

Polymer-Controlled Synthesis of 1-(2-Pyridylazo)-2-naphthol Hierarchical Architectures

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ABSTRACT

The self-assembly of organic 1-(2-pyridylazo)-2-naphthol (PAN) into hierarchical architectures, such as microfibers, microrods, and sheaflike structures, in solution was successfully achieved by reprecipitation method with the assistance of thermoresponsive diblock copolymer poly(*N,N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide) (PDMA-*b*-PNIPAM). It was found that the morphology modification can be readily controlled by varying the polymer concentrations. The optical absorption and fluorescence emission properties of the as-prepared PAN architectures were investigated. Time-dependent spectra of the precipitating solution for sheaflike structures formation were measured to monitor the self-assembly process of PAN molecules. The results showed that the PAN microstructures exhibited intense fluorescence emission, indicating an unusual aggregation-induced emission enhancement (AIEE) phenomenon for PAN, which has great potential for future use in optoelectronic microdevices.

Keywords: Organic Microstructures, Block Copolymer, Self-Assembly, Reprecipitation

1. Introduction

Nano/microstructures based on small organic molecules have attracted considerable attention during the past few years due to the potential applications in diverse fields such as color-tunable display, field-effect transistors, chemical sensors, and optical waveguides [1-7]. Therefore, the fabrication of organic nano/microstructures with controlled sizes and shapes have been an intense and rapidly developing field of research since the properties are intimately related to its morphology [8-18]. Recently, extensive efforts have been devoted to the development of synthetic strategies for preparing organic nano/microstructures such as reprecipitation [19-21], solvent evaporation [22], physical vapor deposition (PVD) [23], and template-directed method [24,25]. For example, tris(8-hydroxyquinoline)aluminum nanowires were successfully synthesized by adsorbent-assisted PVD [23]. Additionally, 1,4-bis(2-(5-phenyloxazolyl))benzene nanowires were also prepared using anodic aluminum oxide (AAO) membrane as a template [25]. However, it is still a big challenge to develop a simple and easy-tuned route for

the fabrication of organic hierarchical architectures because of the uncontrollability of intermolecular interactions and complexities of self-assembly process [18,26].

In recent articles dealing with the preparation of organic nano/microstructures, the reprecipitation method has become one of the most popular methods because of its easy and versatile operation [27,28]. This facile method is based on solvent displacement by pouring microamounts of organic compound solution into macroamounts of poor solvent. The sudden changes of environment then induce the self-assembly of organic molecules. It has been reported that surfactant [24,29] and polymer micelles [19,30] can be employed as an additive or template for the preparation of organic nano/microstructures. For instance, Qi [19] and co-worker prepared uniform dye Sudan microrods with the assistance of Pluronic F127.

In our previous paper [31], we have reported the synthesis of diblock copolymer PDMA-*b*-PNIPAM via reversible addition fragmentation chain transfer (RAFT) polymerization. The expected transition from molecularly dissolved unimers at low temperature to aggregated

micelles above its critical micelle temperature was observed upon heating the copolymer aqueous solution. From the viewpoint of applications, it would be greatly beneficial if the micelles self-assembled in aqueous media may respond to the external changes. This copolymer is well suited to act as a template for the fabrication of organic architectures. The present work is designed to fabricate 1-(2-pyridylazo)-2-naphthol (PAN) hierarchical architectures by reprecipitation method. Although PAN for analytical purposes has been investigated and widely applied in liquid-liquid extraction separation [32-33] and spectrometric determination of metal ions [34-36], there is little work on the synthesis of morphology-controlled PAN superstructures. In this work, hierarchical architectures of organic PAN were prepared through a template-assisted reprecipitation method. By tuning the template concentrations in the reaction system, the morphologies of PAN structure can be manipulated from fibers to rods, and then to sheaflike structures. The optical properties of the prepared products were investigated by absorption and fluorescence spectroscopy.

2. Experimental Section

2.1. Materials

PAN was recrystallized twice from EtOH. Block copolymer PDMA-*b*-PNIPAM and homo-PDMA were synthesized by RAFT polymerization as described elsewhere [31,37]. Copolymer with a molecular weight of 54,000 g/mol (denoted as DMA₂₆₈-NIPAM₂₄₃) was used in this study.

