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Environment-induced nanostructural dynamical-change based on supramolecular self-assembly of cyclodextrin and star-shaped poly(ethylene oxide) with polyhedral oligomeric silsesquioxane core

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ABSTRACT

The star-shaped amphiphilic inorganic—organic hybrid polymer POSS-(PEO)₈ prepared via click chemistry can self-assemble into spherical aggregates by directly dissolving the hybrid polymer in water. The regular spherical aggregates were gradually transformed to deformed spherical aggregates, cylinders and sheets through adding different amount of α -CD molecules into the POSS-(PEO)₈ spherical aggregates solution due to the host-guest inclusion complexation between POSS-(PEO)₈ aggregates and α -CD. Adding different amount of phenol which captured α -CD from PEO chains or increasing the environmental temperature of the self-assemblies solutions which also led to the slipping of α -CD out of PEO can reversibly and dynamically change the sheets to cylinders, deformed spherical aggregates or regular spherical aggregates, showing that the reversibly nanostructural dynamical-change can be induced by altering the environmental conditions of the solutions.

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1. Introduction

The nanostructural controlled-change of assemblies has attracted considerable attention because this behavior of assemblies has the perspective applications in smart nanomaterials and biomedical fields [1–8]. The reversible control features of nanostructures show the characteristic of "living" self-assembly of the assemblies to some content [9–11]. From this view, environmental responsive polymers play an important role in achieving controllability and reversibility. A typical example is that the terpolymeric assemblies transferred from micelles to vesicles by changing external temperature [12]. However, these strategies are still limited to static self-assembly principles, and do not meet the requirement of biological systems for dynamical self-assembly [13]. Therefore, utilizing environmental changes to induce the nanostructural dynamical-change of the assemblies is of very interesting and challenging.

Recently, the supramolecular self-assemblies of host-guest inclusion complexation of linear polymers with cyclodextrins (CDs) show fascinating biologic properties [14–18]. More importantly. they inherit the intrinsic equilibrium nature of the inclusion complexation between formation and dissociation, and the CD molecules can freely slip out from them by an external environmental stimulation, such as chemical reagents, temperature and pH changes [19-22]. Obviously, the polymeric nanostructures accomplished from supramolecular self-assembly can be changed controllably through altering the environmental conditions. Yuan et al. reported the reversible change of supramolecular nanostructures from comb-block copolymer of ehtyl cellulose-graftpoly(ε-caprolactone)-*block*-poly(ethylene oxide) (EC-g-PCL-*b*-PEO) complexed with α -CD through adding competitive guests (phenol) which strip α -CD away from PCL and PEO stepwise, leading to a hierarchical disassembly and forming bottom-up deformable supramolecular objects [23]. In addition, Chen et al. reported the supramolecular micelles self-assembled from poly(ethylene oxide)-block-poly(acrylic acid) (PEO-b-PAA) with α-CD and found the α-CD molecules slipped from PEO chains at higher temperature [24].

The self-assembly behavior of inorganic—organic hybrid polymers based on polyhedral oligomeric silsesquioxane (POSS) has attracted great interest due to the combination of properties





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derived from the inorganic and organic components [25–30]. POSS is a class of unique inorganic component and can be incorporated into polymer matrices to produce novel hybrid polymers with advantageous properties [31-36]. Müller et al. synthesized the tadpole-shaped inorganic-organic hybrid PAA containing POSS (POSS-PAA) and investigated their self-assembly in water [37]. Li et al. studied the hierarchical self-assembly of POSS end-capped polv(dimethylamino methacrylate) (POSS-PDMAEMA) hybrid polymer from single micelle to complex micelle [29]. These POSScontaining inorganic-organic hybrid micelles/aggregates are different from micelles self-assembled from amphiphilic block copolymers. Furthermore, the investigation for host-guest supramolecular self-assembly between POSS-containing hybrid micelle and CDs has been carried out. For example, Zheng et al. reported the preparation and characterization of POSS-PEO-POSS/a-CD inorganic-organic hybrid polyrotaxanes by click chemistry [38]. However, the self-assembly and nanostructural dynamical-change of the assemblies of POSS-containing micelles/aggregates and CD molecules were not concerned.

Herein, in order to investigate the dynamical supramolecular self-assembly between inorganic–organic hybrid spherical aggregates and CD molecules, the star-shaped PEO with POSS core (POSS-(PEO)₈) (Scheme 1) was synthesized via click chemistry which is a kind of coupling reaction with high specificity and efficiency. The supramolecular self-assembly behavior of POSS-(PEO)₈ spherical aggregates and α -CD in water was investigated by altering the amount of α -CD molecules. Environment-induced nanostructural dynamical-change of the hybrid supramolecular self-assemblies was studied by changing the amount of phenol and temperature for POSS-(PEO)₈/ α -CD self-assemblies solution.

