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Supramolecular ABA Triblock Copolymer with Polyrotaxane as B Block and Its Hierarchical Self-Assembly

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ABSTRACT: A series of novel well-defined supramolecular ABA triblock copolymers of polyrotaxane are synthesized via atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DMA) initiated by a polypseudorotaxane initiator of α-cyclodextrins (α-CDs) and PEG. The molecular structure of the ABA triblock copolymer with a polyrotaxane as B block, poly(2-(dimethylamino)ethyl methacrylate)-*b*-PEG[included by α-CDs]-*b*-poly(2-(dimethylamino)ethyl methacrylate) (DMA-*b*-PEGCD-*b*-DMA), was confirmed by two-dimensional rotating frame Overhauser effect spectroscopy (2D ROESY) and X-ray diffraction (XRD) analyses. Self-assembly behaviors of the copolymers in water solution were studied by dynamic light scattering (DLS), static light scattering (SLS), and transmission electron microscopy (TEM). Different from the model triblock copolymer without α-CDs and the polypseudorotaxanes composed of homo-PEG and α-CDs, the supramolecular triblock copolymers in water self-assembled into spheres with an amorphous core. Furthermore, the block copolymers at an acidic aqueous solution where the flanking chains were protonated generated the particles with a core of hexagonally packed polyrotaxanes. It is interesting to notice that the particles further aggregated into large disks induced by the solvent evaporation.

1. Introduction

Polyrotaxanes have attracted much attention in the past decades for their great potential as stimulus-responsive materials, molecular machines, or switches in the fields of nanotechnology and drug delivery.[1,2] They are usually constructed by threading molecular rings (or host molecules) onto a macromolecular chain via host–guest interaction, followed by capping the chain ends with bulky groups.[1] Among all the host molecules, cyclodextrins (CDs) are frequently applied in polyrotaxane system mainly due to their bioavailability and low cytotoxicity.[3] The capping reaction, which should be highly efficient and easy to execute, is important during the synthesis of polyrotaxanes. Many capping reactions, including nucleophilic substitution,[4,5] condensation,[6] and click[7] reactions, have been reported in the literature. Small and bulky molecules are normally used as the capping agents. It is known that the polyrotaxanes of α-CDs and poly(ethylene glycol) (PEG) form crystalline precipitates in water because the stiff polyrotaxane columns are prone to aggregate.[8] Thus, polyrotaxanes end-capped using bulky polymers can be regarded as a supramolecular block copolymer that may self-assemble in solution like amphiphilic block copolymers.[9] It is especially important if it is realized that this polyrotaxane segment is a stiff column that is much bulkier than the traditional stiff polymer chain since the diameter of the α-CD ring is 1.4 nm, i.e., the diameter of the polyrotaxane. As far as we know, there is only one example using bulky polymer chains as the capping agent.[10] But the polymer chain reported is formed by an ill-controlled UV-irradiated polymerization, and no report has been found about the self-assembly of such supramolecular block copolymers. Previously, we have shown that the α-CD inclusion complex of poly(ethylene glycol)-*b*-poly(2-(dimethylamino)ethyl methacrylate) induced micelle-like aggregation in aqueous solution.[11] But the aggregates were ill-defined probably due to the polypseudorotaxane structure.

In this paper, a series of novel and well-defined supramolecular ABA triblock copolymers of polyrotaxane, DMA-*b*-PEGCD-*b*-DMA, were synthesized via atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DMA) initiated by a polypseudorotaxane initiator of bromoisobutyryl-modified PEG and α-CD. The structure of the polyrotaxanes was verified by 2D ROESY using nuclear magnetic resonance and X-ray diffraction (XRD) analyses. It is found that the properties of the copolymers are greatly influenced by threading α-CDs onto the polymer chains, and an interesting hierarchical self-assembly is presented.

2. Experimental Section

2.1. Materials. PEG (*M* 2000), 2-bromoisobutyryl bromide, DMA, and *N,N,N′,N″,N″*-pentamethyldiethyenetriamine (PMDETA, 99%) were purchased from Aldrich. α-CD was provided by Wacker Chemical Corp. and used without further purification. *N,N*-Dimethylformamide (DMF, Beijing Reagent Corp.) was redistilled under vacuum before use. All other reagents were analytical grade and used without further purification. The dialysis bag was produced by Viskase Co. (cutoff 3500).