2.2. Characterization

Scanning electron microscope (SEM) images were recorded using a field emission scanning electron microscope (JEOL, JSM-6360LV), and the samples were loaded on the mica surface, previously sputter-coated with a homogeneous gold layer for charge dissipation during the SEM imaging. The powder X-ray diffraction (XRD) patterns of the samples were measured on a Japan Rigaku D/max-2500 diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). FTIR spectra in KBr pellets were recorded on a PE Spectrum One FTIR spectrophotometer. UV-Vis spectra were measured using PE Lamada 25 spectrometer. Fluorescence spectra were recorded on a PE LS-55 luminescence spectrometer. Dynamic light scattering (DLS) was performed on a Brookhaven Instruments BI-200 SM equipped with a BI-APD correlator and a crystalaser GCL-100-L operating at 532 nm with a fixed scattering angle of 90°, and the temperature was controlled by a PolyScience 9102 digital temperature controller. To ensure that DLS measurements were not affected by dust, all solution samples were filtered

through 200 nm membrane filters.

2.3. Synthesis of PAN Hierarchical Architectures

The organic hierarchical architectures of PAN were prepared through reprecipitation method. In a typical preparation, a solution of PAN in ethanol (2 mM, 400 mL) was injected into 5 mL of aqueous DMA₂₆₈-NIPAM₂₄₃ solution (10 mg/mL) with vigorous stirring at 50°C. After stirring for 5 min, the sample was left undisturbed for about 8 days. The resultant precipitate was centrifuged, washed thoroughly with deionized water, and dried under vacuum at room temperature for characterization. Reprecipitation was also carried out at varied DMA₂₆₈-NIPAM₂₄₃ concentrations and temperatures. For comparison purposes, copolymer DMA₂₆₈-NIPAM₂₄₃ was replaced by homo-PDMA for the reprecipitation of PAN.

3. Results and Discussion

3.1. Preparation of Polymeric Micelles

Polymer micelles were employed to assist the fabrication of PAN hierarchical architectures in this study. To obtain PDMA-*b*-PNIPAM micelles, aqueous solution of the diblock copolymer DMA₂₆₈-NIPAM₂₄₃ with different concentrations was raised from room temperature to their micellization temperature. The expected transition from molecularly dissolved unimers at low temperature to aggregated micelles above their critical micelle temperature (CMT) was observed by DLS measurements. Above the CMT, the NIPAM segment became dehydrated due to an entropy gain resulting from the release of water molecules upon association of the isopropyl groups [38]. The diameter of micelles was also determined by DLS. It is found that the CMT and the micelle diameter are sensitive to the concentration of the diblock copolymer. For example, the CMTs of the DMA₂₆₈-NIPAM₂₄₃ aqueous solution at concentrations of 0.5, 2.0, 5.0 and 10.0 mg/mL are approximately 37°C, 36°C, 34°C and 33°C, respectively, while the hydrodynamic diameters of the formed micelles are approximately 63, 58, 54 and 48 nm, respectively (**Figure 1**). It is important to note that the temperature induced association/dissociation process was reversible over numerous heating and cooling cycles, and micelle sizes remained approximately constant. These observations are consistent with a recent report by McCormick and coworkers [37]. In the following study, the DMA₂₆₈-NIPAM₂₄₃ micelles were used to assist the reprecipitation of PAN hierarchical architectures.

3.2. Reprecipitation of PAN from Aqueous Copolymer Solution

Due to the insolubility of PAN in water, we turn to thermoresponsive amphiphilic PDMA-*b*-PNIPAM polymer

surfactants as a more facile means for maximizing the solubility of PAN particles in water during assembly. Because these aggregates are grown from particles in micelle, the surfactants may favorably prolong their solution lifetime, and sustain growth to larger objects while maintaining the narrow distribution. Upon injecting a 2 mM ethanolic solution of PAN into a hot solution of diblock copolymer DMA₂₆₈-NIPAM₂₄₃ (10 mg/mL), and allowing the resulting mixture to precipitate at 50°C, narrowly dispersed sheaf-like architectures are obtained (**Figure 2(a)**). The product looks like ribbon-sheaf with two fantails consisting of a bundle of outspread ribbons, which are closely bonded to each other in the middle, so we call it a “ribbon-sheaf structure”. Careful observations (**Figures 2(b-d)**) reveal that the individual ribbon-sheaf has a length in the range of 5 - 15 μm and a middle diameter in the range of 0.5 - 1 μm. Interestingly, the architectures are in fact built from ribbons with widths of 200 - 300 nm and lengths of 5 - 15 μm, respectively.

