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ARTICLE

Morphology Transitions of Supramolecular Hyperbranched Polymers Induced by Double Supramolecular Driving Forces

Yang Bai[a], Xiao-dong Fan[a]*, Wei Tian[a]*, Ting-ting Liu[a], Hao Yao[a], Zhen Yang[a], Hai-tao Zhang[a], Wan-bin Zhang[a]

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Tuning the morphology of supramolecular hyperbranched polymers (SHPs) in solution has theoretical and practical significance in SHP applications. This study successfully achieved SHP morphology transitions from branched supramolecular structures to spherical nanosized micelles in mixed solvents. Transmission electron microscopy, dynamic light scattering, 2D ^{1}H NMR ROESY, and fluorescence emission spectroscopy confirmed these transitions. An AB_2-type amphiphilic β-cyclodextrin (β-CD) monomer (Ada-CD_2) possessing double supramolecular interactions was initially synthesized. SHPs based on Ada-CD2 were then formed in DMF/H_2O mixed solvents through the host–guest inclusion interaction between β-CD and Ada. The formed SHPs disassembled with the addition of adamantane carboxylic sodium salt, which was a competitive guest. The SHPs reassembled into core–shell structured micelles based on the hydrophilic–hydrophobic interaction of the amphiphilic Ada-CD_2 monomer.

Introduction

Supramolecular polymers (SPs) with novel structures are attracting considerable attention from various research groups in the last decade.[1–5] These SPs are driven by an intermolecular non-covalent interaction. SPs have potential applications in drug delivery, biomedical engineering, and nanocomposite materials. Various SPs with linear, star-shaped, hyperbranched, dendronized, and cyclic structures are obtained through hydrogen bonding, π–π stacking, metal–ligand interactions, and host–guest recognitions according to their topological architecture differences.[6–21].

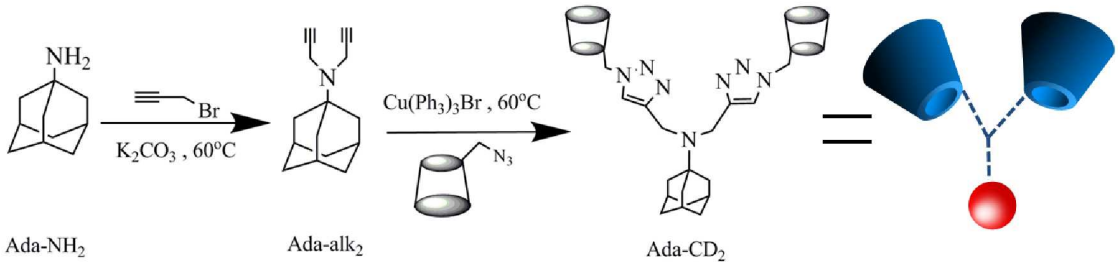
Compared to other SPs, the supramolecular hyperbranched polymers (SHPs) have three-dimensional topological features, little molecular entanglement, low viscosity, high solubility, and plenty of functional terminal groups.[2] Therefore, the SHPs possess the combined advantages of SPs and hyperbranched polymers.[11–21] Some researchers have particularly reported the SHPs based on the host–guest inclusion of cyclodextrin (CD).[12–14] Zhou and Zhu et al. reported a novel class of photoreversible SHPs using the host–guest complexation of azobenzene dimer (A_2 monomer) and *β*-CD trimer (B_3 monomer).[12] Liu's group prepared a novel bifunctional enzyme model using the host–guest interaction of adamantane tetramer (A_4 monomer) and *β*-CD dimer (B_2 monomer).[13] Liu prepared the poly(N-isopropylacrylamide) (PNIPAM) oligomer containing one adamantyl and two CD moieties in the chain terminals (Ad-PNIPAM-CD_2). This "long chain" monomer spontaneously formed a branched polymer through a molecular recognition between Ada and CD moieties.[14] As previously mentioned, most current studies focus on synthesizing different SHPs and adjusting corresponding stimulus-responsive properties. Although this point is very important in expanding SHP applications in different fields, investigations on the tunable morphology transitions are few.

An important issue for the academic field is how to change the polymer structure morphology. The reports in this field are classified into two aspects.[22–24] The first aspect utilizes breaking of a covalent bond and its reaction to the polymer topological structure change. You's group used the Michael addition polymerization to report the synthesis of a polymer, which contained many stimulus-sensitive linkages (disulfide bonds) in the backbone. The structures of the produced polymers were tuned from the linear to the hyperbranched structures by varying the polymerization temperature.[22] The second aspect utilizes a dynamic noncovalent interaction to control polymer architecture and morphology.[23–24] Yan and Zhu obtained polymers with linear and branched structures by

merely adjusting the amount of host molecules (such as β-CD) present.[23] Alternatively, Yuan's group adjusted the CD and copolymer molar ratio, and reported the supramolecular complexes induced from micelles to cylinders, vesicles, and sheets.[24] This study intends to utilize double supramolecular driving forces, i.e., host–guest inclusion and hydrophilic–hydrophobic interaction, in one functionalized β-CD monomer to achieve SHP morphology transitions.