2.2. Synthesis. *Preparation of Polypseudorotaxane as ATRP Initiator.* The bifunctional PEG (Br-PEG$_{44}$-Br) was synthesized following a procedure reported in the literature.[12] To prepare the inclusion complex of bifunctional PEG and α-CD, Br-PEG$_{44}$-Br (1.149 g, 0.50 mmol) was dissolved in deionized water (1.0 mL), and a saturated α-CD aqueous solution (10.70 g, 11.0 mmol α-CD in 63 mL of water) was added. The mixture was sonicated for 30 min, and the white precipitate was collected by centrifugation and washed with deionized water three times to remove free α-CDs. The polypseudorotaxane was obtained by lyophilization and used as a supramolecular ATRP initiator.

ATRP To Prepare ABA Supramolecular Block Copolymers. The typical ATRP procedure was as follows: In a 25 mL Schlenk flask, CuBr (29 mg, 0.20 mmol) and polypseudorotaxane macroinitiator (1.309 g, 0.10 mmol) were added, and the air was exchanged with nitrogen three times. Then, a mixture of the deoxygenated DMA

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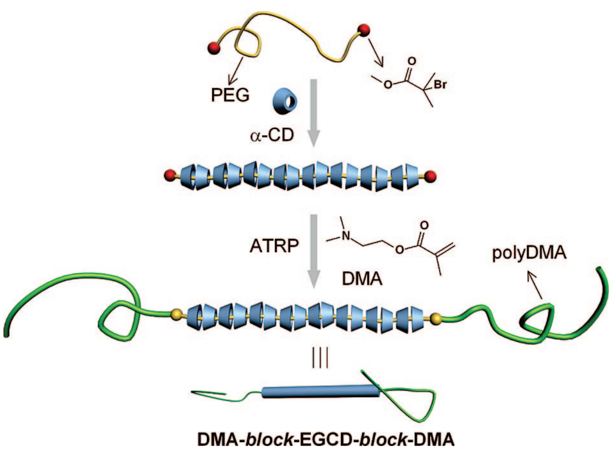
Scheme 1. Synthetic Route for the Polyrotaxane ABA Block Copolymer



(0.795 g, 5.00 mmol) and PMDETA (42 μL, 0.20 mmol) in DMF (12 mL) was transferred into the Schlenk flask under the protection of nitrogen. The reaction proceeded at room temperature for 36 h. The solvent was removed by distillation under vacuum. The product was purified by dialysis against deionized water for a week, and a white powder was obtained after lyophilization.

The model triblock copolymer without cyclodextrins was synthesized following a similar procedure above without cyclodextrins. After termination of the reaction, the polymer was precipitated in ethyl ether and then dissolved by THF. The catalysts were removed by passing through an alumina column. The product was purified by precipitating three times in ethyl ether.

2.3. Characterization. *NMR Characterization.* A Bruker AV 400 MHz proton NMR spectrometer was used for ^1H NMR experiments with DMSO-d_6 or $CDCl_3$ as solvent. The 2D-ROESY experiment was recorded on a Bruker AV 600 MHz proton NMR spectrometer with D_2O as solvent.

XRD Experiments. XRD patterns of the samples were recorded on a Rigaku D/max 2500 X-ray powder diffractmeter with Cu Kα (1.54 Å) radiation (40 kV, 40 mA). The proportional counter detector collected data at a rate of $2\theta = 3° \text{ min}^{-1}$ over the range of $2\theta = 3°-40°$.

DLS/SLS Measurements. Light scattering experiments were performed on a Brookhaven Instrument equipped with BI-200SM goniometer and a BI-TurboCorr digital correlator. A solid-state laser polarized at the vertical direction (CNI Changchun GXL-III, 532 nm, 100 mW) operating at 532 nm was used as light source. In DLS, the intensity−intensity time correlation function $G^{(2)}(\tau)$ in the self-beating mode was measured. It is related to the normalized first-order electric field time correlation function $g^{(1)}(\tau)$ as $G^{(2)}(\tau) = A[1+\beta|g^{(1)}(\tau)|^2]$, where A is the measured baseline, β is a coherence factor, and τ is the delay time. Mathematically, $g^{(1)}(\tau)$ is the Laplace transform of the normalized line width distribution $G(\Gamma)$, $g^{(1)}(\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma\tau}\,d\Gamma$. By using a Laplace inversion program, CONTIN, $G(\Gamma)$ and the average line width, $\bar{\Gamma}$, were obtained. $\bar{\Gamma}$ is used to calculated the translational diffusion coefficient D using the relationship $\bar{\Gamma} = Dq^2$. D can be further converted into the hydrodynamic radius R_h by using the Stokes−Einstein equation $D = k_BT/6\pi\eta R_h$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively. The aqueous solutions of block copolymer were prepared at a concentration of 0.25 mg/mL and filtered through a hydrophilic filter (Millipore, 0.45 μm) to remove dust. The sample at pH 2 was prepared by filtering an acidic aqueous solution (1 N HCl) into the polymer solution. The aqueous solution of model triblock copolymer without α-CDs was prepared at a concentration of 1 mg/mL. The block copolymer of polyrotaxane was also analyzed in DMSO at 0.25 mg/mL on an ALV/DLS/SLS-5022F instrument equipped with a multi-τ digital time correlator (ALV 5000) at the scattering angle of 30°; the data were analyzed by using the commercial CONTIN software provided by ALV.