2. Experimental

2.1. Materials

 dried under vacuum. Methoxy poly(ethylene oxide) with $M_n = 5$ K denoted as mPEO-OH (Fluka, USA) was dried by azeotropic distillation in the presence of toluene. Alkynyl PEO was synthesized by the DCC reaction of mPEO-OH with excess of propargyl 3-carboxylic-propanoate, according to our previous work [80].

2.2. Characterization

Nuclear magnetic resonance (NMR). NMR spectra of samples were obtained from a Bruker DMX 500 NMR spectrometer $CDCl_3$ or D_2O as solvents. The chemical shifts were relative to tetramethylsilane.

Gel permeation chromatography (GPC). The molecular weight and molecular weight distribution were measured on a Viscotek TDA 302 gel permeation chromatography equipped with two columns (GMHHR-H, M Mixed Bed). THF was used as eluent at a flow rate of 1 mL min⁻¹ at 30 °C.

Optical transmittances. The optical transmittances of POSS-(PEO)₈/ α -CD supramolecular assemblies aqueous solutions (1 g L⁻¹, 2 g L⁻¹ and 5 g L⁻¹, deionized water was used as the solvent) at various temperatures were measured at a wavelength of 500 nm on a UV–visible spectrophotometer (Lambda 35, PerkinElmer). The temperature of the sample cell was thermostatically controlled using an external superconstant temperature bath. The solutions were equilibrated for 10 min at each measuring temperature.

Dynamic light scattering spectrophotometer (DLS). The hydrodynamic radius (R_h) of the aggregates of copolymer was investigated using DLS techniques. The experiments were performed on a Malven Autosizer 4700 DLS spectrometer. DLS was performed at a scattering angle 90°. The R_h was obtained by a cumulant analysis.

Transmission electron micrographs (TEM). The morphology of nano-assemblies was observed with a JEOL JEM-2010 TEM at an accelerating voltage of 120 kV. The samples for TEM observation were prepared by placing 10 μ L of nano-assemblies solution on copper grids coated with thin films and carbon. The samples were stained by 1% phosphotungstic acid.

2.3. Synthesis of octa(3-chloropropyl) POSS (POSS-(Cl)₈)

Octa(3-chloropropyl) POSS (POSS-(Cl)₈) was synthesized according to the literature [39]. A typical procedure was as follows. Methanol (1800 mL), 3-chloropropyltrimethoxysilane (79.5 g,



Scheme 1. Synthesis of star-shaped PEO with POSS core by click chemistry.

0.4 mol), and concentrated hydrochloric acid (90 mL) were mixed and the hydrolysis and rearrangement reactions were allowed to carry out for 40 days. POSS-(Cl)₈ was obtained as a white powder after suction filtration and washing with deionized water (yield: 29%).

¹H NMR (CDCl₃, δ, ppm): 0.75–0.89 (2H, SiCH₂CH₂CH₂Cl), 1.82– 1.97 (2H, SiCH₂CH₂CH₂Cl), 3.49–3.59 (2H, SiCH₂CH₂CH₂Cl). ¹³C NMR (CDCl₃, *δ*, ppm): 9.5 (SiCH₂CH₂CH₂Cl), 26.3 (SiCH₂CH₂CH₂Cl), 47.2 (SiCH₂CH₂CH₂Cl). ²⁹Si NMR (CDCl₃, *δ*, ppm): -67.1 (SiCH₂CH₂CH₂CH₂Cl).

2.4. Synthesis of octa(3-azido) POSS (POSS- $(N_3)_8$)

Octa(3-azido) POSS (POSS-(N₃)₈) was prepared via azidation of POSS-(Cl)₈ [40]. Typically, POSS-(Cl)₈ (4 g, 3.84 mmol), NaN₃ (12.35 g, 0.19 mol), and anhydrous DMF (60 mL) were added into a 100 mL round-bottom flask. The reaction was carried out at 120 °C for 48 h. Then the solvent was removed under reduced pressure. The residues were dissolved in THF and passed through a neutral alumina column to remove residual NaN3. A colorless viscous liquid was obtained after drying in a vacuum oven overnight at room temperature.

¹H NMR (CDCl₃, δ, ppm): 0.62–0.83 (2H, SiCH₂CH₂CH₂N₃), 1.58– 1.78 (2H, SiCH₂CH₂CH₂N₃), 3.25–3.39 (2H, SiCH₂CH₂CH₂N₃). ¹³C NMR (CDCl₃, δ, ppm): 9.9 (SiCH₂CH₂CH₂N₃), 22.8 (SiCH₂CH₂CH₂N₃), 53.7 (SiCH₂CH₂CH₂N₃). ²⁹Si NMR (CDCl₃, δ, ppm): -69.3 (SiCH₂CH₂CH₂N₃).