For this purpose, an AB_2-type amphiphilic β-CD monomer (Ada-CD_2) was synthesized using the azide-alkyne cycloaddtion click reaction. This reaction contained one adamantane (Ada) and two β-CD moieties (Scheme 1). In Ada-CD_2, the β-CD cavities interacted with the hydrophobic group of the Ada molecule based on the host–guest recognitions. The hydrophilic–hydrophobic interactions existed because the β-CD and Ada moieties complexed. The coexistence of two supramolecular driving forces in one molecule possibly adjusted the morphology of the formed SHPs. The Ada-CD_2 formed SHPs in the DMF/H_2O mixed solvents. Whereas, the branched morphology changed into spherical nanosized micelles with the addition of the proper amount of adamantane carboxylic sodium salt (Ada-Na).

Results and Discussion



Scheme 1. Schematic illustration of the synthetic routes of the AB_2-type monomer (Ada-CD_2) using the click reaction in an aqueous medium.

To study the supramolecular behaviors, the amphiphilic Ada-CD_2 monomer was synthesized according to the routes in Scheme 1. In the presence of K_2CO_3 (Ada-alk_2), and using the alkylation reaction, two alkyne units were introduced into the preliminary Ada-NH_2. Click chemistry is a very selective and effective synthetic method with mild and clean conditions.[25] Hence, Ada-CD_2 was synthesized using the azide-alkyne cycloaddtion click reaction between Ada-alk_2 and an excess of β-CD-N_3. The organo-soluble $Cu(Ph_3)_3Br$ was used as a catalyst. The excess β-CD-N_3 was further removed by click reaction with alk-wang resin. The Ada-CD_2 FT-IR spectrum (Figure S1(b)) showed that the simultaneous disappearance of azido absorption peaks at 2096 cm^{-1} and alkynyl at 2103 cm^{-1} confirmed the complete reaction of CD-N_3 with Ada-alk_2. Characteristic signals for β-CD at $\delta = 4.45$, 4.8, and 5.7 and proton for the 1,2,3-triazole ring at $\delta = 8.02$ appeared in the ^{1}H NMR spectrum of Ada-CD_2 (Figure S2(III)). This appearance indicates that the 1,3-dipolar cycloaddition reaction occurred. Figure S3 showed that the molecular weight of Ada-CD_2 measured by MALDI-TOF-MS was 2548.36. This value was in accordance with the theoretical value (calculated for $[M + H]^+$: 2548.34). Ada-CD_2 has been successfully obtained.

The SHP formation based on the host–guest inclusion interaction of Ada-CD_2 in DMF/H_2O ($V_{DMF}/V_{H2O} = 1{:}1$) was confirmed using the 2D ^{1}H NMR NOESY spectra (Figure 1). The cross-peak interactions between the β-CD and Ada protons reflected the interaction between 3-H and 5-H in β-CD with the **a**, **b**, and **c** protons in Ada. The notations used were n-H for β-CD protons, and **a**, **b**, and **c** for Ada protons. n was the carbon number. The SHPs formed because of the intermolecular complexation between Ada and β-CD, which was in agreement with that obtained by Liu et al. for the Ada and the CD monomer.[14]

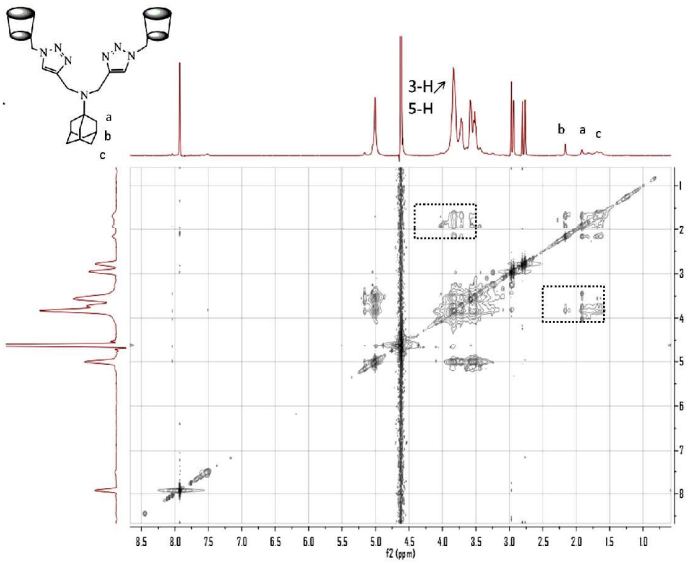


Figure 1. 2D NOESY ^{1}H NMR spectra of Ada-CD_2 in DMF-d_7/D_2O (1.5 mg/mL).