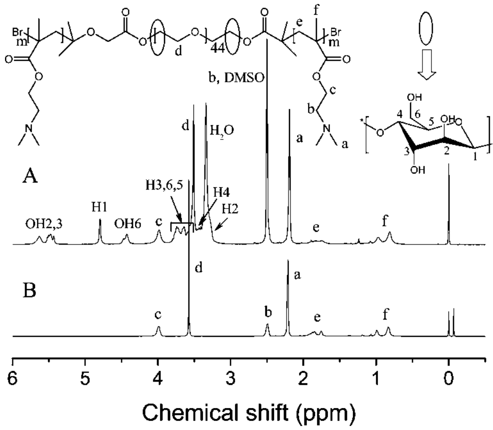


Figure 1. ^1H NMR spectra of (A) DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} with DMSO-d_6 as solvent and (B) DMA_{18}-*b*-EG_{44}-*b*-DMA_{18} with $CDCl_3$ as solvent.

Table 1. Preparation Conditions and Properties of Synthesized Block Copolymers

entry	product	feeding	DMF/mL	time/h
1	DMA_{16}-*b*-$EG_{44}CD_{12}$-*b*-DMA_{16}	1:2:2:50[a]	2	30
2	DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15}	1:2:2:50[a]	12	36
3	DMA_{30}-*b*-$EG_{44}CD_4$-*b*-DMA_{30}	1:2:2:200[a]	20	24
4	DMA_{18}-*b*-EG_{44}-*b*-DMA_{18}	1:2:2:50[b]	1	0.25

[a] [Macroinitiator]:[CuBr]:[PMDETA]:[DMA], [α-CDs]:[EG] = 1:2. [b] Without α-CDs.

TEM Characterization. TEM experiments were carried out on a Hitachi H-800 instrument. The sample was prepared by dropping a few microliters of the aqueous solution (0.25 mg/mL) onto the copper grid coated with a sustaining film, and the morphology was observed after drying. The tilting angle TEM experiment was carried out on a JEOL JEM 2200fs instrument. To further study the morphology of the self-assembly at pH 2, the sample was prepared by dropping solutions onto the grid in a flask that was cooled by liquid nitrogen, followed by removal of water via freeze-drying. After lyophilized, the sample was visualized by TEM.

3. Results and Discussion

3.1. Synthesis of Polyrotaxane Block Copolymers. Because of its well control over molecular weight and chain uniformity,[13] ATRP was used to synthesize the block copolymers of polyrotaxane in this paper. As shown in Scheme 1, a polypseudorotaxane initiator for ATRP was obtained by threading α-CDs onto Br-PEG_{44}-Br, and it was then used to polymerize DMA. The flanking chains of polyDMA were introduced as the stoppers to prevent the dethreading of α-CDs, and the supramolecular block copolymer of polyrotaxane was thus prepared. During the capping process through the polymer chain propagation, some α-CDs were lost from the polypseudorotaxane, and they were removed by dialysis. The composition of the product was estimated by its ^1H NMR spectrum. Figure 1A shows the triblock polyrotaxane DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15}. Figure 1B shows the spectrum of the model block copolymer DMA_{18}-*b*-EG_{44}-*b*-DMA_{18}; the polymerization degree was calculated by comparing the signals at 2.3 ppm ($N(CH_3)_2$) of DMA and the signals of EG unit (3.6 ppm, OCH_2CH_2). The peaks at 2.5 ppm (NCH_2) and 4.1 ppm (OCH_2) in Figure 1B represent the ethyl group of DMA unit. For the triblock copolymer of polyrotaxane (Figure 1A), besides the proton signals of DMA and EG units, the signals of α-CDs were found at 4.8 ppm (H1), 3.5−3.7 ppm (H6, H3, and H5), and 3.3−3.4 ppm (H4 and H2, they were overlapped by H_2O signals). The numbers of α-CDs in the polyrotaxane were calculated by comparing the resonance areas of α-CD (H1 at 4.8 ppm) and DMA.

