Easy Fabrication and Morphology Control of Supramolecular Liquid-Crystalline Polymer Microparticles

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A novel kind of supramolecular liquid-crystalline polymer (SLCP) microparticles was successfully fabricated with an azopyridyl polymer and sebacic acid by combining a simple self-organized precipitation method with hydrogen bonding interactions. Upon slow evaporation of a mixed solution of a volatile good solvent and a nonvolatile poor one, walnutlike microparticles showing wrinkled surfaces and LC natures were obtained. The diacid might play a crucial role in the formation of SLCP particles. Without addition of the diacid, neither wrinkled surfaces nor LC natures were observed in azopyridyl polymer microparticles. The fabricated SLCP microparticle possessed not only photoresponsive properties (due to azopyridyl groups) but also LC ordering, which might enable them to find advanced applications.
strictly experimental conditions. More recently, a self-organization process based on thermodynamically non-equilibrium was considered as a simple and effective way to fabricate novel functional materials, such as fibers,[16] films,[11] vesicles,[20] honeycomb structures.[21,22] Among them, a self-organized precipitation (SORP) method was used to prepare microparticles with many kinds of polymers,[23,24] in which microparticles with narrow size distributions were obtained by evaporating volatile good solvents from polymer solutions after adding nonvolatile poor solvents into the mixed solutions. This method eludes surfactants or stabilizers, which are commonly necessary in conventional methods and lead to remained impurity in products. Combing the simple SORP method with hydrogen bonding to prepare SLCP microparticles may extend the research of SLCP materials on a microscale. Furthermore, the precipitation of polymer microparticles interfered with SLCP self-assembly might bring the fabricated microparticle some interesting properties, such as photoreponse, LC ordering, and walnutlike morphologies. In this paper, an azopyridine-containing polymer (PM6AzPy, as shown in Figure 1) and a dicarboxylic acid (sebacic acid, 8DA) were used as a hydrogen-bond acceptor and a hydrogen-bond donor to fabricate SLCP microparticles. Confining the photoresponsive PM6AzPy with supramolecular assembly on microscales, multifunctional microparticles are also expected.

**Experimental Part**

**Materials**

An azopyridyl monomer (M6AzPy) and polymer (PM6AzPy) were synthesized according to a reported method.[9] The 1H NMR spectra of them are given in Supporting Information (Figure S1). The SLCP was prepared by dissolving PM6AzPy and sebacic acid with equimolar amounts of pyridyl and carboxylic acid groups in THF. After slow evaporation of THF at room temperature, the remainder was dried in vacuum for 24 h, and then the SLCP powder was obtained. THF was dried with sodium and benzophenone and then distilled. Other chemical reagents were purchased and used directly without further purification.

**Microparticle Fabrication**

To prepare SLCP microparticles (P-8DA), distilled water (5.0 mL) was added dropwise into a THF solution (10.0 mL) of PM6AzPy (30.0 mg) and 8DA (8.3 mg) with vigorous stirring, and the transparent mixture was left at room temperature to slowly evaporate THF, allowing for microparticle formation. Then the water layer of suspension was removed, and the remaining microparticle was dried in vacuum for 24 h. PM6AzPy microparticles (P-0DA) were fabricated through a similar process, and the only difference was that no carboxylic diacid was added.

**Characterization**

The surface morphologies of microparticles were investigated with optical microscopy and scanning electronic microscopy (SEM, JSM-5300LV, JEOL). To evaluate LC properties, a differential scanning calorimeter (DSC, Thermo plus EVO DSC 8230) and a polarizing optical microscope (POM, ECLIPSE LV100POL, Nikon) equipped with a hot stage and a digital camera (Nikon, D5000) were performed. The composition and hydrogen-bonded interactions of the fabricated SLCP microparticles were confirmed by nuclear magnetic resonance spectroscopy (NMR, JEOL AL-400) and Fourier transform infrared spectroscopy (FT-IR, Shimadzu IR Prestige-21) with a temperature controller, respectively.

