., Karthaus, O., and Ringsdorf, H., 1998, *Polymer*, **39,** 4509; (*b*) Herrmann-Schönherr, O., Wendorff, J. H., Kreuder, W., and Ringsdoff, H. 1986, *Makromol. Chem. rapid Commun.*, **7,** 97.

[7] Krender, W., and Ringsdoff, H., 1983, *Makromol. Chem. rapid Commun.*, **4,** 807.

[8] HSU, T.-C., Hüser, B., Pakula, T., Spiess, H. W., and Stamm, M., 1990, *Makromol. Chem.*, **191,** 1597.

[9] Disch, S., Finkelmann, H., Ringsdorf, H., and Schuhmacher, P., 1995, *Macromolecules*, **28,** 2424.

[10] Bengs, H., Finkelmann, H., Kupfer, J., Ringsdorf, H., and Schuhmacher, P. 1993, *Makromol. Chem. rapid Commun.*, **14,** 445.

[11] (*a*) Herrmann-Schönherr, O., Wendorff, J. H., Ringsdoff, H., and Tschirner, P., 1986, *Makromol. Chem. rapid Commun.*, **7,** 791; (*b*) Ringsdoff, H., Tschirner, P., Herrmann-Schönherr, O., and Wendorff, J. H., 1987, *Makromol. Chem.*, **188,** 1431; (*c*) Ebert, M., Herrmann-Schönherr, O., Wendorff, J. H., Ringsdoff, H., and Tschirner, P., 1988, *Makromol. Chem. rapid Commun.*, **9,** 445.

[12] Huser, B., Pakula, T., and Spiess, H. W., 1989, *Macromolecules*, **22,** 1960.

[13] (*a*) Xie, P., Xie, Z. S., Wan, Y. Z., Jin, S. Z., Dai, D. R., Hou, J. A., Liu, D. S., and Zhang, R. B., 1996, *Mol. Cryst. liq. Cryst.*, **289,** 59; (*b*) Xie, P., Wan, Y. Z., Zhou, B. S., Hou, J. A., Dai, D. R, Li, Z., Liu, D. S.,

and Zhang, R. B., 1996, *Macromol. Chem. Phys.*, **197,** 745; (*c*) Wan, Y. Z., Huang, Y. X., Xie, P., Li, B., Jin, S. Z., Cao, X. Y., Liu, D. S., Dai, D. R., Li, Z., and Zhang, R. B., 1996, *Macromol. Symp.*, **105,** 249; (*d*) Wan, Y. Z., Xu, L., Ren, L. L., Zhang, L. J., Xie, P., Liu, Y. B., and Zhang, R. B., 1999, *Liq. Cryst.*, **24,** 871; (*e*) Liu, C. Q., Liu, Y., Kong, B., Xie, P., Zhang, R. B., He, C. B., and Chung, N. T. S., 2001, *Liq. Cryst.*, **28,** 35.

[14] Liu, Y., Liu, C., Cui, L., Fan, Z., Xie, P., and Zhang, R., 2000, *Liq. Cryst.*, **27,** 5.

[15] Xie, P., Shen, Z., Liu, Y., Kong, B., Liu, C., Zhang, R. B., Fan, Z., Bai, R., Chung, T. S., and He, C. 2001, *Liq. Cryst.*, **28,** 477.

[16] Bai, R., Li, S., Zou, Y., Pan, C., Xie, P., Kong, B., Zhou, X., and Zhang, R., 2001, *Liq. Cryst.*, **28,** 1873.

[17] Apfel, M. A., Finkelmann, H., Janini, G. M., Laub, R. J., Luhmann, B. H., Price, A, Roberts, W. L., Shaw, T. J., and Smith, C. A., 1985, *Anal. Chem.*, **57,** 651.

[18] (*a*) Boden, N., Bushby, R. J., and Cammidge, A. N., 1995, *J. Am. chem. Soc.*, **117,** 924; (*b*) Bushby, R. J., Cammidge, A. N., Headdock, G., Borner, R. C., and Boden N., 1994, British Patent GB 2 279 072 A (1995, *Chem. Abstr.*, **122,** 239347t).

[19] (*a*) Boden, N., Bushby, R. J., Martin, P. S., Evans, S. D., Owens, R. W., and Smith, D. A., 1999, *Langmuir*, **15,** 3790; (*b*) Boden, N., Bushby, R. J., Cammidge, A. N., El-Mansoury, A., Martin, P. S., and Zhibao Lu, 1999, *J. mater. Chem.*, **9,** 1391.

[20] Li, Z., Cao, X. Y., Xu, H., Xie, P., Cao, M., and Zhang, R. B., 1999, *React. Funct. Polym.*, **39,** 1.

[21] (*a*) Henderson, P., Beyer, D., Jonas, U., Karthaus, O., Ringsdorf, H., Heiney, P. A., Maliszewskyj, N. C., Ghosh, S. S., Mindyuk, O. Y., and Josefowicz, J. Y., 1997, *J. Am. chem. Soc.*, **119,** 4740; (*b*) Gidalevitz, D., Mindyuk, O. Y., Heiney, P. A., Ocko, B. M., Henderson, P., Ringsdorf, H., Boden, N., Bushby, R. J., Martin, P. S., Strzalka, J., McCauley, Jr. J. P., and Smith, A. B., 1997, *J. phys. Chem. B*, **101,** 10 870; (*c*) Vaes, A., Van der Auweraer, M., De Schryver, F. C., Laguitton, B., Jonas, A., Henderson, P., and Ringsdorf, H., 1998, *Langmuir*, **14,** 5250.

[22] (*a*) Albrecht, O., Cumming, W., Kreuder, W., Laschewsky, A., and Ringsdorf, H., 1986, *Colloid polym. Sci.*, **264,** 659; (*b*) Auweraer, M., Catry, C., Feng, C. L., Karthaus, O., Knoll, W., Ringsdorf, H., Sawodny, M., and Urban, C., 1992, *Thin solid Films*, **210/211,** 39.