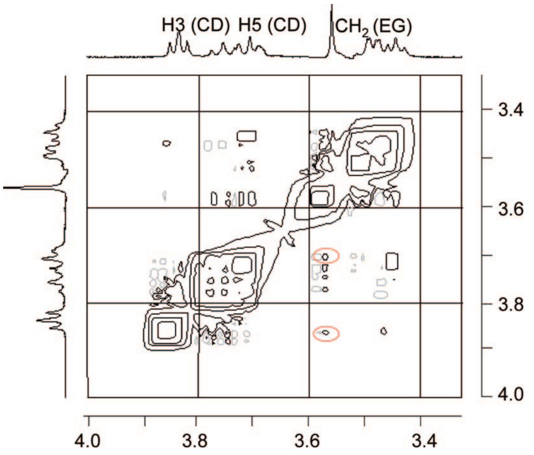


Figure 2. 2D ROESY NMR spectrum of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ in D_2O. Red circles represent the H−H correlation between H3 and H5 of α-CDs and ethylene (CH_2) of PEG, respectively.

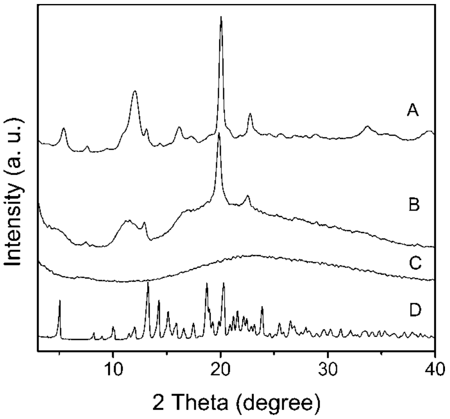


Figure 3. XRD traces of (A) the inclusion complex of homo-PEG and α-CDs, (B) DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ polyrotaxane, (C) DMA$_{18}$-*b*-EG$_{44}$-*b*-DMA$_{18}$, and (D) α-CDs.

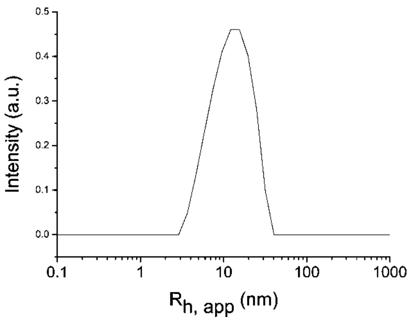


Figure 4. R_h distribution of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ copolymer in DMSO solution (0.25 mg/mL) at a scattering angle of 30° by DLS with CONTIN analysis.

Table 1 shows the obtained block copolymers DMA$_m$-*b*-EG$_{44}$CD$_n$-*b*-DMA$_m$ (*m*: the polymerization degree of the flanking polyDMA chain; *n*: the number of α-CDs threaded onto the PEG chain). Although the molar feed of α-CDs to the Br-PEG-Br chain was 20 (full coverage), the PEG chains of these synthesized polyrotaxanes were covered by α-CD rings ranged from ca. 20% to 60%. Since the polypseudorotaxane macroinitiator dissolved in DMF for the polymerization, the α-CD rings may slip away from the PEG chain dependent upon the concentration. During the propagation, the formed polyDMA segments became so bulky that they detained the α-CD rings from slipping away, and as a result, the block copolymers of polyrotaxane were obtained. Entry 3 in Table 1, which was carried out using more solvent and DMA, gave the block copolymer with the less threaded α-CDs.

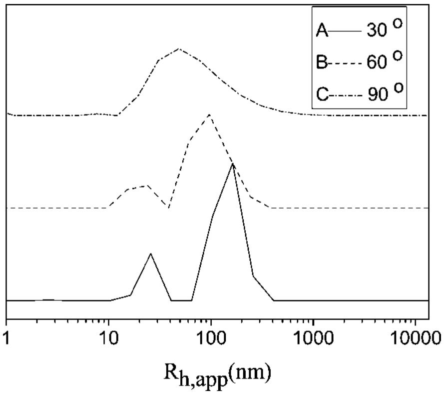


Figure 5. R_h distribution of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ self-assembly in aqueous solution at (A) 30°, (B) 60°, and (C) 90° by DLS with CONTIN analysis.