The crystalline phase of the as-prepared PAN architectures was identified by powder X-ray diffraction. The XRD patterns in **Figure 3** clearly show that the PAN product with a sheaflike structure have an identical crystalline phase similar to that of PAN raw powder, although the precipitated products are not well crystallized.

Figure 4 depicts the FTIR spectrum of the as-prepared PAN microstructures (**Figure 3(b)**), which was almost identical to that of the PAN raw powders (**Figure 3(a)**), suggesting that the polymer can be completely removed by washing with water.

3.3. Polymeric Micelle-Templated Synthesis of Sheaflike Architectures

As mentioned previously, PDMA-*b*-PNIPAM can form

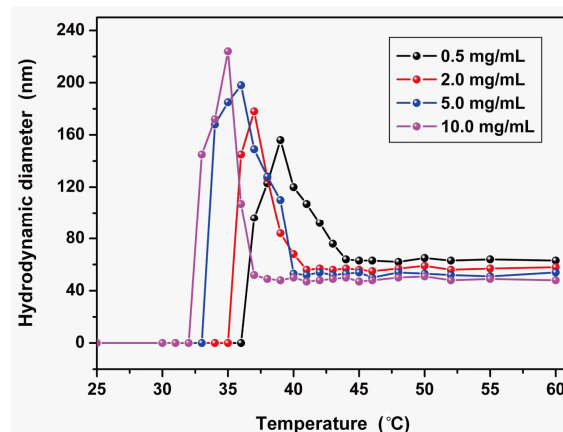


Figure 1. Hydrodynamic diameter (D_h) versus temperature for DMA₂₆₈-NIPAM₂₄₃ aqueous solution for the concentration of 0.5, 2.0, 5.0 and 10.0 mg/mL, respectively.

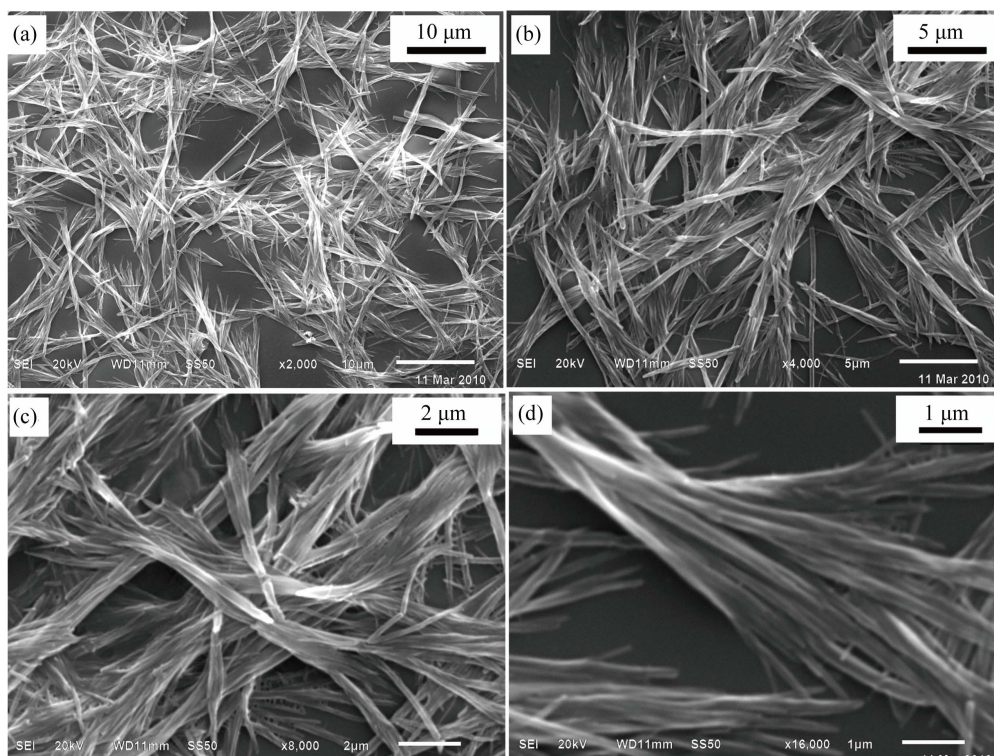


Figure 2. SEM images at different magnifications (a-d) of the PAN sheaflike architectures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution at 50°C.