2.5. Synthesis of star-shaped poly(ethyl oxide) with POSS core $(POSS-(PEO)_8)$

POSS-(PEO)₈ star-shaped hybrid polymer was prepared via click chemistry. A typical procedure was as follows. POSS-(N₃)₈ (0.2 g, 0.184 mmol) and alkynyl PEO (15 g, 2.944 mmol) were dissolved in anhydrous DMF (60 mL). Then CuBr (422 mg, 2.944 mmol) and PMDETA (614 µL, 2.944 mmol) were added into the above solution. After degassed via three freeze-evacuate-thaw cycles and backfilled with argon, the reaction was carried out at 70 °C for 24 h. Then azide-functional Merrifield resin (3 g, 1.4 mmol g^{-1}) was added. The suspension was kept stirring for another 10 h at 80 °C. After suction filtration, the filtrate was diluted with THF, and passed through a neutral aluminum oxide column to remove the copper catalyst. The hybrid polymer was obtained by precipitation into cold hexane and dried in vacuo.

¹H NMR (CDCl₃, δ , ppm): 2.68 (OOCCH₂CH₂COO), 3.39 (OCH₂-CH₂OCH₃), 3.67 (OCH₂CH₂O), 4.26 (CH₂CH₂CH₂-triazole).

2.6. Preparation of self-assembled aggregates of inorganic-organic hybrid polymer

The POSS-(PEO)₈ hybrid aggregates were prepared by the direct dissolution of the inorganic-organic hybrid polymer into water.

3. Results and discussion

3.1. Synthesis of star-shaped inorganic–organic hybrid POSS-(PEO)₈ polymer

Star-shaped inorganic-organic hybrid POSS-(PEO)8 polymer was synthesized by click chemistry of POSS-(N₃)₈ with excess alkynyl PEO. Click chemistry is a kind of "graft onto" method to prepare well-defined polymeric materials with high efficiency. ¹H NMR spectra of POSS-(Cl)₈, POSS-(N₃)₈, and star-shaped POSS-(PEO)₈ were shown in Fig. 1. Compared to those of the two precursors, it can be seen that new signals at 4.26 ppm and 2.68 ppm



Fig. 1. ¹H NMR spectra of (a) POSS-(Cl)₈, (b) POSS-(N₃)₈, and (c) star-shaped POSS-(PEO)₈ (in CDCl₃).

(peaks a and b) appeared, in addition to the signals those belong to PEO arms at 3.67 ppm and 3.39 ppm (peaks c and d) resulting from click reaction. These signals are ascribed to methylene protons in CH₂CH₂CH₂-triazole, OOCCH₂CH₂COO, OCH₂CH₂O, and ethylene protons in OCH₂CH₂OCH₃. The coupling efficiency (CC) of click reaction of azido- and alkynyl-groups was calculated by the integral ratio between peak a (I_a) and d (I_d) in Fig. 1(c), according to eqn (1).

$$CC = (3I_d/2I_a) \times 100\% \tag{1}$$

The CC value is 89.6%, indicating that click reaction for preparing star-shaped hybrid molecules presented high efficiency, although the presence of the steric hindrance during the reaction process. The number-average molecular weight calculated from ¹H NMR spectrum (M_n NMR) was 37,900 g mol⁻¹.

The GPC trace of star-shaped POSS-(PEO)₈ was shown in Fig. 2. As shown in Fig. 2, GPC trace was monomodal. The number-average molecular weight ($M_{n, GPC}$) and M_w/M_n were 33,800 g mol⁻¹ and 1.27, respectively. The value of $M_{n, NMR}$ was higher than that of $M_{n, NMR}$



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Fig. 2. GPC trace of star-shaped POSS-(PEO)₈.

_{GPC} should be ascribed to the unique star-shaped topology of POSS-(PEO)₈.