**Results and Discussion**

PM6AzPy is amorphous due to absence of end groups, and only a glass transition temperature ($T_g$) appeared at about 40 °C in its DSC heating curve.[9] To provide the polymer with LC properties based on hydrogen bonding, a diacid
(8DA) with a long alkyl chain was used to prepare SLCP through a previously reported method. FT-IR spectra in Figure 1 gives direct proof for hydrogen bonding formation between PM6AzPy and 8DA, in which two peaks at 1925 and 2544 cm\(^{-1}\) were observed, corresponding to Fermi resonance bands and vibration of hydroxyl groups, respectively. Here, 8DA could not only serve as end groups by hydrogen bonding with azopyridyl units, but also lead to weak cross-linkages because both ends of 8DA are substituted with carboxylic acid groups. The obtained SLCP exhibited a typical Schlieren texture in its POM image at 86 °C (Figure S2 in Supporting Information). Then PM6A2Py was used to fabricate P-0DA. To detect the formation process of microparticles, the transmittance (at 600 nm) of PM6A2Py in a mixed solution of THF and distilled water was investigated. As shown in Figure 1B, after gradual evaporation of THF at room temperature, the transparent orange solution became turbid due to the scattering effect induced by the formed microparticles. Then P-8DA was fabricated through a similar process, and the only difference was that 8DA was simultaneously dissolved in THF together with PM6A2Py.

Figure 2 shows pictures of fabricated polymer microparticles. Nearly spherical shapes were observed in optical micrograph images of P-0DA and P-8DA (Figure 2A, B), but their POM images exhibited different birefringent behaviors. In Figure 2C, weak refraction surrounding the spherical microparticle P-0DA was observed, which was obviously resulted from the geometric shape nature of amorphous microparticles. Differently, a strong birefringence was observed in the POM image of P-8DA (Figure 2D). Although the supramolecular mesogen was confined on microscales, their LC textures were very similar to that of the SLCP (Figure S2 in Supporting Information), indicating that the obtained P-8DA might be composed of the SLCP.

The LC nature of P-8DA was also confirmed by thermal analysis, as shown in Figure 3A. Both P-8DA and the SLCP exhibited a similar endothermic peak at about 97 °C in their DSC curves, corresponding to an LC-to-isotropic phase transition. On cooling, an exothermic transition peak was observed at 86 °C due to overcooling effect (Figure S3 in Supporting Information). Since P-0DA was amorphous, LC properties of P-8DA should be attributed to the addition of 8DA as end groups through hydrogen bonding, which was further verified by FT-IR measurements. Compared with the
FT-IR spectrum of P-0DA (Figure 3B), two additional peaks were clearly observed in that of P-8DA and the SLCP. One was at 1,925 cm$^{-1}$ corresponding to Fermi resonance bands, and the other was a wide peak at around 2,544 cm$^{-1}$ attributed to vibration of hydroxyl groups, providing direct evidences for hydrogen-bonding formation in P-8DA, which is very similar to Figure 1A. Moreover, the hydrogen bond between PM6AzPy and 8DA exhibited good thermal stability. It still remained at a temperature above the clearing point, and finally disappeared at about 200°C (Figure S4 in Supporting Information).

Similar to other polymer microparticles prepared by the SORP method,[23,24] P-0DA showed a spherical shape with a fine smooth surface in its SEM image (Figure 2E) because the thermodynamic trend of minimization of the interfacial free energy between different phases usually results in spherical particles. More surprisingly, P-8DA exhibited walnutlike structures with wrinkled surfaces in its SEM image (Figure 2F), in contrast to P-0DA. Obviously, the additional 8DA played a major role in appearance of such fascinating morphologies upon supramolecular self-assembly. Generally, small colloids with long “tails” (for example, alkyl groups) were able to form big colloids by entwisting of these tails. Here, 8DA having a long alkyl chain of eight methylene groups between two acid moieties possibly plays a similar role of tails. Meanwhile, it might connect with small particles through hydrogen bonding of carboxylic acid groups in both ends, resulting in formation of walnutlike SLCP microparticles.

In the evaporation process of THF from a THF/water solution of 8DA and PM6AzPy, hydrogen bonds could be formed, enabling the present SORP process to be accompanied with hydrogen-bonding formation, which is a little different from that reported by Shimomura and coworkers[23,24] Since the precipitation of microparticles was followed with the occurrence of hydrogen bonds, walnutlike microparticles with a quasi-spherical shape, and a strong LC birefringence were successfully obtained (Figure 2D,F).