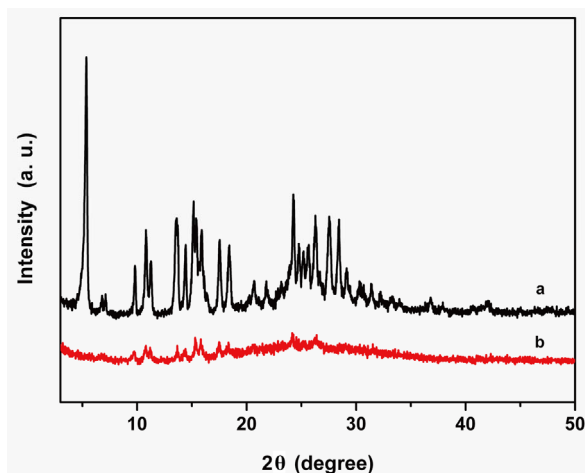


Figure 3. XRD patterns of (a) PAN raw powders, and (b) PAN sheaflike structures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution.

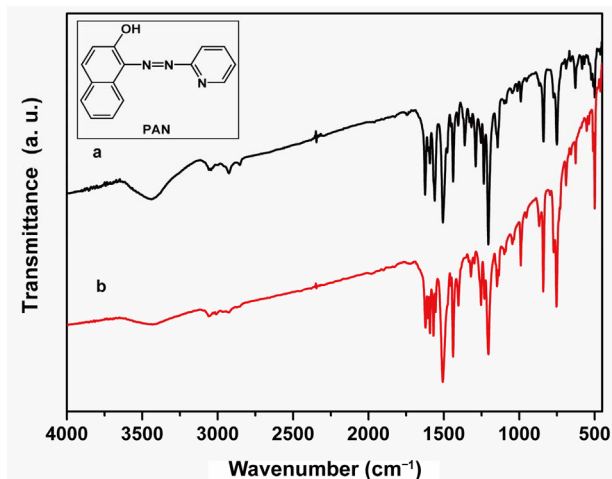


Figure 4. FTIR spectra of (a) PAN raw powders, and (b) sheaflike architectures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution. The inset shows the chemical structure of PAN.

thermally responsive micelles. The structures of copolymer micelles have been well described by the core-shell model, in which a spherical core composed of PNIPAM is surrounded by a shell composed of Gaussian chains of strongly hydrated PDMA [37,39]. In this work, DMA₂₆₈-NIPAM₂₄₃ spherical micelles with a diameter approximately 50 nm were used to control the reprecipitation process of PAN molecules. The presence of DMA₂₆₈-NIPAM₂₄₃ micelles was deemed to favor the formation of PAN sheaflike architectures. This argument was demonstrated by a series of controlled experiments. **Figure 5** shows the SEM images of PAN raw powders and products prepared from pure water or aqueous polymer solutions by reprecipitation method. It is clearly seen that the

raw powders consist of irregular plates ranging from 0.5 to 2 μm in width, and 1 - 4 μm in length (**Figure 5(a)**). Upon reprecipitation from pure water at 50°C, the powders turn to become long fibers with diameters of 150 - 220 nm and typical lengths ranging from 3 to 10 μm (**Figure 5(b)**). **Figure 5(c)** shows the sample prepared from 10.0 mg/mL of DMA₂₆₈-NIPAM₂₄₃ solution at 25°C, from which fiber-like architectures were observed. It was further verified by another controlled experiment in which PDMA homopolymer with equal molecular weight (DMA₅₃₅, Mn = 53000 g/mol) was employed instead of DMA₂₆₈-NIPAM₂₄₃ copolymer. Not surprisingly, SEM image shows that the morphology of the sample prepared from aqueous DMA₅₃₅ solution at 50°C is almost identical to that prepared from DMA₂₆₈-NIPAM₂₄₃ aqueous solution at 25°C (**Figure 5(d)**). These results indicated that the PAN molecules have the tendency to self-assembly in water, but it is difficult to prepare uniform architectures by simple reprecipitation, therefore, it is more important to find suitable ways for the facile fabrication of novel and morphology-controlled organic architectures.