Viscometry was performed to provide direct physical evidence for the non-covalent SHP formation. At low concentrations, a

double-logarithmic plot of specific viscosity yielded a curve with a 0.36 slope as a function of the DMF/H_2O sample solution (V_{DMF}/V_{H2O} = 1:1). The existence of a small oligomer (Figure 2) was confirmed. At high concentrations, the curve slope increased to 1.56. Considering that the conventional linear SPs have slopes of 3–6,[26] the low value (1.56) suggested the SHP formation. The critical polymerization concentration (CPC), above which the SHPs were obtained, was found to be 0.9 mg/mL.

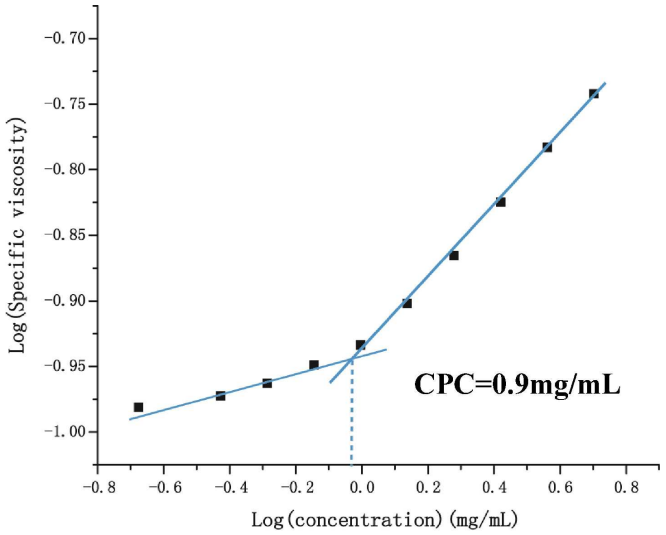


Figure 2. Specific viscosity of the DMF/H_2O mixed solution versus the Ada-CD_2 concentration at 25 °C.

The obtained SHP morphology and size in mixed solvents were observed using transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements. The TEM images of Ada-CD_2 in DMF/H_2O with the same volume ratio (V_{DMF}/V_{H2O} = 1:1) (Figures 3A–3D) showed that the SHP morphology was gradually observed with the increase of Ada-CD_2 concentration, and SHPs were formed. The similar morphology was also observed for SHPs from the host–guest complexation of azobenzene dimer and β-CD trimer.[12] By contrast, the branched SHP morphology in the fixed Ada-CD_2 concentration (e.g., 1.5 mg/mL) was most obvious when the DMF:H_2O volume ratio was set to 1:1 than to the 1:2 or 2:1. The SHP D_z values increased from 592 nm to 1860 nm with the increase of Ada-CD_2 concentration from 0.5 mg/mL to 2 mg/mL (V_{DMF}/V_{H2O} = 1:1) (Figure 4 and Table 1). Table 1 shows the SHP D_z values at the same concentration but different solvent ratios. The SHP D_z values (V_{DMF}/V_{H2O} = 2:1) were smaller than those in the V_{DMF}/V_{H2O} = 1:1 or 1:2. The TEM and DLS results indicated that the SHP formation was dependent on the monomer concentration and the volume ratio of mixed solvents.

