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Synthesis of polyaniline nanostructures in different lamellar liquid crystals and application to lubrication

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Abstract Polyaniline (PANI) nanostructures were synthesized in lamellar liquid crystal (LLC) formed by different surfactants. It was found that PANI presented lamellar nanostructures by using the template of LLC formed by ionic surfactant of sodium dodecyl sulfonate (SDS) or hexadecyltrimethylammonium bromide (CTAB), whereas PANI spheric nanostructures were obtained within the LLC template formed by the nonionic surfactant of Triton X-100. The formation mechanisms of PANI nanostructures were discussed. Besides, the lubricating effect of PANI in LLC template was also investigated, and the results showed that spheric PANI had better lubricative performance than lamellar PANI.

Introduction

Polyaniline (PANI) is attracting much attention because of its low cost, high conductivity, environmental stability, various structures, particular doping/de-doping mechanism and other excellent integrative performance [1, 2]. Recently, PANI has been investigated extensively for application in many fields, including the electrode materials of storage batteries, electroisomerization materials and metal antisepsis materials, etc., where the morphology is believed to play the key role in its applications [3, 4].

Up to now, various techniques have been used to synthesize PANI, mostly focusing on mechanical co-blend, solution co-mixing, electrochemical synthesis, chemical synthesis and so on [5–7]. In the chemical synthesis route, a template is often needed to shape PANI into nanostructures. The nanoporous membranes or channels in zeolites are shown to be effective to the fabrication of PANI nanowires or nanofibers [8]; however, the post-procedures seem to be complicated. The soft template recently is proved to be advantageous in the synthesis of PANI nanostructures. In recent years, researches on utilizing liquid crystal, one of soft templates, as templates to prepare inorganic and organic nano/micro-materials have attracted extensive attention [9, 10]. PANI nanowires have been prepared by potentiodynamic electropolymerization from a reverse hexagonal liquid crystalline phase where one-dimensional aqueous channels can serve as space-confined reactors [11]. Spherical-shaped PANI with mesopores structures was fabricated templated by lyotropic bicontinuous cubic phase consisting of nonionic surfactant NP10 [12]. Noticing that very few researchers have tried to carry out the synthesis of conducting polymers in lamellar liquid crystal (LLC) system [13], in this article, we use LLC formed by different surfactants as template to synthesize PANI. The results show that an ordered micro-environment of LLC templates can be provided for synthesizing PANI with lamellar or spheric morphology. The effect of different surfactants on the resulting PANI morphology was also investigated. FTIR, UV–Vis, XRD and TG analysis were used to characterize the products. The frictional test results show that spheric PANI has better lubricative performance than lamellar structured PANI.

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Experimental

Material

Aniline monomer (Shanghai Chemical Co., >99%) was distilled under reduced pressure. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS, Shanghai Chemical Co., >98%), sodium dodecyl sulfonate (SDS, Acroe, 88%), hexadecyltrimethylammonium bromide (CTAB, Sigma, 99%), Triton X-100 (Aldrich, >99%) and other reagents were used as-received without further treatment.

Determination of partial phase diagrams of LLC regions

We have determined the phase diagrams of SDS/*n*-$C_5H_{11}OH/H_2O$, CTAB/*n*-$C_5H_{11}OH/H_2O$ and Triton X-100/*n*-$C_{10}H_{21}OH/H_2O$ systems [14–16], according to which, in the present paper, we use LLC as templates to synthesize PANI. As seen in Fig. 1, the compositions of SDS/*n*-$C_5H_{11}OH/H_2O$, CTAB/*n*-$C_5H_{11}OH/H_2O$ and Triton X-100/*n*-$C_{10}H_{21}OH/H_2O$ LLC systems, which are used as templates to synthesize PANI, are symbolized as a, b and c, respectively.

Synthesis of PANI in LLC systems

In a typical synthesis, 0.030 g aniline was added to 2.000 g SDS/*n*-$C_5H_{11}OH/H_2O$, CTAB/*n*-$C_5H_{11}OH/H_2O$ or Triton X-100/*n*-$C_{10}H_{21}OH/H_2O$ LLC with magnetic stirring for 2 h to ensure complete mixing and then the system was kept at 25 ± 0.1 °C for another 4 h for phase equilibrium. As the phase equilibrium for LLC is much longer than micelles, then the commonly used addition fashion of APS aqueous solution (in one portion followed by agitation) will disturb the structures of LLC. Therefore, 0.245 g aqueous solution of APS (30 wt%) was added drop by drop for 30 min to initiate the polymerization of aniline and the agitation was not applied, where the molar ratio of APS to aniline was kept at 1:1. The reaction was allowed to polymerize without agitation for 48 h at 25 °C for the complete reaction. After that, the product was washed with deionized water and ethanol till the filtrate became colorless and then dried in a vacuum at 60 °C for 24 h for characterization.