On the other hand, in order to elucidate the effect of copolymer concentrations on the growth of PAN architectures, the preparations were also carried out at different copolymer concentrations under otherwise identical conditions. As shown in **Figure 6(a)**, microfibers of PAN with lengths of 20 - 50 μm were obtained at a low polymer concentration (0.5 mg/mL), which is somewhat similar to the sample precipitated from pure water. Interestingly, one-dimensional double stranded helix architectures were also observed. Upon increasing the DMA₂₆₈-NIPAM₂₄₃ concentrations to the range of 2.0 - 5.0 mg/mL, microrods with diameters about 320 - 420 nm became predominant products, which have an average length less than 20 μm (**Figures 6(b)** and **(c)**). However, when the polymer concentration was increased to 8.0 mg/mL, the corresponding bundle-like architectures of PAN can be observed from **Figure 6(d)**. PAN sheaflike architectures were obtained when the polymer concentration was further increased to 10.0 and 15.0 mg/mL (**Figures 6(e)** and **(f)**). These results indicate that the copolymer concentration is crucial for the formation of PAN architectures. With the increase of polymer concentration, the morphology of PAN architectures can be manipulated from fibers to rods, and finally to sheaflike architectures.

On the basis of the above results, it can be concluded that the DMA₂₆₈-NIPAM₂₄₃ micelles play a key role in the preparation of PAN sheaflike architectures. However, it remains unclear how the block copolymers micelles induce the formation of PAN fiber-like branches and the final sheaflike architectures. In fact, similar nanoparticle-based hierarchical superstructures of organic crystals

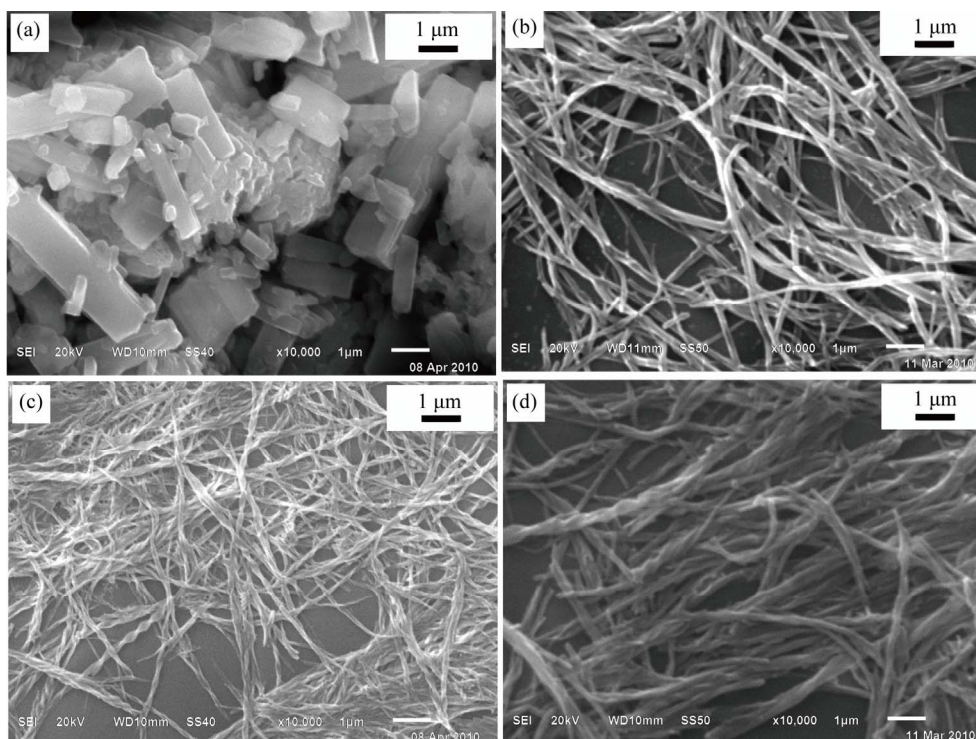


Figure 5. SEM images of (a) PAN raw powders, and the PAN products precipitated from (b) pure water at 50°C, (c) 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution at 25°C, and (d) 10 mg/mL of DMA₅₃₅ aqueous solution at 50°C.