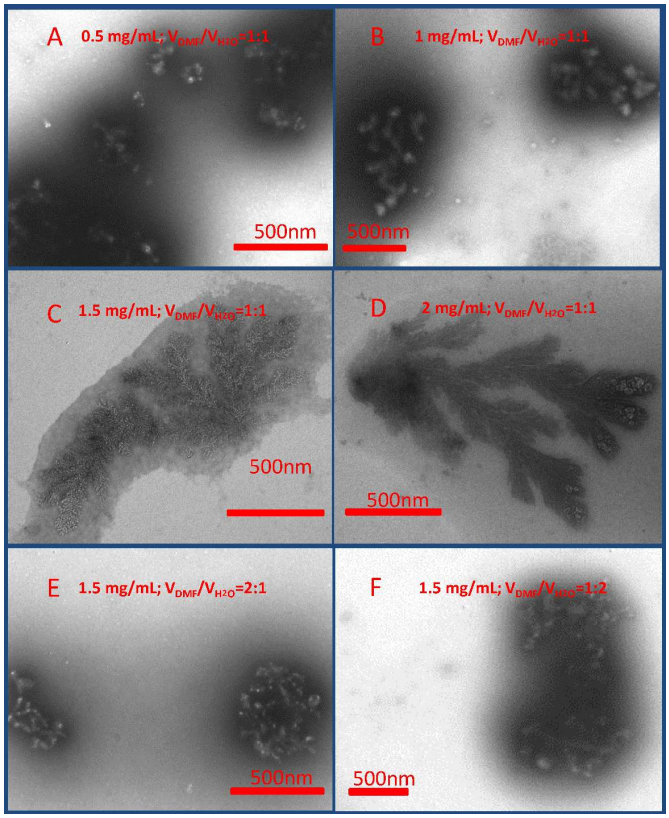


Figure 3. Typical TEM images of Ada-CD_2 in different DMF/H_2O mixed solvents (solution conditions: V_{DMF}/V_{H2O} = 1:1 for A–D, V_{DMF}/V_{H2O} = 2:1 for E, and V_{DMF}/V_{H2O} = 1:2 for F; 0.5 mg/mL for A, 1 mg/mL for B, 1.5 mg/mL for C, E, and F, and 2 mg/mL for D).

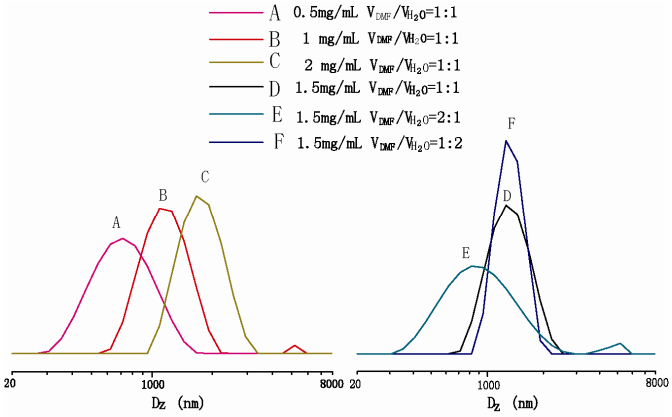


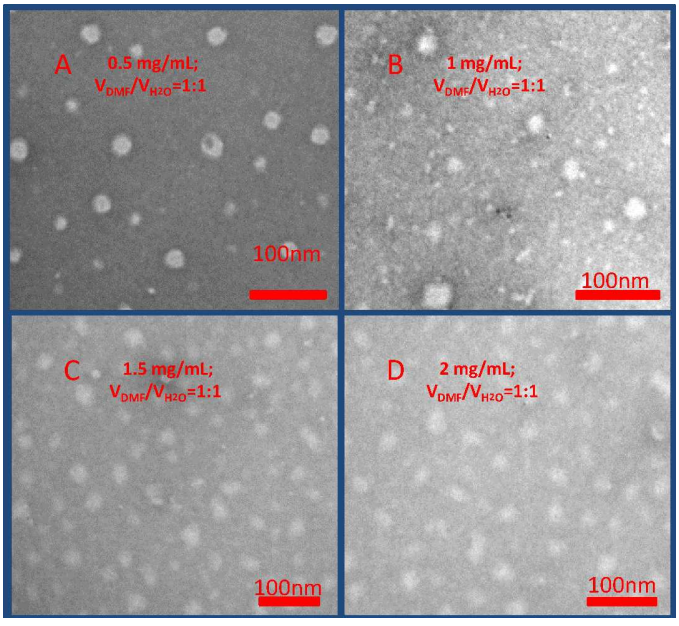
Figure 4. Typical size distributions of Ada-CD_2 in different DMF/H_2O mixed solvents (solution conditions: V_{DMF}/V_{H2O} = 1:1 for A–D, V_{DMF}/V_{H2O} = 2:1 for E, and V_{DMF}/V_{H2O} = 1:2 for F; 0.5 mg/mL for A, 1 mg/mL for B, 2 mg/mL for C, D, and E, and F for 2 mg/mL).

Table 1. DLS results of Ada-CD_2 in mixed solvents at 25 °C.

