Thermotropic Liquid Crystalline Behavior of an Amphiphilic Polymer Lacking Mesogens

Hongbin Li, Xi Zhang, Ruifeng Zhang, and Jiacong Shen*

Department of Chemistry, Jilin University, Changchun, 130023, People's Republic of China

Bing Zhao and Weiqing Xu

Key lab of the molecular spectrum and molecular structure, Jilin University, Changchun, 130023, People's Republic of China

Received April 20, 1995; Revised Manuscript Received July 11, 1995[⊗]

ABSTRACT: The thermotropic liquid crystalline behavior of a new kind of amphiphilic polymer without mesogens is reported. The existence and structure for the polymeric mesophase are confirmed and characterized by DSC, X-ray diffraction, optical polarized microscopy, and temperature-dependent FTIR. Due to strong interactions between pendent long alkyl chains, we conclude that some hydrophobic semirigid rods form and are responsible for mesophase formation. Moreover, the flexible polymer network might act as a unique "spacer" group and also assist in mesophase formation.

Introduction

It is well known that molecules with a form-anisotropic architecture, such as a rod- or disk-shaped structure, often exhibit thermotropic liquid crystalline behavior. Likewise, amphiphilic molecules often form lyotropic liquid crystals in aqueous systems due to the hydrophobic effect. Combining the molecular design of thermotropic and lyotropic mesogens, i.e., incorporating the typical thermotropic liquid crystalline building blocks (rod- or disk-shaped) into amphiphiles, amphotropic liquid crystals are formed.[1] Many amphotropic liquid crystalline materials have been investigated,[2−7] and it seems that all thermotropic liquid crystal behavior of amphiphilic molecules originates from these amphotropic liquid crystal materials. In this paper we report thermotropic liquid crystal behavior for an amphiphilic polymer not bearing mesogens. To the best of our knowledge, this is the first report on this subject.

In previous work,[8−10] we discovered a new kind of amphiphilic polymer composed of hydrophobic microgel cores and hydrophilic chains, or vice versa. They self-rearrange at the air/water interface and are readily transferable as so-called "duckweed" or "reversed duckweed" polymeric Langmuir−Blodgett (LB) films to solid substrates. The term "duckweed" means that the hydrophobic microgels are floating onto the surface of water, and the hydrophilic grafting chains are projecting into the water; "reversed duckweed" means that the hydrophilic networks extend downward into water and the hydrophobic grafting chains are upward packing away from the surface of water. Their unique feature is the combination of order and stability, and they can be used as a matrix for assembling functional or composite ultrathin 2D films. The amphiphilic polymer we use here was composed of a flexible hydrophilic epichlorohydrin−ethylenediamine cross-linked network and several hydrophobic stearic chains (SA). We found that this polymer self-organizes at the air/water interface to form a monolayer with a "reversed-duckweed" structure and that it could be easily transferred onto solid substrates to form LB multilayers which were highly ordered.[11] In this paper, we report the thermotropic liquid crystalline behavior of this kind of amphiphilic polymer.

Experimental Section

Amphiphilic polymers were synthesized according to Figure 1: stearic acid was reacted with a large excess of ethylenediamine under melting conditions to produce the monoamide, which was purified by recrystallization from ethanol. Then the monoamide and ethylenediamine with different molar ratios were mixed under melting conditions, and epichlorohydrin was added to the well-stirred reaction mixture over a period of 20 min to proceed with melt polymerization. Final product was purified by precipitating ethanol solutions of the polymer into ether twice to ensure removal of all unpolymerized substances. The product was dried under vacuum for 24 h at 40 °C.

IR (KBr): 3301 (OH), 2955 (CH_3), 2848, 2919 (CH_2), 1648, 1637 cm^{-1} (C=O, in amide).

