Synthesis and investigation of the self-assembly behavior of guest block copolymers for supramolecular responsive materials

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Abstract. A supramolecular guest copolymer (**PNAP-co-PAM**) based on naphthol-containing monomer (**NAP**) and acrylamide was synthesized via Atom Transfer Radical Polymerization. The structure of supramolecular guest copolymer was characterized by NMR and GPC. And the self-assembly behavior of supramolecular guest copolymer was revealed by optical transmittance, dynamic light scattering (DLS) and SEM. It was proved that the optimum ratio of **NAP** to acrylamide in **PNAP-co-PAM** was 8.2:1 for achieving of the nano-scaled self-assembled materials. This study provides the foundation for construction of supramolecualr responsive host-guest materials..

Introduction

Supramolecular chemistry has developed to a fascinating research field, which is used in the preparation of versatile supramolecular materials[1, 2]. For the construction of supramolecular materials, macromolecule is one of the efficient building block [3, 4]. Especially, versatile synthesized macromolecular building blocks was employed to construct host-guest supramolecular materials[3, 5]. The system of cyclodextrin and adamantane (or azobenzene and naphthol) was the usual supramolecular host-guest system. Un to now, various functional host polymers based on cyclodextrin were extensively synthesized, which were applied to construct supramolecular materials based on host-guest interaction[6, 7]. Contrastively, the synthesis of functional guest polymers was lacking[8]. Typically, few functional guest polymers based on adamantane monomer were prepared and used in the development of functional materials[8, 9]. Considering that the synthesis process of functional guest monomer was simpler than the preparing of host monomer based on cyclodextrin, the exploration of the synthesis of functional guest monomer in an efficient way is a significant goal.

Therefore, to meet such a significant challenge, the exploration of the construction of a novel guest polymer based on naphthol-containing monomer (**NAP**) was carried out. As far as we known, few guest polymer based on 2-naphthol monomer was reported. And just naphthol monomer was observed in the filed of chiral separations[10]. However, considering that naphthol was also the efficient guest molecule for the formation of complex with cyclodextrin via host-guest interaction[11], the successful synthesis of guest polymers based on **NAP** was significant for the development of other functional supramolecular self-assembled host-guest materials.

Experiment

Materials

2-Naphthol, 3-bromo-1-prop-anol, acrylamide, triethylamine, were purchased from J&K scientific Ltd and were used without further purification. DMF, triethylamine, tetrahy-drofuran, ethanol were purchased from Nanning Lantian Reagent Co. Triethylamine and tetrahydrofuran were rigorously dried with sodium. Acryloyl chloride was purchased from Anhui Wotu Reagent Co. **NAP** was denoted by Zhejiang Yuhao Chemical Co.,Ltd. And the structure of **NAP** was determined as this. (^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80-7.19 (7 H, naphthol), 5.87-6.17(3 H, CH_2＝CH－), 4.46(t, 2 H, (naphthol, －O－CH_2－), 4.22(t, 2 H, $COOCH_2$－), 2.27 (m, 2 H, –CH_2–).

Instrumentation

The characterization of the structure of the compound was performed with a Bruker 400 MHz spectrometer using a TMS proton signal as the internal standard. UV-vis spectra were obtained using a Shimadzu 2600 UV-vis spectrophotometer. Scanning electron microscopy (SEM) observations were carried out using a JEOL JSM-6700F scanning electron microscope with a primary electron energy of 3 kV. Dynamic light scattering experiments were performed using a Malvern ZETAS12-ERNANOSERIES instrument. Molecular weights and molecular weight distributions were determined by GPC using THF as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$.

Synthesis of supramolecular guest copolymer (PNAP-co-PAM)