Monomer concentration[a] (mg/mL)	D_z[b] (nm)	PDI[c]	Zeta-potential[d] (mV)	Mixed solvents
0.5	590	0.322	2.92	DMF/H_2O=1:1
1.0	1326	0.310	3.05	DMF/H_2O=1:1
1.5	1542	0.340	3.11	DMF/H_2O=1:1
2.0	1860	0.274	3.23	DMF/H_2O=1:1
1.5	860	0.348	3.13	DMF/H_2O=2:1
1.5	1480	0.282	3.14	DMF/H_2O=1:2

[a]Concentrations of Ada-CD_2 in mixed solvents; [b]Z-average diameter determined by DLS; [c]Polydispersity of particles diameter determined by DLS; [d]Zeta-potential determined by DLS

The proper amount of Ada-Na (0.1 mM, the molar ratio of Ada-Na to CD in Ada-CD_2 = 12.8:1) was added into the Ada-CD_2 solutions to achieve SHP morphology transitions in mixed solvents. Although the spherical nanosized micelles were formed, no supramolecular branched morphology was found in the 0.5 mg/mL monomer concentration and the 1:1 DMF/H_2O volume ratio (Figure 5A). Interestingly, the similar micelle morphology was also observed under other solution conditions (Figures 5B–5F). The average sample diameter (D_{av}) determined by TEM was around 25 nm. The formed micelles showed D_z (about 38–46 nm) and PDI (about 0.24–0.28) values close to the Ada-CD_2 concentration increase from 0.5 mg/mL to 2 mg/mL (V_{DMF}/V_{H2O} = 1:1) (Figure 6 and Table 2). The similar result was drawn with the same monomer concentration but different solvent ratio conditions (Figure 6 and Table 2). In contrast to the SHP formation, these Ada-Na addition-induced nanosized micelles were independent of the monomer concentration and the ratio of mixed solvents.



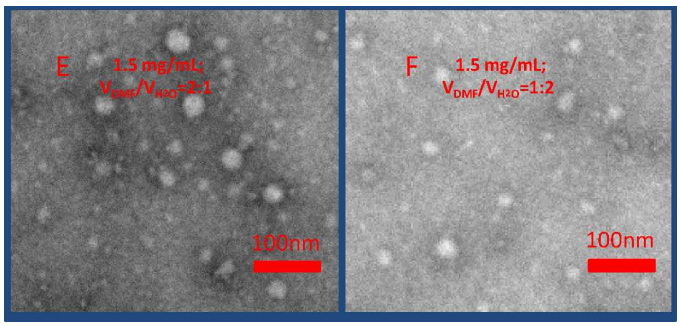


Figure 5. Typical TEM images of Ada-CD_2 in different DMF/H_2O mixed solvents containing 0.1 mM Ada-Na (solution conditions: V_{DMF}/V_{H2O} = 1:1 for A–D, V_{DMF}/V_{H2O} = 2:1 for E, and V_{DMF}/V_{H2O} = 1:2 for F; 0.5 mg/mL for A, 1 mg/mL for B, 1.5 mg/mL for C, E, and F, and 2 mg/mL for D).

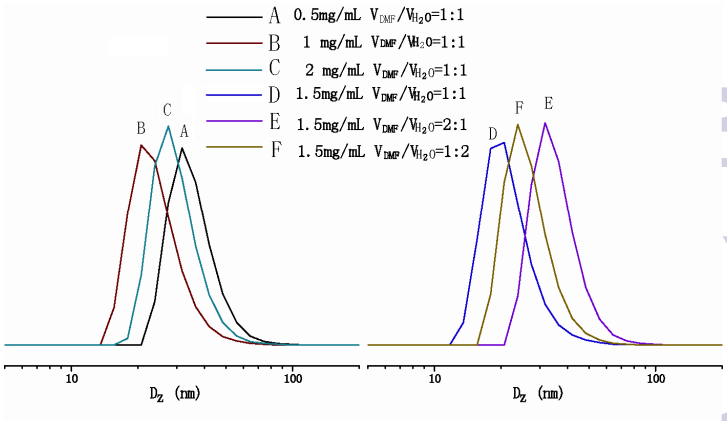


Figure 6. Typical size distributions of Ada-CD_2 in different DMF/H_2O mixed solvents after addition of 0.1 mM Ada-Na (solution conditions: V_{DMF}/V_{H2O} = 1:1 for A–D, V_{DMF}/V_{H2O} = 2:1 for E, and V_{DMF}/V_{H2O} = 1:2 for F; 0.5 mg/mL for A, 1 mg/mL for B, 1.5 mg/mL for D, E, and F, and 2 mg/mL for C).

Table 2. DLS results of Ada-CD_2 in mixed solvents after addition of Ada-Na (0.1mM) at 25 °C.