3.2. Supramolecular self-assembly of star-shaped inorganic organic hybrid POSS-(PEO)₈ and different amount of α -CD

Inorganic-organic hybrid POSS-(PEO)₈ aggregates was easily prepared by the direct dissolution of POSS-(PEO)₈ into water. After adding α -CD molecules into the aggregates, the supramolecular host-guest inclusion complexation between α -CD and PEO occurred, and the hybrid supramolecular self-assemblies formed. Fig. 3(a) shows the photographs of these self-assemblies solutions after adding different amount of α -CD molecules into POSS-(PEO)₈ aggregates solution. It can be seen that the solutions presented an obvious transition from transparency to turbidity with the increase of the amount of α -CD. Without or with small amount of α -CD, the aggregates or supramolecular self-assemblies are stable and the aggregation did not occur, indicating that POSS-(PEO)8 or POSS- $(PEO)_8/\alpha$ -CD supramolecular self-assemblies presented good hydrophilicity under above conditions. But when the adding amount of α -CD molecules increased, the solutions became turbid to some extent, which revealed that the hydrophobicity and aggregation of the supramolecular self-assemblies increased when more α -CD molecules complexed with PEO chains. The morphologies of the self-assemblies may be changed in comparison with those at lower α -CD molecules condition. Adding more α -CD molecules into the solution system, the obvious turbidity can be observed, demonstrating that POSS-(PEO)₈/ α -CD supramolecular self-assemblies aggregated into lager self-assemblies.



Fig. 3. Photographs of (a) POSS-(PEO)₈ hybrid supramolecular self-assemblies solution (1 g L⁻¹) after adding different amount of α -CD. [α -CD]:[EO] = (A) without α -CD, (B) 1:37, (C) 1:19, (D) 1:8, (E) 1:5, (F) 1:4.4, (G) 1:4, (H) 1:3.8, (I) 1:3; (b) POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) hybrid supramolecular self-assemblies solution (1 g L⁻¹) after adding phenol. [phenol]:[α -CD] = (A) without phenol, (B) 0.16:1, (C) 0.32:1, (D) 0.47:1, (E) 0.62:1, (F) 0.77:1, (G) 0.91:1, (H) 1.01:1, (I) 1.13:1; and PEO-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) hybrid supramolecular self-assemblies solutions ((c) 1 g L⁻¹ and (d) 2 g L⁻¹) at different temperature: (A) 25 °C, (B) 40 °C, (C) 45 °C, (D) 50 °C, (E) 55 °C, (F) 60 °C, (G) 65 °C, (H) 70 °C, and (I) 75 °C.

The hydrodynamic radius (R_h) and the Z-average size distributions (polydispersity index, PDI) of POSS-(PEO)₈ aggregates and POSS-(PEO)₈/a-CD supramolecular self-assemblies were characterized by DLS. As shown in Fig. 4(a), the $R_{\rm h}$ and PDI of the selfassemblies increased with increasing of the amount of α -CD molecules in supramolecular system. POSS-(PEO)₈ aggregates presented an average R_h of 91.6 nm and a narrow PDI of 0.082. But for sample E, the molar ratio of α -CD to EO unit is 1:5, the $R_{\rm b}$ and PDI increased to 144.6 nm and 0.127, respectively. Further improved the content of α -CD (sample I, the molar ratio of α -CD to EO unit is 1:3), the self-assemblies showed larger R_h and the wider PDI data (227 nm and 0.206, respectively). The increase of R_h and widening of PDI of the supramolecular self-assemblies with the increase of the amount of α -CD molecules implied that the nanostructure of the self-assemblies changed due to the host-guest inclusion complexation of PEO chains with different amount of α -CD molecules.

TEM images were used to directly observe the morphologies of the inorganic-organic supramolecular self-assemblies. Fig. 5(a) shows the scheme of the self-assembly process of POSS-(PEO)8. The spherical aggregates can be observed after self-assembly, as shown in the TEM image (Fig. 5 (b)). Because the aggregates are much larger than the contour length of PEO, they must have a more complicated structure than conventional micelles. When small amount of α -CD molecules was added to the aggregates solution (such as sample C, molar ratio of α -CD to EO unit is 1:19), the supramolecular self-assembly between PEO chains and α -CD was carried out, and the hydrophobicity of the system increased to some degree due to the presence of small amount of hydrophobic microcrystal domains formed from the host-guest inclusion complexation of α -CD with partial PEO chains. Therefore, the supramolecular self-assemblies presented deformed spherical structure, as shown in Fig. 6(a). After more α -CD molecules complexing with PEO chains (such as sample E, molar ratio of α -CD to EO unit is 1:5), the hydrophobicity of the self-assemblies system increased rapidly owing to more hydrophobic microcrystal domains formed at this condition and the aggregation of self-assemblies were different from those at lower amount of α -CD molecules. From Fig. 6(b), the supramolecular self-assemblies presented cylindrical structure. Further adding more α -CD molecules to the above solution (such as sample I, molar ratio of α -CD to EO unit is 1:3), the POSS-(PEO)₈/ α -CD supramolecules became more hydrophobic due to the presence of large amount of hydrophobic microcrystal domains and self-assemble and aggregate into sheet-structural self-assemblies, as shown in Fig. 6(c). Fig. 7 shows the schematic illustration of the dynamic change of self-assemblies from regular spherical aggregates, deformed spherical aggregates, cylinders to sheets. After adding small amount of α -CD molecules, only small amount of hydrophobic microcrystal domains formed from the host-guest inclusion complexation of α -CD with PEO chains. Therefore, the spherical aggregates would present deformed spherical morphology due to the presence of hydrophobic microcrystal domains. When more α -CD molecules were nested to PEO chains, the polypseudorotaxanes of α -CD-PEO would become more rigid and more hydrophobic microcrystal domains can be formed due to the self-assembly and arrangement of these polypseudorotaxanes. So, the aggregates would be changed to cylinders. Further adding more α -CD molecules to the system, all PEO chains would be nested by α -CD and the polypseudorotaxanes become very rigid. Large amount of hydrophobic microcrystal domains are formed. The cylinders would be further changed to nano sheets due to the presence of large amount of hydrophobic microcrystal domains.