Nuclear magnetic resonance spectroscopy (NMR) measurements were carried out to evaluate the amount of 8DA associated in P-8DA. As shown in Figure 4A, four additional peaks in 8DA were observed besides NMR peaks of PM6AzPy. Three sharp peaks at 1.25, 1.33, and 2.14 ppm, and one wide peak at 2.66 ppm appeared, correlated with methylene protons and carboxylic-acid protons in 8DA, respectively. The molar ratio of acid to azopyridyl groups in P-8DA was estimated as 0.8 by integration of the phenyl proton NMR peak at 7.58 ppm of PM6AzPy to that of the methylene protons of 8DA at 2.14 ppm. It means that only a part (about 80%) of 8DA was incorporated in P-8DA through hydrogen bonding, and there was still some 8DA residual in water. This was supported by optical and POM images of P-8DA in a large area (Figure S5 in Supporting Information), in which 8DA crystals were clearly observed after complete evaporation of the remained water. These results might be attributed to the equilibrium existing between the formation and disassociation of hydrogen bonds.[25] In the formation process of P-8DA by supramolecular self-assembly, carboxylic acid groups might interact with azopyridyl moieties through hydrogen bonding, and microparticles precipitated simultaneously with a certain part of non-hydrogen-bonded PM6AzPy from the mixed solution. 8DA has weak solubility in water, whereas
PM6A2Py precipitates in its aqueous solution. Therefore, a small part of 8DA remained in water after complete evaporation of THF. As a result, the hydrogen-binding reaction occurred between PM6A2Py and 8DA with non-equimolar amounts of azopyridyl and acid groups in fabrication of P-8DA.

Generally, morphology control of microparticles is one of interesting topics of polymer science since it significantly enhances the application areas of polymer materials. To elucidate the formation of walnutlike LC microparticles with wrinkled surfaces, hydrochloride acid and acetic acid were used to replace 8DA in preparation of SLCP microparticles. With similar fabrication processes, hydrochloride acid showed little influence on the formation of PM6A2Py microparticles, and analogous microparticles to P-0DA were obtained with smooth surfaces. Although introduction of acetic acid led to formation of birefringent LC microparticles, no walnutlike morphologies or wrinkled surfaces were obtained. This means that acetic acid with a short alkyl chain could not play a role of the so-called long tails as 8DA did.

Since the 8DA played a key role in the fabrication of SLCP microparticles with walnutlike morphologies, changing the molar ratio of 8DA in the mixed solution might induce different morphologies of the fabricated microparticle. As shown in Figure 4B, microparticles fabricated with a molar ratio of 0.2 showed smooth surfaces, and no birefringence was observed with POM, which is similar to that of P-0DA. When the molar ratio was higher than 0.4, a weak wrinkled surface was obtained and a faint birefringence was measured upon POM observation. Continuing increasing the molar ratio of the acid group, both obvious walnutlike morphologies and strong birefringent texture were obtained in the fabricated microparticles, indicating that SLCP microparticles with walnutlike morphologies can be fabricated when the molar ratio of the acid group in 8DA was higher than 0.6.

Accordingly, the formation processes of walnutlike SLCP microparticles can be plausibly illustrated as following.[23,26,27] First, the polymer was dissolved as random coil structures in the mixed solution containing the diacid, and hydrogen bonds were reversibly formed between azopyridyl and carboxylic acid groups. Second, the concentration of poor solvent was gradually increased due to slow evaporation of THF, and compact folding of polymer chains led to the formation of small nuclei. Third, small particles appeared as the growth of polymer nuclei with further evaporation of THF. Finally, P-8DA was achieved through self-assembly of small particles by interactions of entwisting and hydrogen bonding, leading to walnutlike SLCP microparticles in Figure 2. With addition of a lower molar ratio of diacid in the fabrication process, such entwisting interactions are weak, resulting in microparticles with a smooth morphology.

Conclusion

In summary, walnutlike SLCP microparticles with wrinkled surfaces were successfully fabricated by combining a simple SORP method with hydrogen-bonding formation. The diacid played a crucial role in formation of the SLCP microparticle upon self-assembly, whose molar ratio can be used to adjust the morphology of the fabricated microparticle. With addition of a lower molar ratio of the diacid, neither walnutlike morphologies nor LC properties were obtained in microparticles. The fabricated microscaled materials possessed both photoresponsive azopyridyl groups and SLCP ordering, as well as walnutlike morphologies, which promises them to find advanced applications in photonics[9,11,28] nanotechnology, and other fields, which is still underway in our lab.

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