Monomer concentration[a] (mg/mL)	D_z[b] (nm)	PDI[c]	Zeta-potential[d] (mV)	Mixed solvents
0.5	42	0.286	-4.96	DMF/H_2O=1:1
1.0	38	0.252	-4.96	DMF/H_2O=1:1
1.5	39	0.240	-5.11	DMF/H_2O=1:1
2	46	0.262	-5.13	DMF/H_2O=1:1
1.5	45	0.302	-4.85	DMF/H_2O=2:1
1.5	40	0.296	-4.89	DMF/H_2O=1:2

[a]Concentrations of Ada-CD_2 in mixed solvents; [b]Z-average diameter determined by DLS; [c]Polydispersity of particles diameter determined by DLS; [d]Zeta-potential determined by DLS

The Ada-CD_2 with the 0.5 mg/mL concentration and Ada-Na was dissolved in the DMF/H_2O mixed solvents

(V_{DMF}/V_{H2O} = 1:1) to obtain the critical aggregation concentration (CAC) of the formed nanosized micelles. These mixed solvents contained a certain amount of pyrene. The solution was then diluted to various desired concentrations (from 1 mg/mL to 1×10^{-5}) while the pyrene concentration was kept at around 6×10^{-6} mol/l. The CAC value (about 0.05 mg/mL) was then obtained from the baseline and the tangent intersection of the rapidly decreasing I_1/I_3 curves (Figure 7). This event indicated the micelle formation. The CAC values of the Ada-CD_2 solutions under other conditions were also 0.05 mg/mL, which were determined by the similar method in Figures S4 and S5. This result was in accordance with TEM and DLS, further confirming the micelle formation independence under different solution conditions.

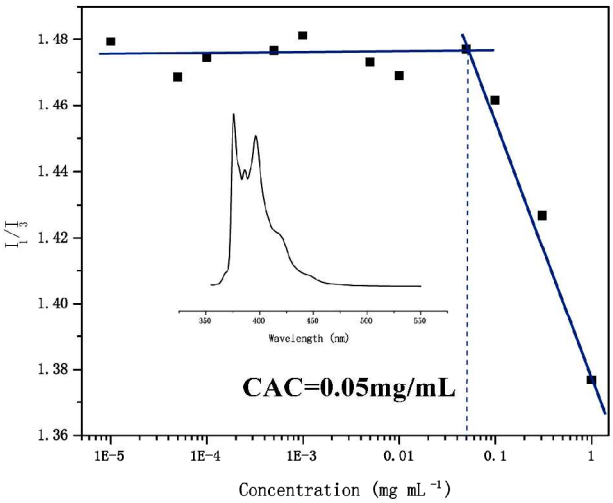
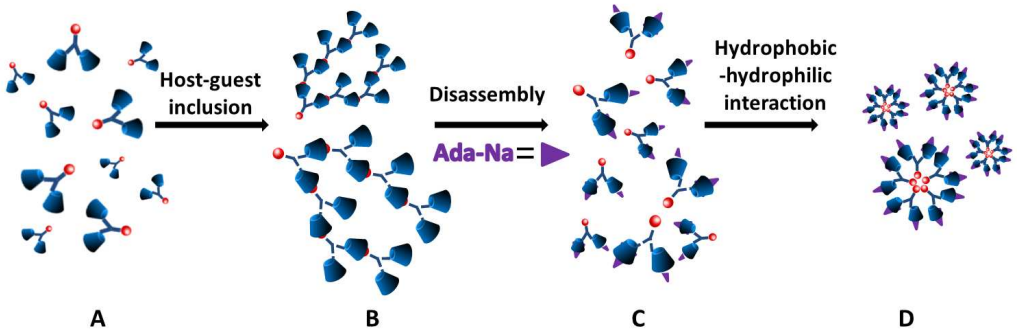


Figure 7. Relationship between the fluorescence intensity ratio and the Ada-CD_2 concentration in DMF/H_2O (1:1) solutions after the addition of Ada-Na at 25 °C (inset: the pyrene fluorescence emission spectrum).

The core–shell structure of these nanosized micelles was further confirmed by zeta-potentials. For instance, the micelle zeta-potential value was −4.96 mV, whereas the corresponding SHPs had the value of 2.92 mV under the same solution conditions (0.5 mg/mL Ada-CD_2 concentration and V_{DMF}/V_{H2O} = 1:1). The negative charges were located on the micelle surfaces. The surface charge presence generally caused the micelles' higher absolute zeta-potential value. Therefore, the current micelles' negative charges were attributed to the presence of the β-CD moieties encapsulated in Ada-Na molecules carrying carboxyl groups. Tables 2 and 1 show the micelle and SHP zeta-potential results, respectively. The tables show a similar result with the preceding example. Therefore, this study proposed that the hydrophobic Ada group spontaneously aggregated to form the "core", whereas the hydrophilic β-CD moieties formed the "shell" of the nanosized micelles in the DMF/H_2O mixed solvents.