The macroinitiator **PAM-Br** was synthesized according to our previously report[12]. GPC analysis of **PAM-Br** revealed a Mn of 8764, Mw of 13671 and a polydispersity, Mw/Mn, of 1.56. And the degree of polymerization of **PAM-Br** was 119. Then, three kinds of supramolecular guest copolymer was synthesized, which were denoted as **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$ and PNAP-co-PAM$_4$**, respectively. GPC analysis of **PNAP-co-PAM$_{14}$** revealed a Mn of 22711, Mw of 38679 and a polydispersity, Mw/Mn, of 1.70. And the molar ratio of acrylamide to **NAP** in **PNAP-co-PAM$_{14}$** was 14.2:1. GPC analysis of **PNAP-co-PAM$_8$** revealed a Mn of 20342, Mw of 35502 and a polydispersity, Mw/Mn, of 1.75. And the molar ratio of acrylamide to **NAP** in **PNAP-co-PAM$_8$** was 8.2:1. GPC analysis of **PNAP-co-PAM$_4$** revealed a Mn of 21327, Mw of 37654 and a polydispersity, Mw/Mn, of 1.76. And the molar ratio of acrylamide to **NAP** in **PNAP-co-PAM$_4$** was 4.1:1.

Preparation of solution of PNAP-co-PAM.

The solution of **PNAP-co-PAM** was prepared for the optical transmissions, DLS and SEM analysis. The concentration of **PNAP-co-PAM** was 0.5 $mg \cdot mL^{-1}$.

Results and Discussion

Synthesis of PNAP-co-PAM

To explore of the preparation of functional guest monomer in an efficient way, the synthesis of a novel guest polymer based on NAP was carried out. Herein, considering that Atom Transfer Radical Polymerization (ATRP) was an efficient controlled/living radical polymerizations for the designing of versatile functional materials with complex architectures and compositions[13], a series of **PNAP-co-PAM** were synthesized by ATRP. Typically, the synthesis route of **PNAP-co-PAM** was illustrated in Fig. 1. Firstly, the macroinitiator **PAM-Br** was synthesized using acrylamide as monomer at 30^{o}C. Secondly, based on the macroinitiator of **PAM-Br**, the block copolymer (**PNAP-co-PAM**) was synthesized using acrylamide and **NAP** as monomers at 30^{o}C. Through altering the molar ratio of acrylamide to **NAP**, a series of **PNAP-co-PAM** (**PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$**) were obtained. Herein, the molar ratio of acrylamide to **NAP** in **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$** were 14.2:1, 8.2:1 and 4.1:1, respectively.

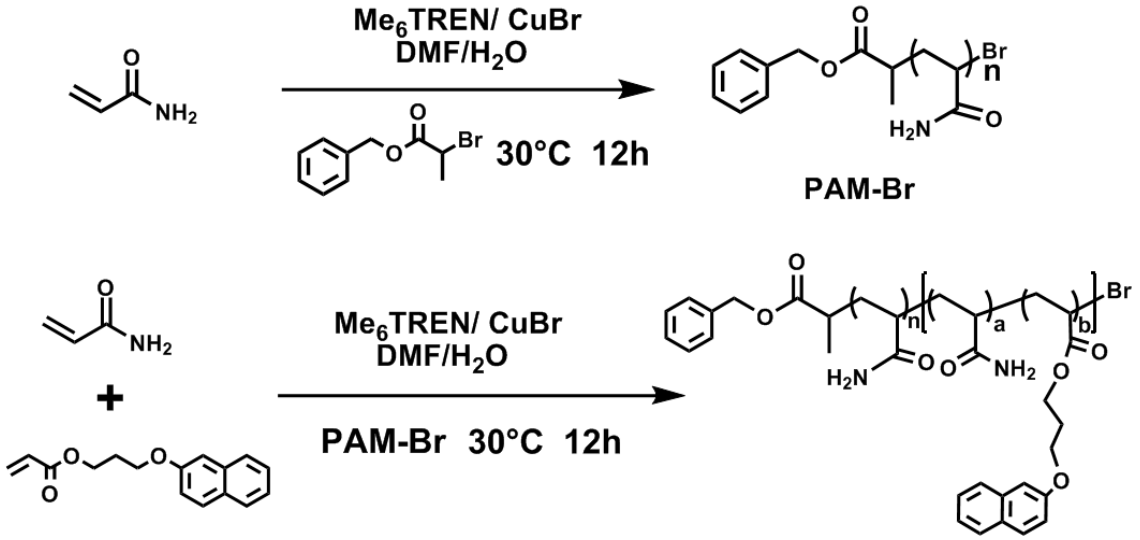

Fig. 1. The representation of the synthesis route of **PNAP-co-PAM**.