3.2. Characterization of Polyrotaxane Block Copolymer. The inclusion structure of triblock copolymer of polyrotaxane DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ was verified by 2D ROESY experiment in D_2O as shown in Figure 2. The correlation peaks between the protons H3 and H5 of inner annular α-CD and the ethylene protons (CH_2) of PEG chains indicated that α-CDs were threaded onto the PEG chains. The necklace structure was confirmed by XRD analysis as indicated in Figure 3. Different from those of the model polymer DMA$_{18}$-*b*-EG$_{44}$-*b*-DMA$_{18}$ (plot C) and α-CDs (plot D), the diffraction of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ at $2\theta = 19.8°$ (plot B) clearly represents the characteristic channel-type crystalline of inclusion complexes formed between PEG and α-CDs, which was the same as the inclusion between homo-PEG and α-CDs (plot A). Therefore, the flanking polyDMA chains are bulky enough to prevent the dethreading of α-CDs.

The apparent hydrodynamic radius ($R_{h,app}$) of polyrotaxane triblock copolymer was also obtained by DLS with CONTIN analysis. The parent block copolymer, DMA$_{18}$-*b*-EG$_{44}$-*b*-DMA$_{18}$, is a double hydrophilic polymer that does not aggregate in water as indicated by DLS results (Figure S1). The $R_{h,app}$ value of this copolymer at the concentration of 1 mg/mL in the aqueous solution was about 3 nm. However, the polyrotaxane block copolymer in water formed larger particles as observed from DLS curve, indicating the polyrotaxane block copolymer aggregates easily, and the detailed results will be shown in the following section. We found that the supramolecular block copolymer in DMSO formed a molecular dispersed solution as shown in Figure 4. The $R_{h,app}$ of the DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ unimer in DMSO at the concentration of 0.25 mg/mL was ca. 16 nm. Thus, threading CDs onto the polymer chains has greatly influenced the properties of the model copolymer in solution, owing to the stiffness of the polyrotaxane segment.

3.3. Self-Assembly of Copolymer DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ in Water. The deionized water solution of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ at 0.25 mg/mL had a slightly blue tint, indicating the occurrence of aggregation. CONTIN analysis of the DLS results at 30° shows a bimodal size distribution (Figure 5, plot A), with both of the modes having an angular dependence. After the extrapolation to zero angle, the $R_{h,app}$s of the fast and the slow modes were obtained to be 20 and 276 nm, respectively. The fast mode was believed to be the unimer of polyrotaxane block copolymer (see Figure 4), and the slow mode was attributed to the aggregates formed by the polyrotaxanes. Therefore, the incorporation of α-CDs onto the PEG

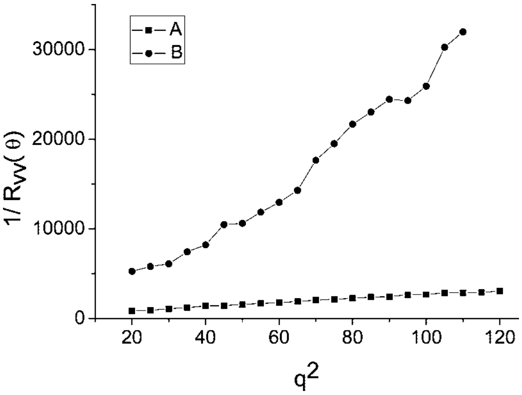


Figure 6. Angular dependence of the scattered intensity of DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} in (A) aqueous solution and (B) acidic (pH = 2) solution.

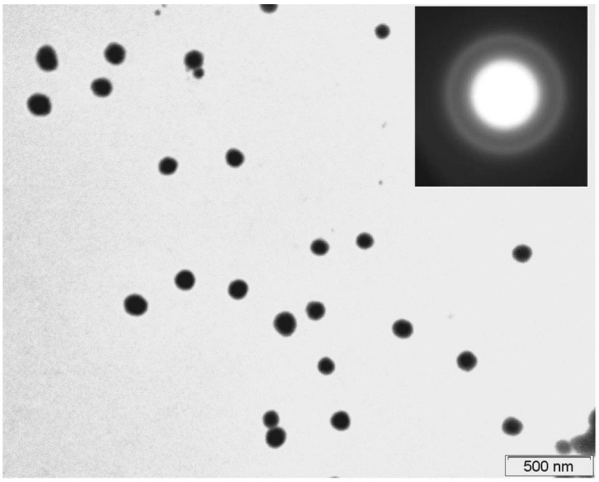


Figure 7. TEM image of the self-assembly of DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} in aqueous solution. The inset was the SAED image of the self-assembly.