The possible morphology transition mechanism of Ada-CD_2 in mixed solvents from SHPs to micelles was proposed (Scheme 2). The host–guest and hydrophilic–hydrophobic interactions obviously coexisted as double supramolecular driving forces in the Ada-CD_2 molecular structure as it was dissolved in the mixed solvents. In the preliminary stage, the host–guest interaction, as the main driving force, played an important role in the SHP formation because according to the literature, the β-CD possessed a high inclusion constant of 20,000 M^{-1} with Ada.[15] Thus, covalently linked double β-CD units drove one Ada molecule into their cavities, which further resulted in the SHP formation (Schemes 2A–2B). The molecular recognition between the β-CD and the two guests happened when the Ada-Na was added to the Ada-CD_2 solutions. The guests were Ada linked with the β-CD moiety and free Ada-Na molecules. According to a previous study[27], the Ada-Na addition, instead of Ada only, led to the formation of a new inclusion complexation between the β-CD and the Ada-Na. Thus, SHPs based on the host–guest interaction between the β-CD and the Ada disassembled (Schemes 2B–2C). The hydrophilic–hydrophobic interaction induced the Ada-CD_2 self-assembly in the mixed solvents when the cavities of the β-CD were occupied by Ada-Na molecules. As a result, the nanosized micelles were formed (Schemes 2C–2D). After the preceding process, the Ada-CD_2 branched morphology in the mixed solvents transitioned into spherical nanosized micelles.



Scheme 2. Schematic representation of the possible morphology transition mechanism of Ada-CD_2 from SHPs to nanosized micelles in mixed solvents.

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Conclusions

SHPs were formed in the DMF/H_2O mixed solvents based on an AB_2-type amphiphilic β-CD monomer. The formed SHPs transitioned into spherical nano-micelles with the Ada-Na addition. The coexistence of two supramolecular driving forces, i.e., the host–guest and the hydrophilic–hydrophobic interactions, in the monomer contributed to the morphology transitions. In addition, the SHP formation was dependent on the monomer concentration and the ratio of mixed solvents. Whereas, the micelle existence was independent of the solution conditions. The SHP morphology transitions induced by double supramolecular driving forces introduced a convenient and effective method of preparing supramolecular aggregations with tunable morphologies for potential applications in drug delivery and biomedical engineering.

Experimental section

Materials

Mono-6-deoxy-6-azido-*β*-cyclodextrin (*β*-CD-N_3) and Alk-wang resin were prepared according to literature.[28,29] Ada-NH_2, (99%, Alfa Aesar), Cu(Ph_3)$_3$Br (Acros, 99%), wang-resin were all purchased from the companies attached and used without further purification. N,N-dimethyl formamide (DMF), was dried with 3Å grade molecular sieve before use. K_2CO_3, acetone, ethyl acetate, petroleum ether from Shanghai Sinopharm Chemical Reagent Co., Ltd, were used as received.

Synthesis and characterization of the Ada-CD_2 monomer are found in ESI.

SHP Construction using Ada-CD_2 as monomer

In a typical experiment, 10 mg Ada-CD_2 was first dissolved in deionized water and stirred for 24 h at room temperature. The isopyknic DMF was then added. After stirring for another 1 h, the solution was ultrasonically treated for 30 min. The samples in the V_{DMF}/V_{H2O} = 1:1 were 2 mg/mL, 1.5 mg/mL, 1 mg/mL, and 0.5 mg/mL. The samples in the V_{DMF}/V_{H2O} = 2:1 and V_{DMF}/V_{H2O} =1:2 were 1.5 mg/mL.

Preparation of Nanosized micelles

The 0.1 mM Ada-Na (the molar ratio of Ada-Na to CD in Ada-CD_2 = 12:1) was added to the sample solutions (V_{DMF}/V_{H2O} = 1:1, 0.5 mg/mL) and stirred for 1 h. The similar operation was applied to the other sample solutions (V_{DMF}/V_{H2O} = 1:1, 2 mg/mL, 1.5 mg/mL, and 1 mg/mL; V_{DMF}/V_{H2O} = 2:1 and V_{DMF}/V_{H2O} = 1:2, 1.5 mg/mL).

Investigation on the morphology and size of supramolecular aggregates

The supramolecular aggregate morphology was visualized using a Hitachi H-600 electron microscope at an acceleration voltage of 75 kV. Samples were prepared by placing a 10-μl solution on copper grids, followed by staining with phosphotungstic acid. DLS measurements were carried out in a Malvern Zetasizer Nano ZS dynamic light scattering instrument. The light source was a He–Ne laser operating at 632 nm. The samples were placed in the cell for at least 5 min prior to the measurement to allow for thermal equilibration.

The 2D ^{1}H NMR ROESY spectra were recorded on a Bruker-Avance III NMR Spectrometer (400 MHz) with D_2O and DMF-d_7 as solvents.

Viscosity studies were performed using an Ubbelohde viscometer at 25 °C in DMF/H_2O (1/1, v/v).

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Notes and references

[a] The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an, 710072, P. R. China.