Characterization of the self-assembly behavior of PNAP-co-PAM

As a supramolecular guest copolymer, the reveal of the self-assembly behavior of **PNAP-co-PAM** is significant for the further application in various functional self-assembled materials. Herein, optical transmittance, dynamic light scattering (DLS) and SEM were employed to investigate the the self-assembly behavior of **PNAP-co-PAM**.

As shown in Fig. 2. the optical transmittance of the solutions of **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$** at 600 nm were 67.32%, 8.97% and 1.82%, respectively. And the hydrodynamic diameters of **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$** were determined using dynamic light scattering (DLS), which were given in Fig.3. It was proved that the hydrodynamic diameters of the solutions of **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$** were about 18 nm, 110 nm and 950 nm, respectively. Moreover, the actual morphologies of **PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$** were investigated by SEM and illustrated in Fig. 4. It was suggested that the spherical nanoparticles were observed. However, the spherical nanoparticles of **PNAP-co-PAM$_{14}$** were scarce observed and the size of them was smaller. And the size of the spherical nanoparticles of **PNAP-co-PAM$_4$** were too large. Comparatively, the size of the spherical nanoparticles of **PNAP-co-PAM$_8$** were about 100 nm, which was suitable for the preparing of nano-scaled supramolecular materials.

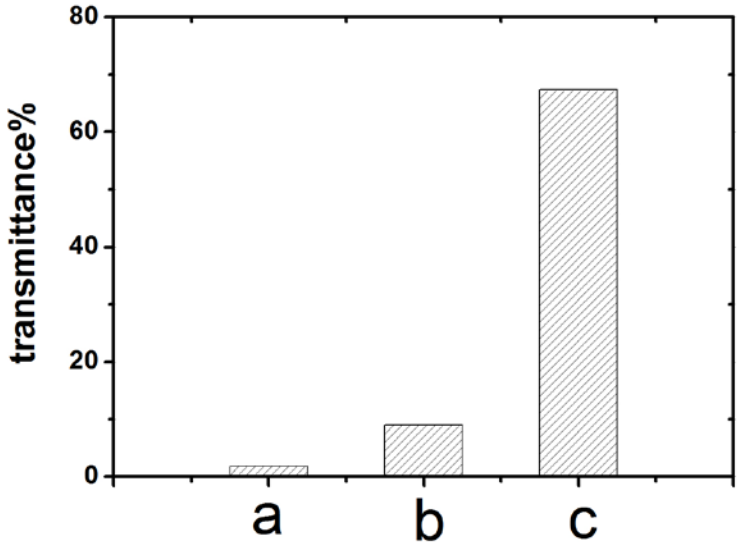

Fig. 2. The optical transmittance of three kinds of supramolecular guest copolymers at 600 nm. (**a**) **PNAP-co-PAM$_{14}$**; (**b**) **PNAP-co-PAM$_8$**; (**c**) **PNAP-co-PAM$_4$**.

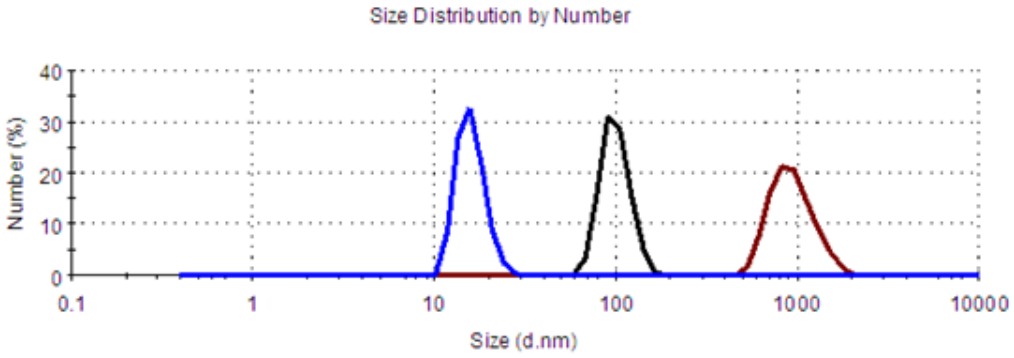

Fig. 3. Hydrodynamic diameters of three kinds of supramolecular guest copolymers determined using a Malvern ZETAS12-ERNANOSERIES instrument. (**a**) **PNAP-co-PAM$_{14}$**; (**b**) **PNAP-co-PAM$_8$**; (**c**) **PNAP-co-PAM$_4$**.