under the direction of block copolymers have been previously observed [30,40-42]. It can also be recalled that, a two-stage growth mechanism for the polymer-directed synthesis of penniform BaWO₄ nanostructures have been proposed by Shi *et al.* [43], implying that polymer micelles played a very important role in the formation of hierarchical architectures. For example, Nguyen and co-workers had demonstrated the growth of narrowly dispersed porphyrin nanowires and their hierarchical assembly into macroscopic columns with the assistance of an amphiphilic Pluronic F127 [30,41]. In our present study, sheaflike architectures of PAN were obtained when the copolymer concentration was above 8.0 mg/mL. The presence of copolymer micelles provided suitable sites for the nucleation and growth of PAN aggregates, inducing the formation of sheaflike PAN architectures. Nevertheless, more detailed researches are required to examine the growth process for the formation of PAN hierarchical architectures under the direction of PDMA-b-PNIPAM.

3.4. Time-Dependent Absorption Spectra of PAN Products Self-Assembled from Copolymer Solution

To better understand the growth process of PAN hierarchical architectures, the optical properties of both the PAN molecules dissolved in ethanol and the as-prepared

PAN architectures dispersed in water were characterized. **Figure 7** displayed the UV-Vis absorption spectra of raw PAN ethanol solution and the PAN sheaflike architectures dispersed in water. The spectrum of PAN ethanol solution (20 mM, curve a) exhibits a peak at 460 nm and two shoulders at 550 nm and 398 nm, which might be attributed to the π - π^* and n - π^* transitions (**Figure 7(a)**). The absorption spectrum of PAN sheaflike structures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution and redispersed in water is characterized by two peaks at 393 nm and 468 nm (**Figure 7(b)**).

The formation process of PAN sheaflike architectures was studied by time-dependent absorption spectra as shown in **Figure 8**. Immediately after the injection of 400 mL ethanol solution of PAN (2 mM) into the aqueous solution of copolymer DMA₂₆₈-NIPAM₂₄₃ (10 mg/mL), an absorption peak and two absorption shoulders were observed at 468 nm, 562 nm and 398 nm, respectively. However, with the increase of aging time, these two absorption bands decreased gradually, accompanied by the final disappearance of the absorption shoulder at 562 nm, indicating the existence of aggregation for PAN molecules, which may result from the changed solvent polarizability and intermolecular interactions between PAN molecules. Meanwhile, the base-lines of spectra were gradually heightened with the extension of aging time, implying that the scattering from