The structural data are characterized and shown in Table 1. The number-average molecular weight was determined by membrane osmometry (Knauer model). The alkyl chain content of the amphiphilic polymer was determined by weighing the amount of stearic acid obtained by thorough hydrolysis of 0.5 g of polymer in HCl solution. The stearic acid obtained was washed with water and dried under vacuum for 24 h at 50 °C.

Liquid crystalline phases were characterized by X-ray diffraction (D/max γA, using copper Kα radiation of wavelength 1.542 Å), by optical polarized microscopy (Opton R P01, Germany), by differential scanning calorimetry with a heating rate of 5 K/min (Perkin-Elmer DSC 2c), and by temperature-dependent FTIR (Bruker IFS66V). The FTIR temperature controller is homemade and gives a temperature stability of better than 0.1 K when the sample is heated to the desired temperature (20 min wait for equilibration). The method for determining the FTIR band half-width and peak position is the second-derivative method (program supplied with the Bruker IFS66V FTIR instrument).

Results and Discussion

Liquid crystal behavior is generally induced either by temperature or by the influence of a given solvent. Here, the thermotropic liquid crystal behavior for this amphiphilic polymer was analysed by DSC, X-ray diffraction, optical polarized microscopy, and FTIR. Figure 2 shows the heating DSC scans for three samples, exhibiting phase behavior ranging from 280 to 430 K. From the DSC data, we found that sample ES-1 had a transition peak corresponding to the melting process, T = 360.4 K with ΔH = 94.4 J/g; ES-2 had two transition peaks, T_1 = 368.7 K, ΔH_1 = 121.5 J/g, T_2 = 386.5 K, ΔH_2 = 3.0 J/g; and ES-3 had three transition

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-8178$09.00/0

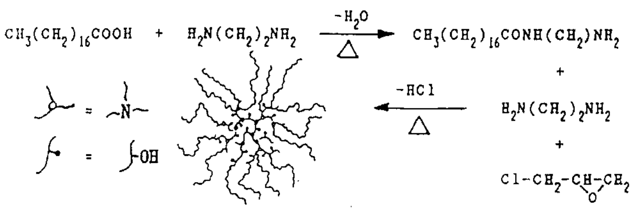


Figure 1. Approach for synthesizing the amphiphilic polymer.

Table 1. Structural Data for Amphiphilic Polymers Based on the Synthesis Shown in Figure 1

sample	$\bar{M}_n \times 10^{-4}$	SA content (wt %)	SA/molecule
ES-1	1.21	48.5	20.6
ES-2	0.85	62.7	18.9
ES-3	0.75	75.8	20.8

peaks, $T_1 = 362.1$ K, $\Delta H_1 = 75.5$ J/g, $T_2 = 381.9$ K, $\Delta H_2 = 9.6$ J/g, $T_3 = 408.9$ K, $\Delta H_3 = 31.0$ J/g. From these data, we inferred that ES-1 does not show liquid crystalline properties. However, ES-2 and ES-3 had one and two LC transition peaks, respectively. From the results we could see that the structure and balance between the hydrophilic and hydrophobic polymer parts had a great influence on the phase transition. Taking ES-3 as an example, we used temperature-dependent X-ray diffraction and optical polarized microscopy to study the existence and the structure of the mesophases. Figure 3 shows the temperature-dependent X-ray diffraction pattern for ES-3. We could see that ES-3 had a typical crystal structure at room temperature, with little amorphous component. When heated into the first LC phase, sample diffraction was dominated in the small-angle region by a series of well-pronounced Bragg peaks (up to third order), which at $2\theta = 1.8°$ corresponded to a layer spacing of 49.1 Å, indicating a well-established layer structure. Furthermore, in the wide-angle region, there was a sharp peak at approximately $2\theta = 21.2°$, corresponding to a spacing of 4.2 Å, which supports the ordering of "mesogens" within a smectic layer, which is typical for a higher ordered phase.[12] When heated into the second liquid crystalline region, the peak in the small-angle region decreases and shifts to 2.1°, corresponding to a layer spacing of 42 Å. The sharp peak at 21.2° disappears and only a broad diffuse halo is observed, typical for fluid analog packing of mesogens within each smectic layer. Upon further heating into the isotropic phase, the peak in the small-angle region disappears. From the data for the temperature dependence of X-ray diffraction, we conclude that this liquid crystal exhibits smectic phases, and the first liquid crystalline phase is more ordered than the second liquid crystalline phase. However, we cannot conclude which specific smectic phases are present. Smectic phase assignment is also in agreement with the results of the optical polarized microscopy. Figure 4 shows the typical texture—a smectic garlic clove texture—at 393 K. In order to investigate the details of the liquid crystalline phase transition, temperature-dependent FTIR spectroscopy was employed. While infrared spectroscopy cannot be used to absolutely identify a certain phase, it does permit the precise monitoring of subtle changes in the absorption bands characteristic of specific functional groups. According to previous results, the frequencies for CH_2 asymmetric and symmetric stretching bands are sensitive to the degree of their conformation and bandwidths are a reflection of the alkyl chain mobility.[13,14] Figure 5 shows the temperature-dependent behavior of the symmetric and asymmetric CH_2 stretching bands. Figure 6 plots the temperature dependence for frequencies of the symmetric and asymmetric CH_2 stretching bands.