Fig. 4. Z-average size distributions of (a) POSS-(PEO)₈ spherical aggregates (sample A) and POSS-(PEO)₈/ α -CD supramolecular self-assemblies (sample E and I) at 25 °C and (b) POSS-(PEO)₈/ α -CD supramolecular self-assemblies after adding different amount of phenol molecules (sample B, sample F and sample I, molar ratios of phenol to α -CD are 0.16:1, 0.77:1, and 1.13:1 respectively).

3.3. Phenol-induced nanostructural dynamical-change of supramolecular self-assemblies

Phenol molecules have stronger host-guest inclusion complexation ability with α -CD than POSS-(PEO)₈/ α -CD system. Therefore, phenol molecules can strip α-CD away from PEO chains if phenol is added to the POSS-(PEO)₈/ α -CD supramolecular self-assemblies solution. In order to investigate the nanostructural dynamicalchange of self-assemblies, different amounts of phenol molecules were added to POSS-(PEO)₈/α-CD hybrid supramolecular selfassemblies solution ($[\alpha$ -CD]:[EO] = 1:3, 1 g L⁻¹). The molar ratio of phenol to α -CD was changed from 0 to 1.13:1. Fig. 3(b) shows the photographs of supramolecular self-assemblies solution after adding different amount of phenol. Without or with small amount of phenol, the solutions were turbid, but the solutions became more transparent after adding more amount of phenol molecules to the self-assemblies solutions. These phenomena indicated that phenol molecules captured the α-CD molecules from PEO chains to form phenol/ α -CD inclusion complexes, which resulted in the destroy of hydrophobic microcrystal domains and the dynamicalchange of the nanostructures of POSS-(PEO)₈/α-CD hybrid supramolecular self-assemblies.

The changes of R_h and PDI of self-assemblies also can reveal the effect of phenol on the morphologies of supramolecular selfassemblies. Fig. 4(b) shows the R_h and PDI of self-assemblies after adding different amount of phenol molecules. As for sample B, the molar ratio of phenol to α -CD is 0.16:1, and the R_h and PDI were 226.5 nm and 0.253, respectively. When the ratio of phenol to α -CD was improved to 0.77:1 (sample F), the R_h and PDI decreased to 177.3 nm and 0.241, respectively. Further increasing the ratio of phenol to α -CD to 1.13:1, the R_h and PDI of the self-assemblies declined to 91.8 nm and 0.09, respectively. These results demonstrated that the nanostructural dynamical-change of POSS-(PEO)₈/ α -CD hybrid supramolecular self-assemblies can be achieved through adding phenol to make α -CD slip out of PEO chains gradually.

Fig. 6((d)–(f)) shows the TEM images of POSS-(PEO)₈/ α -CD supramolecular self-assemblies ($[\alpha$ -CD]:[EO] = 1:3) after adding different amount of phenol molecules. It can be seen that selfassemblies presented sheet structure (Fig. 6(d)), indicating small amount of phenol only changed the self-assemblies morphologies slightly. Adding more phenol molecules into the solution (such as molar ratio of phenol to α -CD: 0.77:1), the sheet nanostructures were transferred into cylindrical self-assemblies (Fig. 6(e)). When the molar ratio of phenol to α -CD was improved to 1.01:1 (Fig. 6(f)). the self-assemblies were changed into deformed spherical aggregates. With the increase of phenol molecules in solutions, the α-CD molecules slipped out from PEO also increased. Then the hydrophilicity of POSS-(PEO)₈/ α -CD gradually increased due to the destroy of hydrophobic microcrystal domains, which led to the transition of self-assemblies from sheets, cylinders to deformed spherical aggregates or regular spherical aggregates, as schemed in Fig. 7.