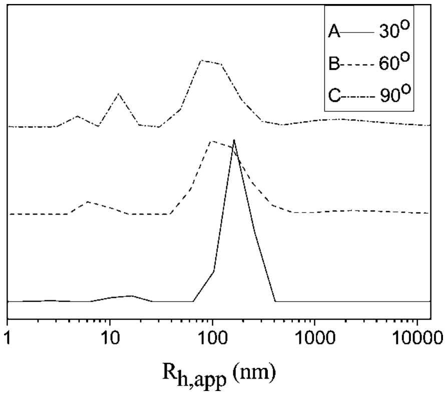


Figure 8. R_h distribution of DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} aqueous solution at pH = 2 at the scattering angle of (A) 30°, (B) 60°, and (C) 90° by DLS with CONTIN analysis.

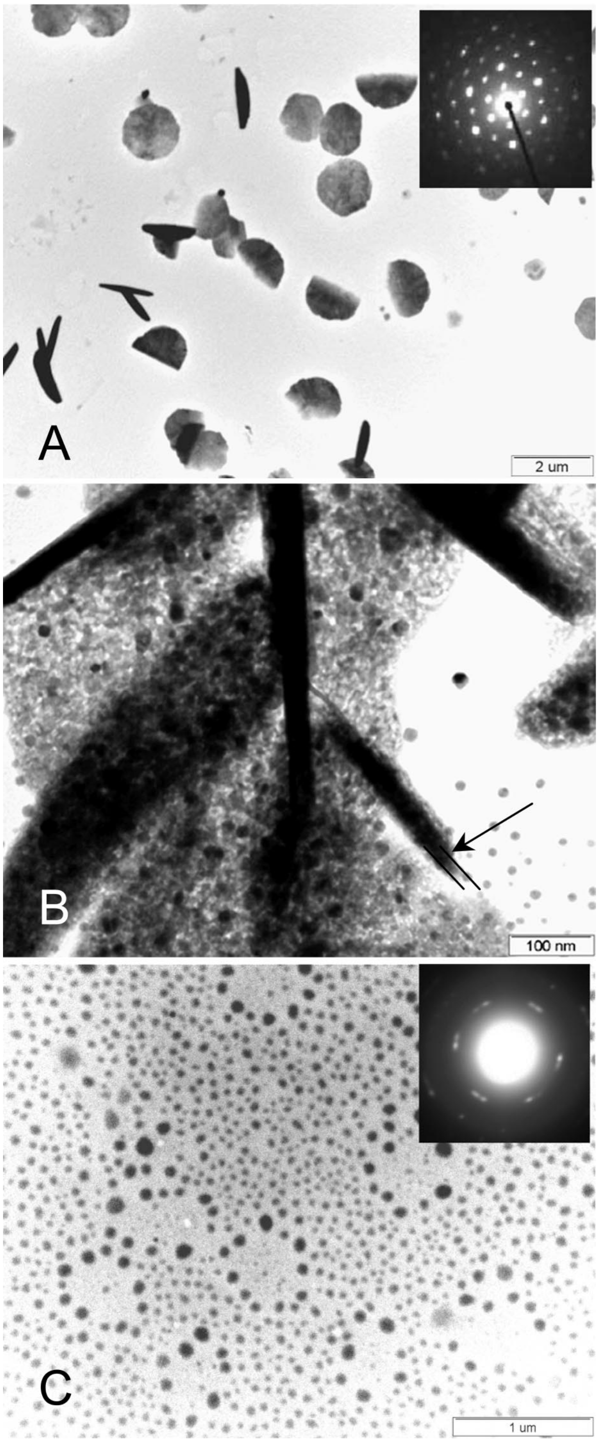


Figure 9. TEM images of the self-assemblies of DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} in pH = 2 aqueous solutions (A and B) prepared by direct dropping the solution onto the grid at room temperature and (C) prepared by freeze-drying. The insets in (A) and (C) are the SAED patterns. The arrow in (B) indicates the maximum thickness of the disk.

chains not only affects the conformation of single polymer chain but also induces aggregation between the polyrotaxanes.

SLS analysis at lower scattering angle (below 40°) yields an apparent gyration radius ($R_{g,app}$) of 151 nm for the larger aggregates (Figure 6A). Combining the results from DLS and SLS, the $R_{g,app}/R_{h,app}$ ratio for the aggregates is 0.55, indicating a solid spherical conformation.[14] This finding is confirmed by the TEM image shown in Figure 7, though the diameter of the spheres observed was ca. 100−150 nm, smaller than that obtained from DLS analysis, which was probably caused by the shrinkage of the particles on the grids in dryness. The inset in Figure 7 shows the selected area electronic diffraction (SAED) pattern of the self-assembled spheres, representing an amorphous assembly of the polyrotaxane blocks.