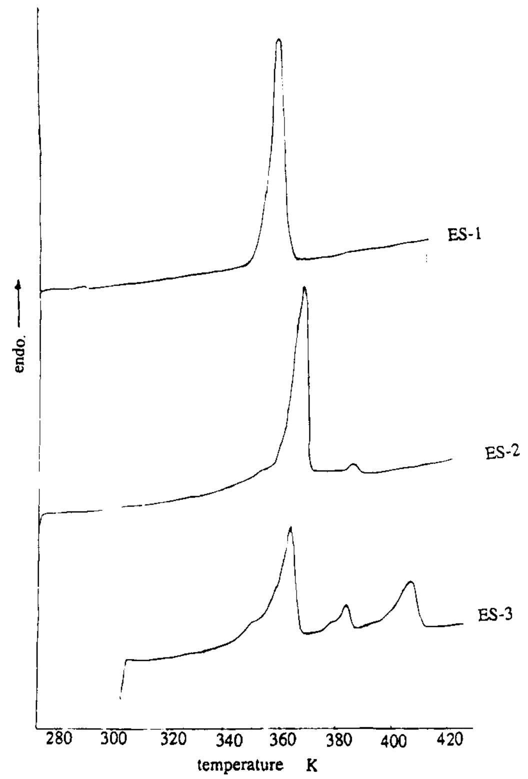


Figure 2. DSC thermograms of amphiphilic polymers ES-1, ES-2, and ES-3.

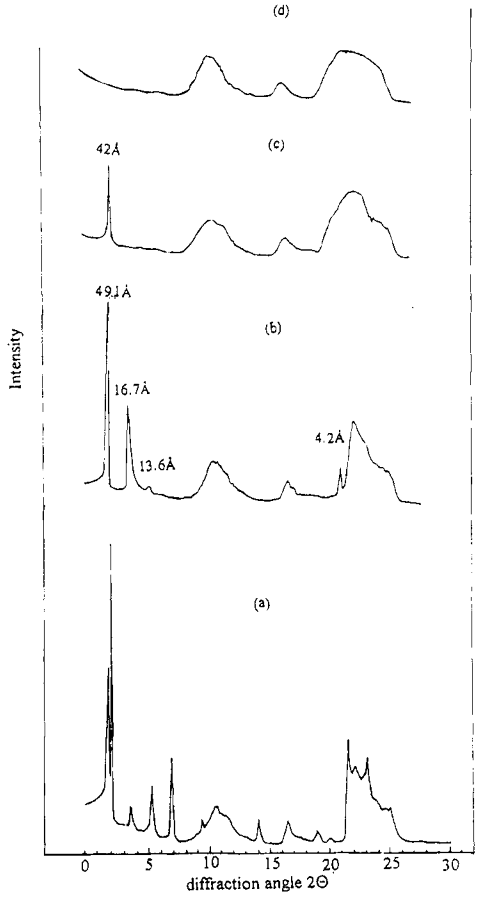


Figure 3. Temperature dependence of X-ray diffraction pattern for ES-3: (a) at room temperature; (b) at 381 K; (c) at 393 K; (d) at 423 K.

