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Effect of hydrogen bonding on the liquid crystalline behavior of Poly(p-phenylene terephthamide) in sulfuric acid

Sheng Zhou [1], Chang-Sheng Li [1], Xing-He Fan, Zhihao Shen*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

Many factors affect the formation of lyotropic liquid crystals (LLCs) in the poly(p-phenylene terephthamide) (PPTA)/H_2SO_4 system. In this systematic work, we prove that the hydrogen bonding between PPTA and H_2SO_4 plays a very important role for the LLC formation by using a combination of several characterization methods. Texture features and transition temperatures of different phases owing to hydrogen bonding in the PPTA/H_2SO_4 system were obtained by using polarized light microscopy and differential scanning calorimetry. ^{13}C NMR and FTIR spectroscopy were applied to investigate the chemical structures in different phases, especially the hydrogen bonding between PPTA and H_2SO_4. The effect of molecular weight on phase transition was also examined. Moreover, guest compounds such as H_2O, CH_3SO_3H, and carbon nanotube added will destroy the hydrogen-bonding network in the PPTA/H_2SO_4 system, resulting in different phase behaviors. All these results demonstrate that hydrogen bonding between PPTA and H_2SO_4 is the key factor for the highly ordered arrangement of polymer chains in the LLC state that is a nematic phase.

1. Introduction

High-performance fibers are usually spun in the lyotropic liquid crystal (LLC) state that is a nematic (N) phase to form highly oriented molecular chains. Poly(p-phenylene terephthamide) (PPTA)/H_2SO_4 is one of these typical systems developed by DuPont. PPTA fiber [1–4] has excellent mechanical properties, chemical resistance, and heat resistance. Compared with carbon fiber, PPTA fiber has a lower tensile strength or tensile modulus, but it offers favorable balance of key properties and exhibits high performance for ballistic armor, composite materials, optical fibers, mechanical rubber products, and so on. However, generally high-modulus PPTA fibers can only be spun from LLC solutions in H_2SO_4. And hydrogen bonding between the polymer and the solvent formed in the spinning solution is replaced by intermolecular hydrogen bonding after being treated in the coagulating bath or by thermal treatment [5]. Hydrogen bonding is important for the mechanical properties of high-performance fibers, such as shear modulus [6] and compressive strength [7]. Understanding the interactions between PPTA and H_2SO_4 in the LLC state will help us improve the processing or develop a new solvent system to manufacture such a high-performance polymer.

Stepanyan and coworkers proposed two possible reasons for the formation of the LLC phase in the PPTA/H_2SO_4 system by simulating the crystalline structure of PPTA [8]. On the one hand, the low rotational energy of the PPTA molecular chain permits the highly ordered organization of PPTA. On the other hand, there is a competition between van der Waals force and hydrogen bonding, both of which affect the formation of the LLC phase, with the van der Waals force having a stronger effect in the crystalline structure. However, the conformations of PPTA in the crystalline structure and in solution are different, and the hydrogen bonding interaction between PPTA and H_2SO_4 may be very strong in the solution.

There are two or three phases, namely crystal solvent (CS), LLC phase, and isotropic phase, in this system dependent on the PPTA concentration and temperature [9]. Among them, the CS, a complex compound formed by H_2SO_4 and PPTA, was proposed by Gardener [10]. Several methods have been explored to investigate the structures of these phases, such as differential scanning calorimetry (DSC) [9], X-ray diffraction (XRD) [9–11], NMR [12–14], and polarized light microscopy (PLM) [9,15–19]. These results prove that H_2SO_4 molecules and PPTA chains are arranged in a sheet-like

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* Corresponding author.
E-mail address: zshen@pku.edu.cn (Z. Shen).
[1] These two authors contributed equally.

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structure owing to hydrogen bonding rather than electrostatic forces [20], which means that hydrogen bonding between PPTA and the solvent is an important issue [5–7]. Because of the influence of the concentration and temperature, the addition of guest compounds will affect the hydrogen bonding between PPTA and H_2SO_4. Effects of water on the phase diagram were investigated by Rommel and Foerster [9]. The melting temperature of the CS becomes higher when the water content is increased whereas the clearing temperature decreases. Polymer degradation is also affected by the water content. The structures and the morphologies of PPTA films are also affected by the differences in the coagulating bath [21–23]. Carbon nanotube (CNT) is believed to be the strongest fiber [24], with the theoretical tensile strength and modulus of 100 GPa and 1 TPa, respectively. It also has a high electrical conductivity, a high thermal conductivity, and other useful functions [25]. Continuous CNT fibers were obtained by Behabtu [25], and the tensile strength was to be ca. 1 GPa. On the other hand, CNT has been added in commercial fibers to improve the mechanical and functional properties [26–30]. Both CNT and PPTA can be dissolved in H_2SO_4 to form an N LLC, and thus the mechanical properties of the composite fibers depend on the interaction between the rigid polymer and CNT. Adding the guest compounds will affect the phase behavior and properties of the PPTA/H_2SO_4 system, with the assumption that the guest compounds will influence the hydrogen-bonded network between PPTA and H_2SO_4.