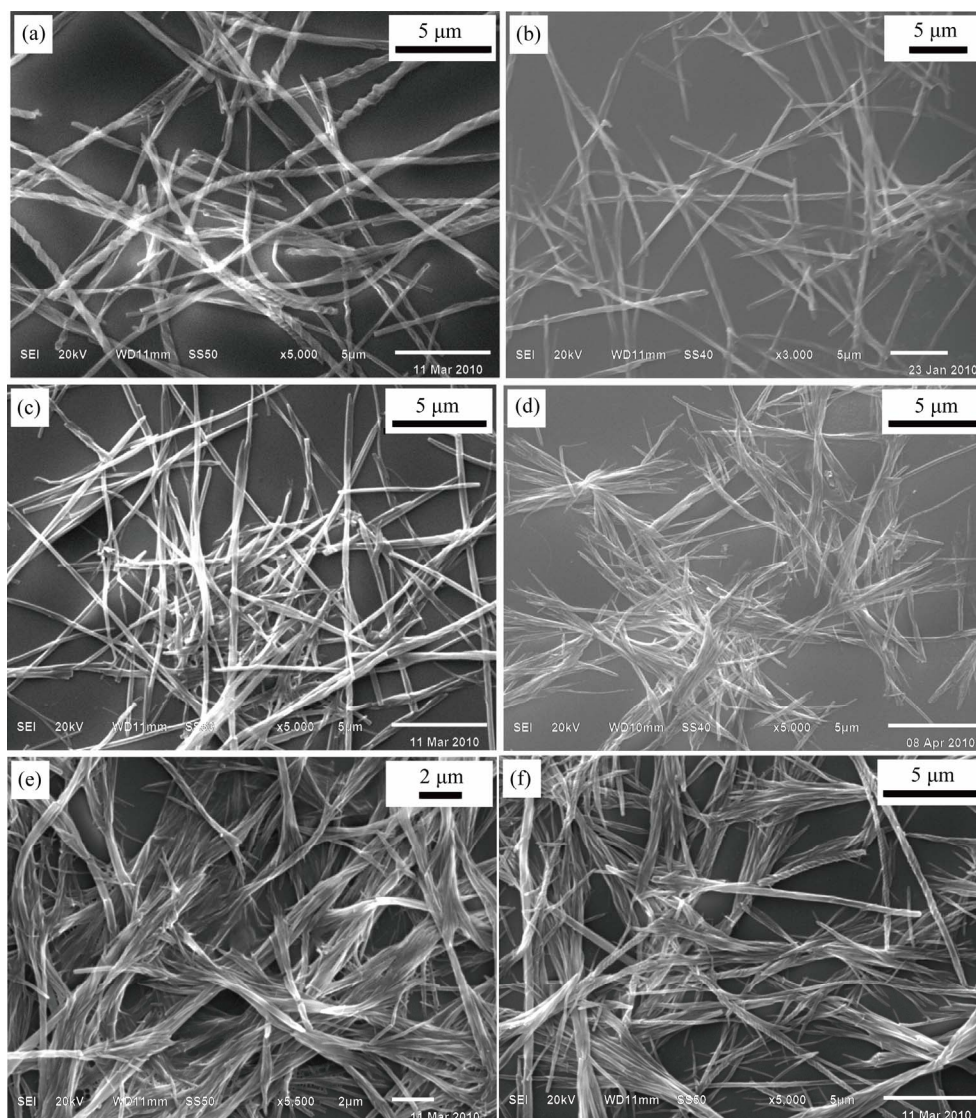


Figure 6. SEM images of PAN products precipitated from DMA₂₆₈-NIPAM₂₄₃ aqueous solutions with different polymer concentrations: (a) 0.5; (b) 2; (c) 5; (d) 8; (e) 10; and (f) 15 mg/mL.

larger particles could also be detected for longer aging times. Upon further aging of the precipitating solution for 8 days, PAN sheaflike architectures were obtained (**Figure 7(b)**), which exhibit two absorption peaks at 393 nm and 468 nm.

The fluorescence emission properties of both the PAN ethanol solution and PAN sheaflike architectures redispersed in water were also characterized as shown in **Figure 9**. The PAN ethanol solution shows two emission peaks around 330 and 350 nm when excited at 273 nm (**Figure 9(a)**). Different from that of PAN ethanol solution, two main emission peaks at 332 and 423 nm are observed in the spectrum of PAN sheaflike architectures when excited at 273 nm (**Figure 9(b)**). It is important to note that there is a strong red shift of emission peak from

350 to 423 nm.

To gain insight into the above mentioned phenomenon, we investigated the time-dependent fluorescence emission spectra obtained after injecting 400 mL ethanol solution of PAN (2 mL) into an aqueous solution of DMA₂₆₈-NIPAM₂₄₃ (10 mg/mL), which is shown in **Figure 10**. Immediately after the injection, three very weak emission peaks at around 332, 423, and 484 nm were observed. With increasing aging time, the emission intensities of spectra increase gradually but the peak positions are immovable, suggesting an unusual aggregation induced emission enhancement (AIEE) process, which is consistent with the previous observation [44-46]. Both of the decreasing rotations of rigid molecular planes and the change of solvent polarity are considered to be beneficial

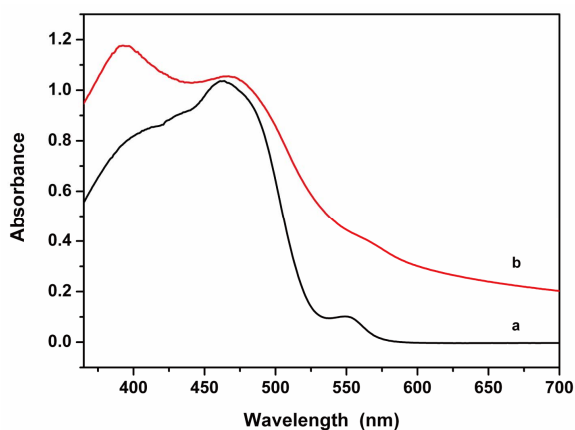


Figure 7. UV-Vis absorption spectra of (a) PAN ethanol solution, and (b) PAN sheaflike architectures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution and redispersed in water.