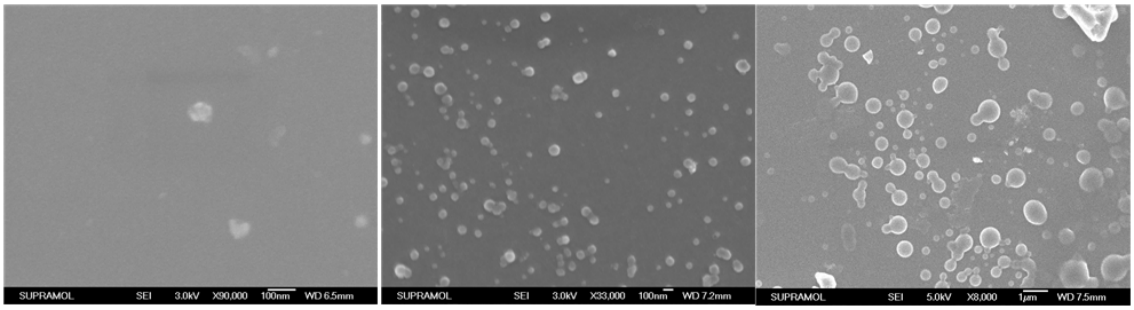

Fig. 4. SEM images of three kinds of supramolecular guest copolymers. (**a**) **PNAP-co-PAM$_{14}$**; (**b**) **PNAP-co-PAM$_8$**; (**c**) **PNAP-co-PAM$_4$**.

Discussion of the self-assembly behavior of PNAP-co-PAM

As **NAP** was a hydrophobic monomer, **PNAP-co-PAM** (bearing **NAP** as functional monomer) would exhibited the enhanced hydrophobic property. Therefore, the self-assembled aggregates would be formed when **PNAP-co-PAM** was presented in water solution. Considering that the mole contents of **NAP** and the hydrophobic properties in various **PNAP-co-PAM** (**PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$**) were different, the different aggregate structure might be observed. Herein, for **PNAP-co-PAM$_{14}$**, the mole content of **NAP** was relatively low. Therefore, the optical transmittance of **PNAP-co-PAM$_{14}$** at 600 nm was 1.82%, the hydrodynamic diameters was about 18 nm, and few aggregate was observed by Fig. 4 **a**. It meant that the content of **NAP** was too low to form the efficient aggregate. Contrastly, much more large-scaled aggregates were observed when the molar ratio of acrylamide to **NAP**, was 4.1:1. Under this condition, the optical transmittance of **PNAP-co-PAM$_4$** at 600 nm was 67.32%, the hydrodynamic diameters was about 950 nm. The self-assembled aggregate of **PNAP-co-PAM$_4$** was not suitable for preparing of nano-scaled materials. Significantly, for **PNAP-co-PAM$_8$**, the optical transmittance of **PNAP-co-PAM$_8$** was 8.97%, the hydrodynamic diameters was about 110 nm, and uniform aggregates were observed by Fig. 4 **b**. The self-assembled aggregates of **PNAP-co-PAM$_8$** were suitable for constructing of nano-scaled materials as a guest polymer. The successful synthesis of **PNAP-co-PAM$_8$** was significant for the development of other functional supramolecular self-assembled host-guest materials.

Conclusions

To explore of the synthesis of functional guest monomer in an efficient way, a novel guest polymer, **PNAP-co-PAM**, based on naphthol-containing monomer (**NAP**) was synthesized. Based on the characterization of various **PNAP-co-PAM** (**PNAP-co-PAM$_{14}$**, **PNAP-co-PAM$_8$**, **PNAP-co-PAM$_4$**), **PNAP-co-PAM$_8$** was selected as the suitable guest polymer for constructing of nano-scaled materials. The optical transmittance of **PNAP-co-PAM$_8$** was 8.97%, the hydrodynamic diameters was about 110 nm, and uniform aggregates were observed by SEM. The successful

synthesis of **PNAP-co-PAM$_8$** was significant for the development of other functional supramolecular self-assembled host-guest materials.

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