Characterization

Micrographs of the textures were obtained at Leica DFC 320 Polarized light microscope.

The morphology of PANI was characterized by scanning electron microscope (SEM, XL-30E, Philip Co., Holland) and transmission electron microscope (TEM, Tecnai-12 Philip Apparatus Co., USA).

The Fourier transform infrared (FTIR) spectra of the various samples were recorded in the range of 400–4000 cm^{-1} using Fourier transform infrared spectrometer (TENSO2 27, Bruker Co., Germany). The samples were prepared in pellet form using spectroscopic grade KBr.

The UV–Vis absorption spectra of PANI were measured with a Shimadzu UV-2501 ultraviolet spectrophotometer at room temperature.

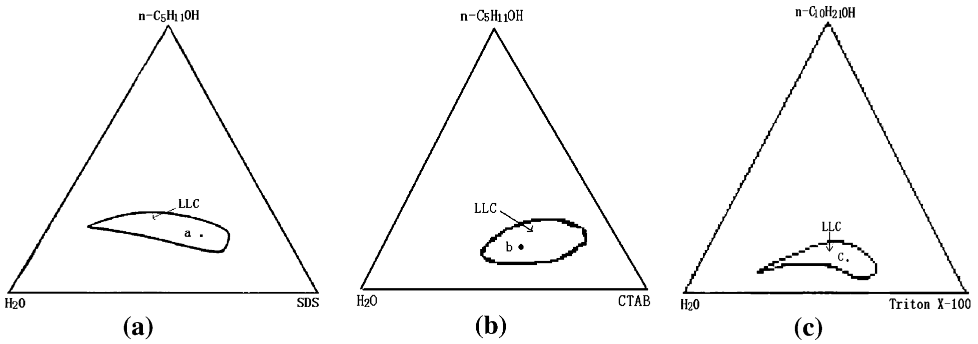
Power X-ray diffraction (XRD) patterns of products were measured on a German Bruker AXS D8 ADVANCE X-ray diffractometer.

Thermal studies were performed using a STA 409PC thermogravimetric analyzer (NETZSCH Co., Germany) in N_2 atmosphere and approximately 5 mg of each sample were analyzed from 20 to 800 °C at a heating rate of 10 °C/min.

The lubrication properties of the LLC with and without PANI were evaluated with a high-speed ring-block wear tester at 25 °C. The rotating speed was 800 ± 8 rpm, the test duration 180 s and the load applied 200 N. The 49-mm-diametered ring used is made of SAE 2100 steel, with a HRc of 59-61. The block used is Al–Si alloy (Si: 12–15%). Before each test, the ring and the block were cleaned with petroleum ether. At the end of each test, the wear scar width was measured with a digital microscope.

Results and discussion

Three kinds of LLC formed by different surfactants, including anionic SDS, cationic CTAB and nonionic Triton



(a) (b) (c)

Fig. 1 Partial phase diagrams of LLC regions of different systems: **a** SDS/*n*-$C_5H_{11}OH/H_2O$; **b** CTAB/*n*-$C_5H_{11}OH/H_2O$; and **c** Triton X-100/*n*-$C_{10}H_{21}OH/H_2O$. Composion of samples: **a** SDS 53.17%, H_2O 28.63%, *n*-$C_5H_{11}OH$ 18.20%; **b** CTAB 53.17%, H_2O 28.63%, *n*-$C_5H_{11}OH$ 18.20%; **c** Triton X-100 53.40%, H_2O 35.60%, *n*-$C_{10}H_{21}OH$ 11.00%

X-100, are used as template for fabrication of PANI. The partial diagrams of LLC regions as shown in Fig. 1 were taken from our previous reports [14–16]. The choice of the compositions of surfactant/alcohol/water is based on the following considerations: (1) the addition of aniline will not disturb the LLC phase; (2) after injection of APS aqueous solution, the additional water will not destroy the LLC template. Only if the above-mentioned requirements are met, LLC will actually act as template throughout the polymerization processes. Therefore, the amount of aniline added is relatively low and thereafter low quantity of APS aqueous solution is required. The compositions of surfactant/alcohol/water as given in Fig. 1 should satisfy the requirements according to our preliminary experiments.