3.4. Self-assembly of Copolymer DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} in Acidic Aqueous Solution. It is known that polyDMA may be protonated under acidic conditions. The aggregation behavior of DMA_{15}-*b*-$EG_{44}CD_8$-*b*-DMA_{15} in aqueous solution

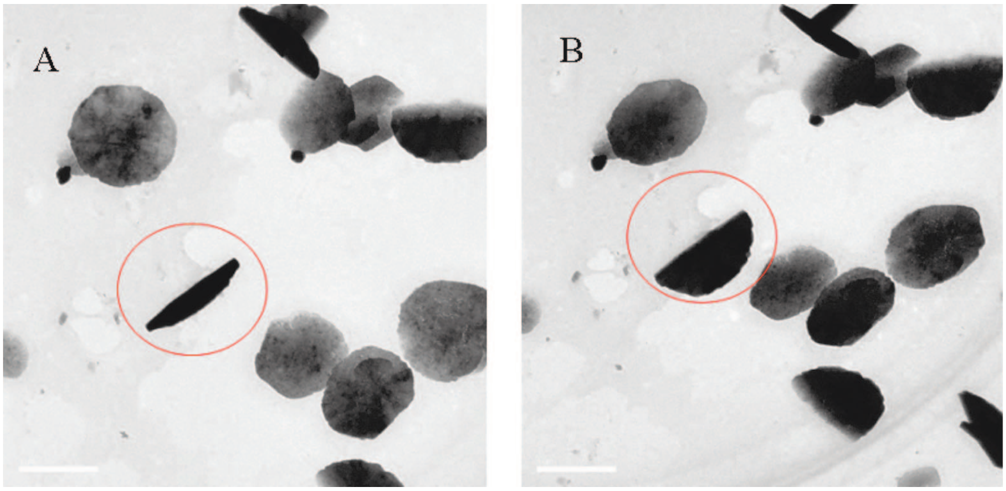
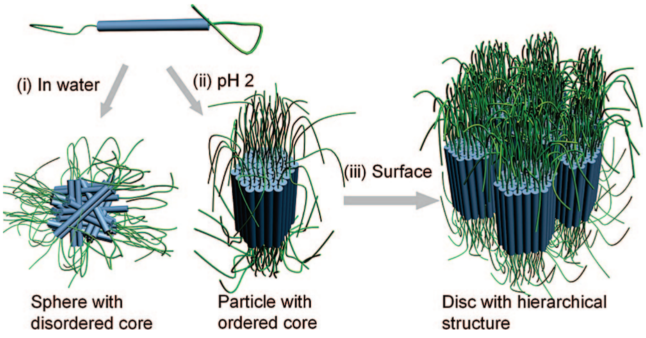


Figure 10. Titling TEM images of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ at pH = 2. Image A was taken without titling, and image B was taken at a titling angle of −42°. The labeled section indicates a coiling disk. The bar is 500 nm.

Scheme 2. Sketch Map for Mechanism of the pH-Dependent Self-Assemblies



of pH = 2 was also studied by DLS. As shown in Figure 8 for angular dependence, a bimodal distribution similar to that in water at 30° scattering angle was observed, except that the $R_{h,app}$ values of the two modes were reduced to 13 and 193 nm, respectively, and the ratio of the smaller aggregate was greatly reduced. The SLS result, as shown in Figure 6B, generated a $R_{g,app}$ of 191 nm for the larger aggregates by fitting the data points at lower scattering angles. Thus, the $R_{g,app}/R_{h,app}$ ratio was 0.99, which is much higher than the value (0.78) of a sphere. This result indicates that the larger aggregates formed by DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ in the acidic conditions adopted a structure of low density. Such aggregates with loose structure were also confirmed by the excessive scattered intensity. As shown in Figure 6, the excessive scattered intensity of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ in acidic condition was almost 4 times lower than that in natural conditions.