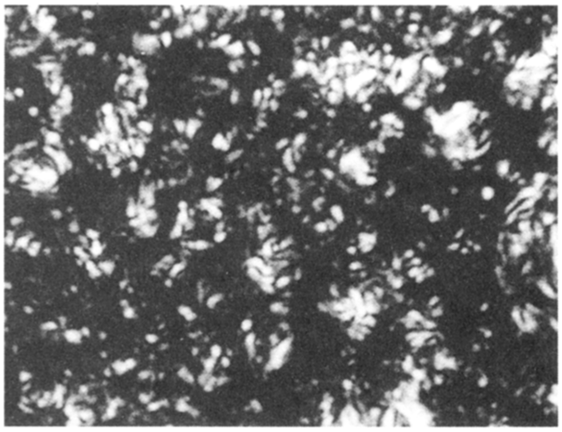


Figure 4. Optical micrograph of ES-3 obtained by polarized microscopy at 393 K (magnification: ×400).

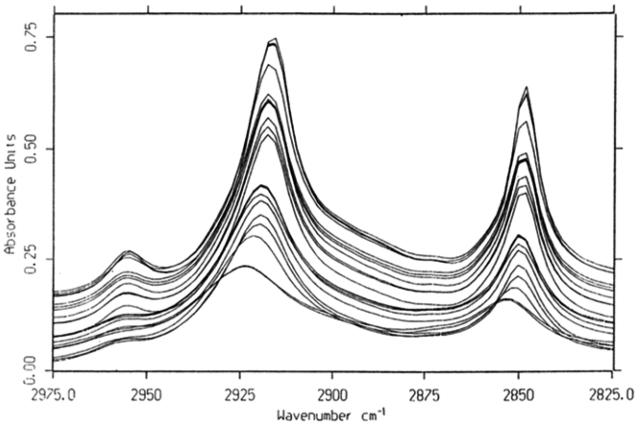


Figure 5. Temperature-dependent behavior of the symmetric and asymmetric CH_2 stretching band. The bottom spectrum is at 428 K and the top spectrum is at 288 K. There are 28 individual spectra, each about 5 K apart.

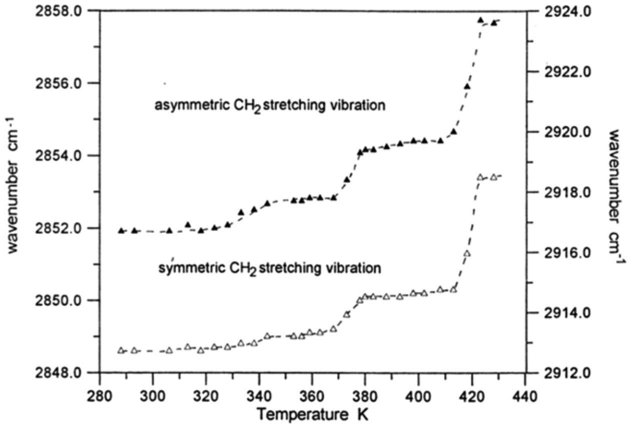


Figure 6. Temperature dependence of the frequency of the symmetric and the asymmetric CH_2 stretching vibration.