Morphology and formation mechanism

Polarized light micrograph are used to characterize the LLC phases. The patterns show characteristic birefringence of cruciate flower textures of Triton X-100/n-$C_{10}H_{21}OH/H_2O$ LLC before (Fig. 2a) and after (Fig. 2b) addition of aniline. The SDS/n-$C_5H_{11}OH/H_2O$ and CTAB/n-$C_5H_{11}OH/H_2O$ LLC systems before and after addition of aniline monomer also give the characteristic birefringence of LLC phase, where the polarized light micrograph patterns are not given. The results indicate that the addition of aniline monomer does not disrupt the LLC phase.

Figure 3 shows the SEM images of PANI synthesized in different LLC systems. Figure 3a indicates that PANI with parallel arrayed lamellar structures is formed by using SDS/n-$C_5H_{11}OH/H_2O$ LLC as template. As seen in Fig. 3b, PANI synthesized in CTAB/n-$C_5H_{11}OH/H_2O$ LLC system also shows ordered lamellar structures. The formation mechanism of PANI with lamellar structures synthesized within the two LLC systems can be explained as follows: since the amino group of aniline is hydrophilic, which makes aniline locate in the solvent layer of LLC. Therefore, after adding APS as an oxidant, the polymerization reactions only take place in the solvent layer owing to the hydrophilic properties of APS. Confined by the two-dimensional water layer, polymerization of aniline will be conducted in water layer and then the nucleation and growth of PANI will be limited in two dimensions that lead to the formation of lamellar structured PANI. As the water layers in LLC are orderly arranged (parallel with each other in short distance), therefore, it is not surprising that parallel arrayed PANI lamellar structures can be formed with the template of LLC.

PANI prepared in Triton X-100/n-$C_{10}H_{21}OH/H_2O$ LLC system is spheric structures as shown in Fig. 3c. On the one hand, for the –EO group of Triton X-100 and the amino group of aniline can form hydrogen bonds, which makes aniline solubilized in the amphiphilic bilayer. On the other hand, the hydrophobic chain of Triton X-100 is long and therefore they can curl and twist. Thus, the growth of PANI not only occurs in the amphiphilic bilayer but also can pierce into the LLC templates. Eventually, three-dimensional PANI spheres (~40 nm in diameter) can be formed.

Polymer characterization

The UV–Vis absorption spectra of PANI are shown in Fig. 4. As for PANI synthesized in SDS/n-$C_5H_{11}OH/H_2O$ LLC system, the UV–Vis spectrum shows two bands at 380 and 883 nm (Fig. 4a). As commonly known, doped PANI shows three characteristic absorption bands at 320–360 nm, 400–420 nm, and 800 nm wavelengths. The first absorption band arises from π–π^* electron transition within benzenoid segments. The second and third adsorption bands are related to doping level and formation of polaron, respectively [17]. The first two bands are often combined into a flat or distorted single peak with a local maximum between 360 and 420 nm. Then the PANI synthesized in SDS/n-$C_5H_{11}OH/H_2O$ LLC system is considered to be in the doped emeraldine salt form. However, PANI synthesized in CTAB/n-$C_5H_{11}OH/H_2O$ (Fig. 4b) and Triton X-100/n-$C_{10}H_{21}OH/H_2O$ (Fig. 4c) LLC systems shows only two bands at 350–400 nm and 550–650 nm, which are assigned to the π–π^* benzenoid transition and the benzenoid to quinoid excitotic transition, respectively [17], indicating the emeraldine base form of PANI. This can be rationalized by the fact that cationic