Fig. 8(I) shows the ¹H NMR spectra of POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) supramolecular self-assemblies solution (in D₂O) conducted after adding different amount of phenol. In D₂O, POSS-(PEO)₈/ α -CD supramolecules presented high hydrophobicity and only free α -CD molecules and naked PEO segments those did not inclusion complex with α -CD can be observed in spectrum. After adding certain amount of phenol molecules, α -CD molecules slipped out from PEO, and more free α -CD molecules and naked PEO segments dissolved in D₂O were observed. At high phenol concentration (d), the peaks of free α -CD and naked PEO segments without adding



Fig. 5. (a) The schematic self-assembly process of POSS-(PEO)₈ and (b) TEM image of POSS-(PEO)₈ spherical aggregates.



Fig. 6. TEM images of POSS-(PEO)₈/ α -CD supramolecular self-assemblies after adding different amount of α -CD molecules. The molar ratio of α -CD to EO unit: (a) 1:19, (b) 1:5, (c) 1:3; PEO-(PEO)₈/ α -CD ([α -CD];[EO] = 1:3) supramolecular self-assemblies after adding different amount of phenol molecules. The molar ratio of phenol to α -CD: (d) 0.16:1, (e) 0.77:1, (f) 1.01:1; and PEO-(PEO)₈/ α -CD ([α -CD];[EO] = 1:3) supramolecular self-assemblies at different temperature: (g) 40 °C, (h) 50 °C, (i) 65 °C.

phenol (a). All these further confirmed that phenol can lead to the sliding of α -CD out from PEO chains and the nanostructural dynamical-change of the supramolecular self-assemblies.

3.4. Temperature-induced nanostructural dynamical-change of supramolecular self-assemblies

Temperature has the obvious effect on the stability of POSS-(PEO)₈/ α -CD supramolecular inclusion complexes. When the temperature was higher than a critical value, the POSS-(PEO)₈/ α -CD became unstable, and the α -CD molecules slipped out from PEO chains gradually. Fig. 3((c) and (d)) shows the photographs of POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) self-assemblies solutions ((c) 1 g L⁻¹ and (d) 2 g L⁻¹) at different temperature. As shown in Fig. 3(c), at lower temperature (\leq 45 °C), the self-assemblies solutions were turbid. When these solutions were heated to higher temperature, they became more transparent. This indicated that the α -CD molecules can slip out from PEO chains when temperature increased. If the concentration of the self-assemblies solution was improved, the turbidity was more apparent and the turbiditytransparency transition occurred at higher temperature (as shown in Fig. 3(d)). From the view of turbidity-transparency transition, the self-assemblies solutions showed the feature of thermosensitivity.

Fig. 6((g)–(i)) shows the TEM images of POSS-(PEO)₈/ α -CD supramolecular self-assemblies ($[\alpha-CD]$:[EO] = 1:3) at different temperature. It can be seen that self-assemblies presented sheet structure (Fig. 6(g)) at 40 °C. The sheet nanostructures were transferred into cylindrical self-assemblies (Fig. 6(h)) at 50 °C. When the temperature increased to 65 $^{\circ}C$ (Fig. 6(i)), the selfassemblies were changed into deformed spherical aggregates. With the environmental temperature increased up to a critical value, the α -CD molecules started to slip out from PEO. The different dissociation degree of α -CD from PEO chains at different temperature led to the transition of self-assemblies from sheets, cylinders to deformed spherical aggregates or regular spherical aggregates due to the destroy of hydrophobic microcrystal domains, as schemed in Fig. 7. However, during the process of heating, the cylindrical structure tended to transform to micellar structure, indicating that cylindrical structure was unstable and transitional nano-structure.

Fig. 8(II) shows the ¹H NMR spectra of POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) supramolecular self-assemblies solution (in D₂O) conducted at different temperature. In D₂O, POSS-(PEO)₈/ α -CD



Fig. 7. A schematic illustration of the dynamic supramolecular self-assembly transformation from POSS-(PEO)₈ and POSS-(PEO)₈/α-CD nanostructures from regular spherical aggregates, deformed spherical aggregates, cylinders to sheets.



Fig. 8. ¹H NMR spectra of PEO-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) supramolecular self-assemblies solution (in D₂O) (I) after adding different amount of phenol molecules. The molar ratio of phenol to α -CD: (a) without phenol, (b) 0.32:1, (c) 0.62:1, (d) 0.91:1; and (II) at different temperature: (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C.

supramolecules presented high hydrophobicity and only free α -CD molecules and naked PEO segments in spectrum at 30 °C. When the temperature increased to 40 °C, the peaks of α -CD and PEO increased slightly. When the temperature increased to 50 °C, the intensity of the peaks of α -CD and PEO increased to some extent, indicating some α -CD molecules slipped out from PEO at this temperature, and more free α -CD molecules and naked PEO segments dissolved in D₂O were observed. When the temperature increased to 60 °C, the peaks intensity became stronger due to more α -CD molecules slipped out from PEO at this temperature. All these confirmed that high temperature can lead to the sliding of α -CD out from PEO chains and the nanostructural dynamical-change of the supramolecular self-assemblies.