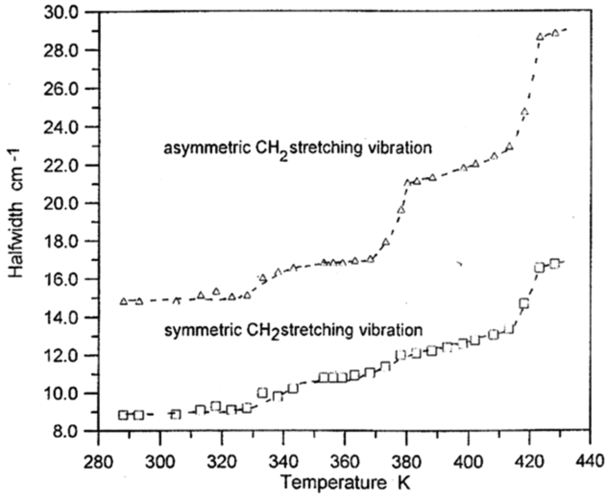
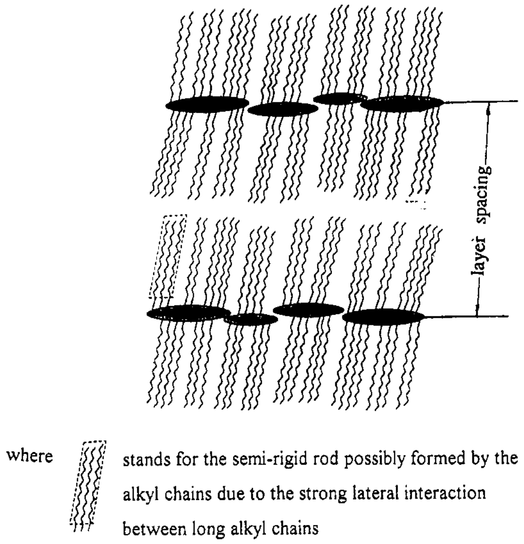


Figure 7. Temperature dependence of the half-width of the CH_2 stretching band.

Figure 7 shows the temperature dependence for the half-width of the CH_2 stretching bands. We observe that the respective phase transition temperatures, T_1, T_2, and T_3, could be precisely monitored by infrared spectroscopy. Near the transition temperatures, the frequency of the CH_2 stretching greatly changes, shifting to higher frequency and accompanied by an increase in bandwidth. Changes observed in the alkyl chain bands at the first transition temperature are very similar to those observed at the second transition temperature, but smaller in magnitude. Both of these are smaller than those seen at the melting temperature. From the FTIR data, we see that during the liquid crystalline transition processes, additional conformation disorder is introduced and an increase in alkyl chain fluidity results. From plots of the frequency versus temperature, changes in the stretching frequency and bandwidth occur at some degrees below the actual phase transition temperatures, which means that the short-range order changes below the actual phase transition temperatures. And, the asymmetric stretching vibration was more sensitive to the phase transition than the symmetric stretching vibration. Polarized microscopy allows the observation of long-range order in liquid crystals, whereas infrared spectroscopy is capable of providing quantitative information about the short-range order.[15] According to the results above, taken together, we conclude that changes in long-range order at the phase transition were initiated by changes in short-range order some degrees below the actual transition temperature.

The thermotropic liquid crystalline behavior of this kind of amphiphilic polymer lacking mesogens is very interesting and unusual, given the fact that thermotropic liquid crystal materials often contain a form-anisotropic structure, i.e., mesogens. We think that the thermotropic liquid crystal behavior of this amphiphilic polymer might originate from collective strong interactions between the polymers' long alkyl chains. Due to this interaction, some semirigid rods are formed which have similar effects to rodlike mesogens and helices in polypeptides,[16] and due to this strong interaction, the polymer tends to form a layer structure and exhibit a smectic phase when heating. Once the semirigid rod is destroyed, the mesophase will disappear and come into the isotropic phase. This could be the reason why there does not exist a nematic phase between the smectic phase and the isotropic phase. In X-ray diffraction, the observed wide-angle region sharp peak might correspond to the ordering of the semirigid rods in the layer, and the broad diffuse halo might correspond to the fluid packing of the semirigid rods.