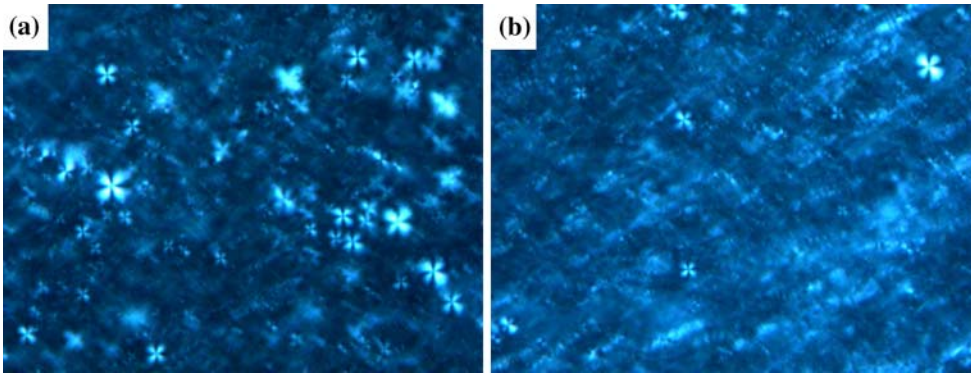


Fig. 2 The typical polarized light microphotograph of Triton X-100/n-$C_{10}H_{21}OH/H_2O$ LLC systems **a** before and **b** after addition of aniline

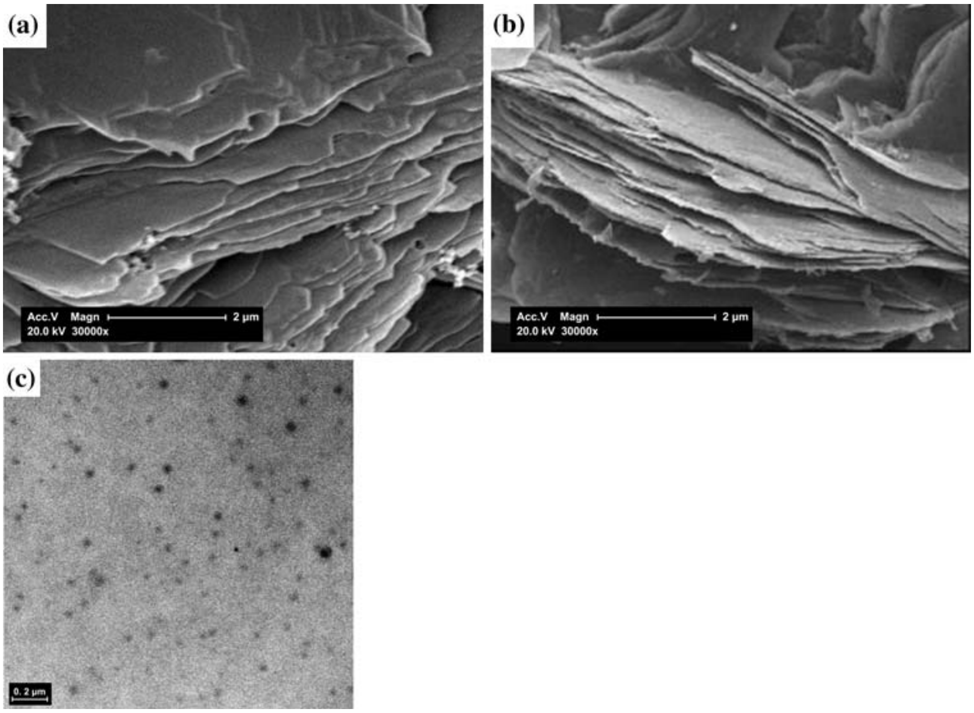


Fig. 3 **a**, **b** SEM and **c** TEM images of PANI synthesized in different LLC systems: **a** SDS/n-$C_5H_{11}OH/H_2O$; **b** CTAB/n-$C_5H_{11}OH/H_2O$; **c** Triton X-100/n-$C_{10}H_{21}OH/H_2O$

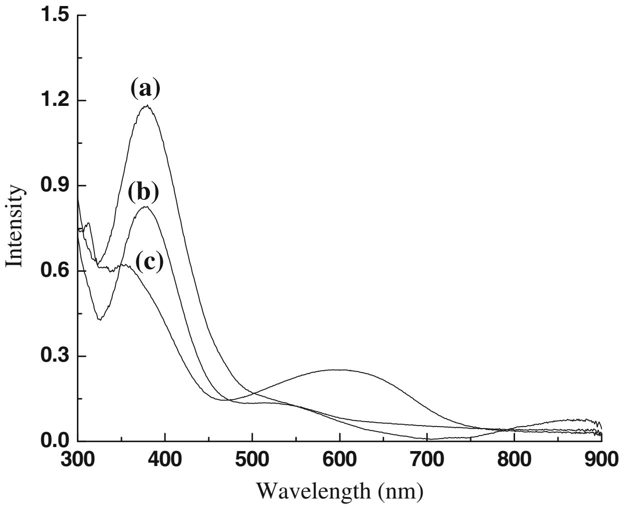


Fig. 4 UV–Vis spectra of PANI synthesized in different LLC systems: (a) SDS/n-$C_5H_{11}OH/H_2O$; (b) CTAB/n-$C_5H_{11}OH/H_2O$; (c) Triton X-100/n-$C_{10}H_{21}OH/H_2O$