Surprisingly, the TEM experiment, which was conducted by dropping the solution (0.25 mg/mL) at pH 2 directly onto the grid, exhibited disklike plates of 500 nm to 2 μm in diameter in the image shown in Figure 9A (and Figure S2 in Supporting Information). Note that the "shuttle" shape in Figure 9A was actually the standing or crimpled disks as shown in the titling images (Figure 10). The SAED pattern in the inset of Figure 9A shows a highly ordered hexagonal symmetry, where the R_1^2:R_2^2:R_3^2:R_4^2:R_5^2 = 1:3:4:7:9 (R is the distance from the center to diffraction spot of different circles). This pattern is the same as that obtained from the crystals formed by homo-PEG and α-CDs.[15] It is interesting to notice that a magnified image (Figure 9B) shows that the big disks were not homogeneous but composed of many small particles. Furthermore, the thickness of the disks, calculated from the standing and curling plate as pointed by the arrow in Figure 9B, was less than 10 nm, close to the theoretical length of the stretched chain of DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$.[16] All these results suggested that the polyrotaxane blocks oriented side-by-side and packed into a monolayer of crystalline structure.

The size of the disks measured from TEM images was much larger than that from DLS, which was probably related with the solvent evaporation on the substrate surface during sample preparation. To eliminate this effect, we also prepared the TEM sample by dropping a solution onto the grid in a flask that was cooled by liquid nitrogen, followed by removal of water via freeze-drying. As shown in Figure 9C, spherical structures, with the size (50−130 nm) similar to that measured by DLS, were observed in the TEM image. The inserted SAED image in Figure 9C still shows the similar symmetric hexagonal patterns. Although the pattern was not as highly ordered as that in Figure 9A, it was enough to tell the difference with that in pure aqueous solution (Figure 7). These results also indicated that the supramolecular structure formed by DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ under acidic conditions was able to further aggregate into disks on the surface during the water evaporation process, in which the polyrotaxanes packed into a highly ordered form.

The self-assembly behaviors of the other copolymers with different number of α-CDs were also studied in the aqueous solution and acidic solution characterized by TEM. Both of the copolymers have the similar self-assembly behaviors as copolymer DMA$_{15}$-*b*-EG$_{44}$CD$_8$-*b*-DMA$_{15}$ (Figure S3 and Figure S4). Even the copolymer DMA$_{30}$-*b*-EG$_{44}$CD$_4$-*b*-DMA$_{30}$ with only four α-CDs threaded onto PEG chains has the similar self-assembly, demonstrating that the property of the DMA-*b*-EG-*b*-DMA copolymers was greatly influenced by α-CDs.

3.5. Proposed Mechanism of the pH-Dependent Self-Assemblies. The above observation is very interesting since such behaviors must be related with the special supramolecular structure of the block copolymers studied, and a mechanism of the pH-dependent self-assembly was proposed. In aqueous solution of polyDMA, of which the pH is ca. 8.5, more than 90% of the amino groups are not protonated since the pK of polyDMA is ~7.0.[17] Besides to increase the solubility of the assembled polyrotaxanes, the polyDMA segments could form hydrogen bonds with the hydroxyl groups of α-CD rings, leading to the formation of solid spheres instead of the highly ordered packing of polyrotaxane segments, as illustrated in Scheme 2i. This structure is supported by the SAED result (inset in Figure 7). However, the hydrogen interactions may be destroyed when the polyDMA segments are fully protonated in an acidic solution. The rigid polyrotaxane segments tend to pack in parallel to form ordered crystalline columns mainly by hydrophobic and packing interactions. As a result, the micellar aggregates with a polyrotaxane-packed core and polyDMA corona in range of 50−150 nm are produced in solution (Scheme 2ii). Because of the repulsive interactions between the protonated and hydrated polyDMAs, the polyrotaxane segments only form a bundle, and the further growth of the bundle to form the disks is prohibited, though the line tension of the edge could be still high. During the evaporation of water on the copper grid surface, the hydration disappears, and the bundles are able to aggregate further in two dimensions to decrease the edge energy but fail to merge into a uniform plate. As a result, the highly ordered polyrotaxanes bundles pack into the monolayer coarse disks with large size.

4. Conclusion

In conclusion, a series of novel supramolecular ABA triblock copolymers with polyrotaxane as the middle block have been synthesized via ATRP. It is interesting to find that, under acidic conditions, they form micelles with a core of hexagonally packed polyrotaxanes, which further organize into disks induced by water evaporation. It is notable that there are three levels of supramolecular structures from the polyrotaxane block copolymer, to bundle-like aggregates in solution, and then to the disk on the surface. The copolymers with different number of α-CDs show the similar self-assembly in aqueous solution. Thus, this study has revealed, for the first time, a hierarchical self-assembly of a supramolecular block copolymer.

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Supporting Information Available: Figure S1 to Figure S4. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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