Fig. 9(a) shows the transmittance change of POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) self-assemblies solutions (1 g L⁻¹, 2 g L⁻¹ and 5 g L⁻¹) with the increase of temperature. For the solution with the concentration of 1 g L⁻¹, the initial transmittance was about 30%. At lower temperature range (\leq 42 °C), the transmittance changed slightly. But when the temperature was higher than 42 °C, the transmittance increased rapidly. For the solution with the concentration of 2 g L⁻¹, the initial transmittance was zero. When the temperature was improved to about 48 °C, the solution transmittance started to increase rapidly. But only the temperature was higher than 65 °C, the transmittance was up to about 70%. For the

solution with the concentration of 5 g L⁻¹, the initial transmittance was also zero. Only when the temperature increased to about 65 °C, the solution transmittance began to increase obviously. But even the temperature was up to 85 °C, the transmittance was only about 52%. The transmittance measurements showed that the transmittance change of the self-assemblies was related with the adjustment of the environmental temperature and the solution concentration has much effect on the transmittance change.

Fig. 9(b) shows the R_h change of for POSS-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) supramolecular self-assemblies with the change of environmental temperature. It can be seen that the R_h of the self-assemblies was large at lower temperature (for example, 234.9 nm at 29 °C). At lower temperature range, the R_h only changed slightly (for example, 238.9 nm at 41 °C). When the temperature further increased, the R_h of the self-assemblies decreased sharply (for example, 224.1 nm at 45 °C and 156.1 nm at 57 °C). The R_h change curve of supramolecular self-assemblies further indicated that changing environmental temperature can make α -CD flip out from PEO chains, which led to the nano-structural dynamical-change of POSS-(PEO)₈/ α -CD supramolecular self-assemblies.

The α -CD molecules slipped out from PEO chains at high temperature can reversibly inclusion complex with PEO chains to reconstruct POSS-(PEO)₈/ α -CD supramolecular self-assemblies



Fig. 9. Temperature dependence of (a) transmittance for PEO-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) hybrid supramolecular self-assemblies solutions (1 g L⁻¹, 2 g L⁻¹ and 5 g L⁻¹) and (b) hydrodynamic radium (R_h) for PEO-(PEO)₈/ α -CD ([α -CD]:[EO] = 1:3) hybrid supramolecular self-assemblies solution (1 g L⁻¹).



Fig. 10. Z-average size distributions of POSS-(PEO)₈/α-CD supramolecular selfassemblies ([α -CD]:[EO] = 1:3) at 25 °C (sample I) and heating sample I to 75 °C then cooling to 25 $^{\circ}$ C (cooled sample I).

when the system was cooled to room temperature. As shown in Fig. 10, the R_h and PDI of sample I (1 g L⁻¹, the ratio of molar ratio of α -CD to EO unit is 1:3) were 227 nm and 0.206, respectively at 25 °C. As a contrast, the solution was heated to 75 °C and then cooled to 25 °C, and the R_h and PDI were observed as 218 nm and 0.319, respectively. The result can confirm the dynamic and reversible change of supramolecular self-assemblies through altering the environmental temperature.

4. Conclusions

Star-shaped inorganic-organic hybrid POSS-(PEO)₈ was successfully synthesized by click chemistry. POSS-(PEO)₈ can be selfassemble into spherical aggregates in water. The host-guest inclusion complexation between POSS-(PEO)₈ aggregates and α-CD molecules to form POSS-(PEO)₈/α-CD supramolecular selfassemblies. The nanostructure of the POSS-(PEO)₈/α-CD supramolecular self-assemblies can be gradually transformed from regular spherical aggregates, deformed spherical aggregates, cylinders to sheets through adding different amount of α -CD molecules into the POSS-(PEO)₈ spherical aggregates solution. Different amounts of phenol molecules were used to capture α -CD from PEO chains and lead to reversible change of the self-assemblies from sheets, cylinders to deformed spherical aggregates or regular spherical aggregates. Moreover, increasing the temperature of supramolecular self-assemblies solution also can lead to the slipping of α -CD out of PEO and dynamically change the nanostructures from sheets. cylinders to deformed spherical aggregates or regular spherical aggregates. The reversibly nanostructural dynamical-change can be induced by altering the environmental conditions of the solutions.