The effect of hydrogen bonding on the formation of the LLC phase will be reflected on the phase behavior. And the concentration, the molecular weight (MW) of PPTA, and temperature will all affect hydrogen bonding. Although many methods have been employed to investigate the phase transition temperatures and structures of the PPTA/H_2SO_4 system, there are still many challenges because of the corrosive nature of the solution, and few characterization methods were used to study the changes of hydrogen bonding between PPTA and H_2SO_4. Orientation of the LLC can be determined by several methods, such as XRD [31] and NMR. However, XRD is difficult to be used for the PPTA/H_2SO_4 system owing to strong corrosion and water absorption. Molecular organization in the PPTA/H_2SO_4 and poly(*p*-benzamide) (PBA)/H_2SO_4 solutions was also investigated by NMR [12,13]. However, the ^{13}C signals were hardly detected because of the degradation of PPTA in such studies. In addition, it is difficult to prepare PPTA/H_2SO_4 solutions with high concentrations of PPTA or with high-MW PPTA samples.

In this work, we systematically studied the effect of hydrogen bonding on the LLC phase behaviors by using a combination of several characterization methods. DSC and PLM were used to determine the phase transition temperatures. NMR was used to detect the chemical shifts of ^{13}C in different phases, and FTIR was employed for the first time to study the evolution of hydrogen bonding during the phase transformation. Several guest compounds, including H_2O, CH_3SO_3H, and CNT were added to study their influences on the hydrogen-bonding interaction between PPTA and H_2SO_4. The results confirm that the hydrogen bonding between PPTA and H_2SO_4 has a dramatic influence on the formation of the LLC phase.

2. Experimental

2.1. Materials and preparation

PPTA resins were supplied by Tayto. Co., Ltd. (Yantai, China), and the inherent viscosities of the four samples used in this study were 3.4, 5.5, 6.3, and 8.0 dL/g. CNT was supplied by Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). The average inner and outer diameters were 10–30 and 50 nm, respectively. The content of −COOH is ca. 3.8%. Both PPTA and CNT were dried under vacuum at 100 °C before use. CH_3SO_3H was purchased from BASF Co., Ltd.

The sample was denoted as IV*x*-*y*, where *x* is the inherent viscosity and *y* is the weight concentration of PPTA in H_2SO_4. For example, in the IV5-18 sample, the inherent viscosity of PPTA is 5.5 dL/g, and the weight concentration of PPTA is 18%.

PPTA/H_2SO_4 solutions were prepared according to the method in literature [32]. Fuming sulfuric acid (20% SO_3) was added into H_2SO_4 (96%) to reduce its water content. PPTA was also added into H_2SO_4 directly to investigate the influence of water, with the system denoted as PPTA/H_2SO_4-H_2O. The system with CH_3SO_3H was denoted as PPTA/H_2SO_4-CH_3SO_3H. CNT was dispersed in H_2SO_4 with magnetic stirring and continuous ultrasonic treatment for 72 h. The weight content of CNT relative to PPTA is ca. 0.5%.

2.2. Characterization

The transition temperatures in the range of −10 °C to 90 °C of the PPTA/H_2SO_4 systems were determined by DSC with TA Q2000 (Thermal Analysis, USA) under a N_2 atmosphere at a heating rate of 5 °C/min. High-pressure pans were utilized to improve corrosion resistance to H_2SO_4. The DSC results are highly reproductive even after one month of storage. Textures of samples were observed by PLM using a Nikon DS-Ri1 microscope equipped with an Instec HCS302 hot stage. The glass slide was heated to 80 °C in order to improve the repeatability [23]. The samples were slightly sheared and then sealed by high-temperature tapes. ^{13}C NMR measurements were performed with a Bruker 500 MHz spectrometer in 5 mm NMR tubes. The samples were isothermally treated at 30, 45, 60, or 90 °C for 30 min before testing. FTIR experiments were carried out in the transmission mode with a Nicolet iN10 (USA).

3. Results and discussion

3.1. PLM characterization on phase structures and phase transition temperatures

PLM is an efficient method to determine the phase transition temperatures and phase structures of bulk liquid crystals. Fig. 1 displays the evolution of the texture of the PPTA/H_2SO_4 (IV5-18) system during the heating process. At ambient temperature, the birefringence of the sample is weak. The sample should be in the CS state. When the temperature is increased to 90 °C, a *Schlieren*-like texture is observed, indicating that the PPTA/H_2SO_4 system develops into the N phase after the melting of the CS phase when the hydrogen bonding between PPTA and H_2SO_4 is formed. The birefringence becomes stronger after the temperature reaches 90 °C, and it vanishes when the temperature is higher than 159 °C following the destruction of the hydrogen-bonded network. As the temperature is increased, although the anisotropic phase changes into the isotropic phase, the high viscosity of the solution results in a slow phase transition when no shear stress is applied. Banded texture was also observed at 90 °C when a shear force was applied. However, the typical feature of the N phase was hardly observed. It may result from the high viscosity of this system. When the temperature is ca. 50 °C during cooling, the *Schlieren*-like texture is formed in a large area. It is interesting that the CS phase tends to form the features typical of spherulites after cooling. As shown in Fig. 1d, four-branched flower-like texture is formed when the sample is cooled to ambient temperature. The texture of the N phase in Fig. 1e is nearly the same as that of the CS phase when no shearing force is applied. Therefore, sometimes it is difficult to determine the CS-N transition temperature from PLM results [9]. The texture of the PPTA/H_2SO_4 system is strongly affected by the sample preparation method and whether a shear force is applied. It