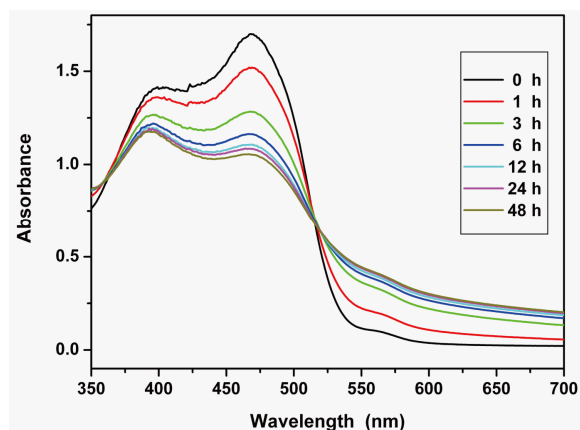


Figure 8. Time-dependent absorption spectra of PAN products self-assembled from 10 mg/mL DMA₂₆₈-NIPAM₂₄₃ aqueous solution.

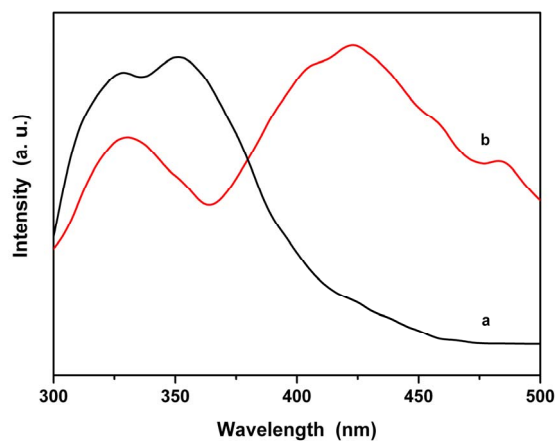


Figure 9. Fluorescence spectra of (a) PAN ethanol solution, and (b) PAN sheaflike architectures precipitated from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution and redispersed in water. $\lambda_{\text{ex}} = 273 \text{ nm}$.

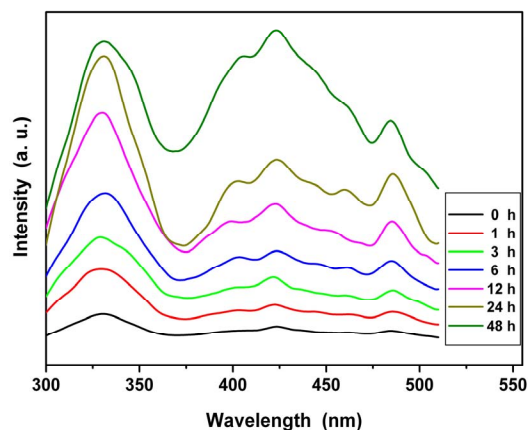


Figure 10. Time-dependent fluorescence spectra of PAN products self-assembled from 10 mg/mL of DMA₂₆₈-NIPAM₂₄₃ aqueous solution. $\lambda_{\text{ex}} = 273 \text{ nm}$.

for the enhancement of fluorescence intensity in this work.

4. Conclusions

PAN hierarchical architectures were synthesized by reprecipitation method with the assistance of thermoresponsive diblock copolymer PDMA-*b*-PNIPAM in this study. By varying the copolymer concentrations, the morphology of PAN can be readily changed from microfibers to microrods and sheaflike architectures. It is revealed that the formation of copolymer micelles play an important role in the growth of PAN sheaflike architectures but the detailed formation mechanism should be further investigated. The PAN sheaflike architectures exhibit an unusual aggregation-induced emission enhancement (AIEE) phenomenon compared with the PAN ethanol solution. Furthermore, the self-assembly process for PAN molecules was investigated by the time-dependent absorption spectra. The approach reported here may provide an effective method for packing small organic molecules into desired microstructures, which may find potential application in optoelectronic microdevices. It is also worthwhile to explore the extension of the present technique to the preparation of other organic hierarchical architectures.

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