Furthermore, we think that the existence of the flexible network also assists in inducing the formation of the liquid crystal phase. It is well-known that "spacer" groups are important to phase formation in side-chain polymeric liquid crystals since they effectively decouple the interaction between the side chains and the polymer main chain during the self-organization process.[17] As to the amphiphilic polymer ES-3, the flexible network might act as a particularly good spacer



where stands for the semi-rigid rod possibly formed by the alkyl chains due to the strong lateral interaction between long alkyl chains

Figure 8. A plausible model for polymeric liquid crystalline phase behavior based on the experimental data.

because the network remains so flexible that it could not influence the side-chain packing. Additionally, the hydrophilic parts tend to self-associate and repulse the nonpolar hydrophobic parts. This might allow the semirigid rods' alignment in layers to form the observed thermotropic smectic liquid crystalline phases. According to the results above, a plausible model for polymer liquid crystal phase formation is schematically depicted in Figure 8.

Conclusion

The thermotropic liquid crystal behavior of an amphiphilic polymer lacking mesogens was studied by DSC, polarized microscopy, temperature-dependent X-ray diffraction, and FTIR. The thermotropic liquid crystalline behavior of this amphiphilic polymer lacking mesogens originated from the strong interaction between the long alkyl chains, and some semirigid rods were formed which acted as the mesogens. Furthermore, the flexible network acting as a unique spacer group might also play an important role in the liquid crystalline phase formation. The FTIR results showed that the changes in the long-range order were initiated by changes in the short-range order some degrees below the actual transition temperatures.

References and Notes

(1) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 116.
(2) Jeffrey, G. A. *Acc. Chem. Res.* **1986**, *19*, 168.
(3) Marcus, M. A.; Finn, P. L. *Mol. Cryst. Liq. Cryst. Lett. Sect.* **1985**, *2*, 159.
(4) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Matiis, P. M.; Styring, P. *Nature* **1986**, *323*, 791.
(5) Tseng, S. L.; Valente, A.; Gray, D. G. *Macromolecules* **1981**, *14*, 7157.
(6) Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S. I.; Takarabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401.
(7) Aharoni, S. M. *Macromolecules* **1979**, *12*, 94.
(8) Yin, R.; Cha, X.; Zhang, X.; Shen, J. C. *Macromolecules* **1990**, *23*, 5158.
(9) Cha, X.; Yin, R.; Zhang, X.; Shen, J. C. *Macromolecules* **1991**, *24*, 4985.
(10) Shen, J. C.; Zhang, X.; Zhang, R. F. *Thin Solid Films* **1992**, *210/211*, 628.
(11) Zhang, X.; Zhang, R. F.; Shen, J. C.; Zou, G. T. *Makromol. Rapid Commun.* **1994**, *15*, 373.
(12) Poth, H.; Zentel, R. *Liq. Cryst.* **1994**, *16*, 754.
(13) Mantsch, H. H.; Martin, A.; Cameron, D. G. *Biochemistry* **1981**, *20*, 3139.
(14) Sapper, H.; Cameron, D. G.; Mantsch, H. H. *Can. J. Chem.* **1981**, *59*, 2543.
(15) Kruk, G.; Kocot, A.; Wrzalik, R.; Vij, J. K.; Karthaus, O.; Ringsdorf, H. *Liq. Cryst.* **1993**, *14*, 807.
(16) Daly, W. H.; Negulescu, I. I.; Russo, P. S. In *Macromolecular Assemblies in Polymeric Systems*; ACS Symposium Series 493; Stroevee, P.; Balazs, A. C., Eds.; American Chemical Society: Washington, DC, 1992; p 292.
(17) Hahi, B.; Wendorff, J. H.; Portugun, M.; Ringsdorf, H. *Colloid Polym. Sci.* **1981**, *259*, 875.

MA9505437