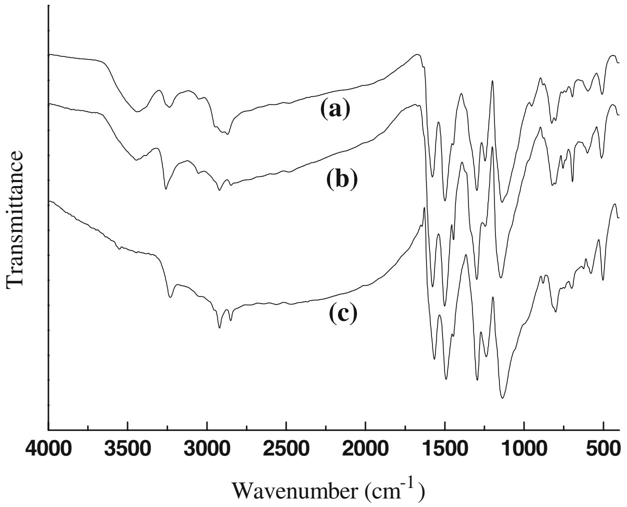


Fig. 5 FTIR spectra of PANI synthesized in different LLC systems: (a) SDS/n-$C_5H_{11}OH/H_2O$; (b) CTAB/n-$C_5H_{11}OH/H_2O$; (c) Triton X-100/n-$C_{10}H_{21}OH/H_2O$

dodecyl sulfonate which comes from SDS can act as dopant while CTAB and Triton X-100 cannot supply such counterions for doping PANI.

Figure 5 shows the typical FTIR spectra of PANI. The characteristic bands of PANI [18, 19], such as N–H stretching vibration (3225 cm^{-1}), C=C stretching deformation of the quinoid (1580 cm^{-1}) and benzenoid rings (1498 cm^{-1}), C–N stretching of secondary amine in polymer main chain (1298 cm^{-1}), C–N stretching in bipolaron structure (1245 cm^{-1}), and out-of-plane deformation of C–H in the 1,4-disubstituted benzene ring (826 cm^{-1}), are observed. For PANI synthesized in different LLC systems, the FTIR spectra are almost the same, which indicates that the chemical structures of PANI are the same regardless of the morphology of PANI and the compositions of the soft templates.

Figure 6 shows the XRD patterns of PANI synthesized in different LLC systems. The two broad bands centered at $2\theta = 21$ and 25° are observed in all PANI samples, which indicates that PANI are amorphous [20, 21]. The behavior of

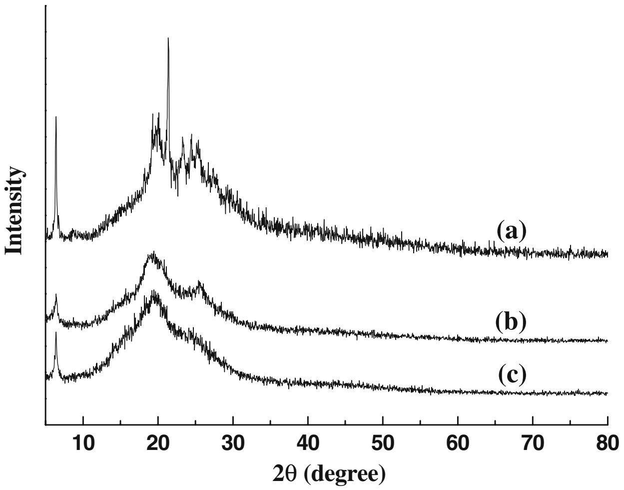


Fig. 6 XRD patterns of PANI synthesized in different LLC systems: (a) SDS/n-$C_5H_{11}OH/H_2O$; (b) CTAB/n-$C_5H_{11}OH/H_2O$; (c) Triton X-100/n-$C_{10}H_{21}OH/H_2O$

the crystalline peak at $2\theta = 6.5°$ may be originated from the ordering of the polymer chains [22]. As the intensity for PANI synthesized in SDS is higher than others, it can be concluded that the doping anionic introduced in PANI chains is beneficial for the ordering of polymer chains. Moreover, comparing with the three figures, it is evident that PANI synthesized in SDS/n-$C_5H_{11}OH/H_2O$ and CTAB/n-$C_5H_{11}OH/H_2O$ LLC systems with lamellar structures has better crystallinity than that of PANI synthesized in Triton X-100/n-$C_{10}H_{21}OH/H_2O$ LLC system with spheric structures. This may be caused by the regular arranged lamellar structures of PANI.