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References

- [1] Rank A. Hauschild S. Förster S. Schubert R. Langmuir 2009;25(3):1337-44.
- [2] Chen Y, Dong CM. J Phys Chem B 2010;114(22):7461-8.
- Chen S, Yang B, Guo C, Ma JH, Yang LR, Liang X, et al. J Phys Chem B [3] 2008;112(49):15659-65.
- Kim SY, Lee KE, Han SS, Jeong B. J Phys Chem B 2008;112(25):7420-3.
- Johnsson M, Wagenaar A, Engberts JBFN. J Am Chem Soc 2003;125(3):757-60.
- [6] Zhu J. Havward RC. J Am Chem Soc 2008:130(23):7496-502.
- Weiss TM, Narayanan T, Gradzielski M. Langmuir 2008;24(8):3759-66. [7]
- [8] Wang L, Yu X, Yang S, Zheng JX, Van Horn RM, Zhang WB, et al. Macromolecules 2012:45(8):3634-8.
- Rowan SJ. Nat Mater 2009;8(2):89-91. [9]
- [10] Szostak JW, Bartel DP, Luisi PL. Nature 2001;409(6818):387-90.
- [11] Zhu T, Szostak JW. J Am Chem Soc 2009;131(15):5705-13.
- [12] Sundararaman A, Stephan T, Grubbs RG. J Am Chem Soc 2008;130(37): 12264 - 5
- [13] Grzybowski BA, Stone HA, Whitesides GM. Nature 2000;405(6790):1033-6. Ren LX, Ke FY, Chen YM, Liang DH, Huang J. Macromolecules 2008;41(14): [14]
- 5295-300. [15] Zhang XL, Huang J, Chang PR, Li JL, Chen YM, Wang DX, et al. Polymer
- 2010;51(19):4398-407
- Tian W, Fan XD, Kong J, Liu YY, Liu T, Huang Y. Polymer 2010;51(12):2556-64. [16] Osman SK, Brandl FP, Zayed GM, Teßmar JK, Göpferich AM. Polymer 2011;52(21):4806-6812.
- [18] Zhang JX, Ma PX. Polymer 2011;52(21):4928-37.
- Isobe Y, Sudo A, Endo T. Macromolecules 2006;39(23):7783-5. [19]
- Isobe Y, Sudo A, Endo T. J Polym Sci Part A: Polym Chem 2008;46(6):2305-8. [20]
- Choi HS, Lee SC, Yamamoto K, Yui N. Macromolecules 2005;38(23):9878-81. [21]
- [22] Kidowaki M, Zhao C, Kataoka T, Ito K. Chem Commun 2006;39:4102-3.
- [23] Yan Q, Yuan JY, Kang Y, Yin YW. Polym Chem 2010;1(4):423-5.
- [24] Huang J, Ren L, Chen YM. Polym Int 2008;57(5):714-21.
- [25] Du F, Tian J, Wang H, Liu B, Jin B, Bai R. Macromolecules 2012;45(7):3086-93. Li Y, Guo XH, Wang Z, Chen Z, Wesdemiotis C, Quirk RP, et al. ACS Macro Lett [26]
- 2012;1(7):834-9.
- Zhang WA, Yuan J, Weiss S, Ye X, Li C, Müller AH. Macromolecules [27] 2011;44(17):6891-8.
- [28] Ni C, Wu G, Zhu C, Yao B. J Phys Chem C 2010;114(32):13471-6.
- [29] Ma L, Geng H, Song J, Li J, Chen G, Li Q. J Phys Chem B 2011;115(36): 10586-91.
- [30] Zhang WA, Liu L, Zhuang X, Li X, Bai J, Yu C. J Polym Sci Part A: Polym Chem 2008;46(21):7049-61.
- [31] Tanaka K, Chujo Y. J Mater Chem 2012;22(5):1733-46.
- Kanehashi S, Tomita Y, Obokata K, Kidesaki T, Sato S, Miyakoshi T, et al. [32] Polymer 2013;54(9):2315-23.
- [33] He J, Yue K, Liu Y, Yu X, Ni P, Cavicchi KV, et al. Polym Chem 2012;41(23): 6919-21.
- Wang K, Cai L, Wang SF. Polymer 2011;52(13):2827-39. [34]
- [35] Lin YC, Kuo SW. Polym Chem 2012;3(4):882-91.
- [36] Wanke CH, Feijó JL, Barbosa LG, Campo LF, de Oliveira RVB, Horowitz F. Polymer 2011;52(8):1797-802.
- [37] Zhang WA, Fang B, Walther A, Müller AHE. Macromolecules 2009;42(7): 2563-9
- [38] Zheng Y, Wang L, Yu R, Zheng SX. Macromol Chem Phys 2012;213(4):458-69.
- [39] He YH, Yang X, Zhang WA, Zheng SX. Polymer 2006;47(19):6814-25.
- [40] Ge Z, Wang D, Zhou Y, Liu H, Liu S, Macromolecules 2009:42(8):2903-10.