The thermal properties of PANI were measured as shown in Fig. 7. Typically, the TGA curves of PANI have a three-step weight-loss behavior: the first step loss can be attributed to the loss of water or solvent; the second step loss, following the first step, is due to the loss of dopant and low molecular weight fragments of the polymer; and the third step loss results from the thermal degradation and decomposition of the polymer backbone [23]. The thermal degradation of PANI that synthesized within SDS LLC in the doped form shows the lowest initial degradation temperature, which might be attributed to the loss of low molecular weight dopant. Besides, it can be seen evidently that PANI nanoparticles synthesized in Triton X-100/n-$C_{10}H_{21}OH/H_2O$ LLC system have the best thermal stability.

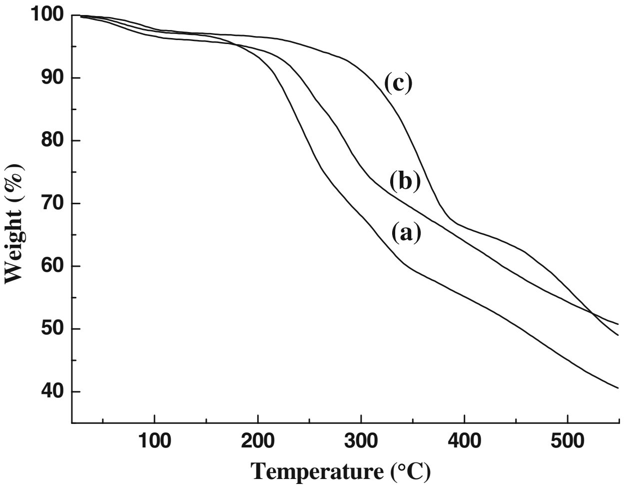


Fig. 7 TGA curves of PANI synthesized in different LLC systems: (a) SDS/n-$C_5H_{11}OH/H_2O$; (b) CTAB/n-$C_5H_{11}OH/H_2O$; (c) Triton X-100/n-$C_{10}H_{21}OH/H_2O$

Table 1 The wear scar width of LLC and LLC/PANI

Composition	LLC (μm)	LLC/PANI (μm)
1. SDS/n-$C_5H_{11}OH/H_2O$	640	598
2. CTAB/n-$C_5H_{11}OH/H_2O$	665	628
3. Triton X-100/n-$C_{10}H_{21}OH/H_2O$	550	480

Lubrication properties

The lubrication properties of LLC and LLC/PANI systems were characterized by high-speed ring-block wear tester. The wear scar width on the block surface is listed in Table 1. Under the same load, the smaller the wear scar width, the better the lubrication performance [24–26]. Results show that the presence of PANI in LLC systems can induce a better lubricant performance. Also, when PANI presents spheric morphology, the lubricant performance of LLC/PANI is better than that of LLC/PANI where PANI shows lamellar morphology.

If F is the friction of polymer, we have

$$F = F_a + F_d \qquad (1)$$

where F_a is cohere item and F_d is the elastic shape change item. Here F_a may be disregard, and frictions of move and slip process depend on F_d [27]. It is known that F_d is descended with the decrease of tangent area. Because the tangent area with LLC/spheric PANI on block is small as compared with LLC/lamellar PANI, thereby the friction of LLC/spheric PANI is small and the antiwear performance is much better, from which we can also confirm that the PANI with spheric structures have preferably lubricative performance.

Conclusion

PANI nanostructures have been successfully synthesized by using LLC as templates. The location of the solubilized aniline influences the resultant morphology of PANI. The

LLC template formed by ionic surfactant produces PANI with lamellar structure, whereas that formed by nonionic surfactant produces PANI with spheric structures. Therefore, the LLC templates can effectively control the growth of PANI. FTIR, UV–Vis, XRD and TGA are used to reveal the chemical structures, crystallinity and thermal stability of PANI. Results of friction test show that spheric PANI has better lubricative performance than lamellar structured PANI.

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