*Corresponding author. E-mail: xfand@126.com (X. Fan), happytw_3000@nwpu.edu.cn (W. Tian).

Electronic Supplementary Information (ESI) available: Synthesis, characterization of Ada-CD_2 monomer can be found in ESI. See DOI: 10.1039/b000000x/

1 (a) F. W. Zeng, S. C. Zimmerman, *Chem. Rev*, 1997, **97**, 1681. (a) R. Villalonga, R. Cao, A. Fragoso, *Chem. Rev*, 2007, **107**, 3088.

2 R. J. Dong, Y. F. Zhou, X. Y. Zhu, *Acc. Chem. Res*., 2014, **47**, 2006-2016

3 (a) S. L. Li, T. X. Xiao, C. Lin, L. Y. Wang, *Chem. Soc. Rev*., 2012, **41**, 5950. (b)M. A. Palacios, R. Nishiyabu, M. Marquez, P. Anzenbacher, *J. Am. Chem. Soc*, 2007, **129**, 7538.

4 (a)S. Y. Dong, B. Zheng, F. Wang, F. H. Huang, *Acc. Chem. Res.*, 2014, **47**, 1982. (b) J. M. Lehn, *Science*, 2002, **295**, 2400.
5 (a)Y. L. Liu, Z. Q. Wang, X. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 5922. (b) L. L. Zhu, D. Zhang, D. H. Qu, Q. C. Wang, X. Ma, H. Tian, *Chem. Commun*., 2010, **46**, 2587. (c) X. Ma, R. Y. Sun, W. F. Li, H, Tian, *Polym. Chem*., 2011, **2**, 1068.
6 Q. Yan, J. Y. Yuan, Z. N. Cai, Y. Xin, Y. Kang, Y. W. Yin, *J. Am. Chem. Soc*, 2010, **132**, 9266.
7 J. Y. Wu, H. K. He, C. Gao, *Macromolecules,* 2010, **43**, 2252.
8 B. V. Schmidt, T. Rudolph, M. Hetzer, H. Ritter, F. H. Schacher and C. Barner-Kowollik, *Polym. Chem*., 2012, **3**, 3139.
9 J. T. Yan , X. Q. Zhang , X. Q. Zhang , K. Liu , W. Li , P. Y. Wu and A. F. Zhang, *Macromol. Chem. Phys*., 2012, **213**, 2003.
10 M. Munteanu, U. Kolb, H. Ritter, *Macromol. Rapid. Commun.*, 2010, **31**, 616.
11 Y. Liu, C. Y. Yu, H. B. Jin, B. B. Jiang, X. Y. Zhu, Y. F. Zhou, Z. Y. Lu and D. Y. Yan. *J. Am. Chem. Soc*., 2013, **135**, 4765.
12 R. J. Dong, Y. Liu, Y. F. Zhou, D. Y. Yan and X. Y. Zhu, *Polym. Chem*., 2011, **2**, 2771.
13 S. J. Yu, W. Zhang, J. Y. Zhu, Y. Z. Yin, H. Y. Jin, L. P. Zhou, Q. Luo, J. Y. Xu, J.Q. Liu, *Macromol. Biosci.*, 2011, **11**, 821.
14 Z. S. Ge, H. Liu, Y. F. Zhang, S. Y. Liu, *Macromol. Rapid Commun.*, 2011, **32**, 68.
15 L. Galantini, A. Jover, C. Leggio, F. Meijide, N. V. Pavel, V. H. S. Tellini, J. V. Tato, C. Tortolini, *J. Phys. Chem. B.*, 2008, **112**, 8536.
16 B. R. Yu, S. W. Guo, L. P. He, W. F. Bu, *Chem. Commun*., 2013, **49**, 3333.
17 B. R. Yu, B. Y. W, S. W. Guo, Q. Zhang, X. R. Zheng, H. T. Lei, W. S. Liu, W. F. Bu, Y. Zhang, X. Chen, *Chem. Eur. J.*, 2013, **19**, 4922.
18 F. H. Huang, H. W. Gibson, *J. Am. Chem. Soc*., 2004, **126**, 14738.
19 G. Fernandez, E. M. Perez, L. Sanchez, N. Martin, *J. Am. Chem. Soc.,* 2008, **130**, 2410.
20 X. Y. Wang, H. M. Deng, J. Li, K. Zheng, X. S. Jia, C. J. Li, *Macromol. Rapid Commun.*, 2013, **34**, 1856.
21 (a) A. Miyawaki, Y. Takashima, H. Yamaguchi, A. Harada, *Tetrahedron*, 2008, **64**, 8355. (b) W. Tian, X. D. Fan, T. Liu, Y. Y. Liu, L. Sun, M. Jiang, Y. Huang, *Chem J Chin Univ*, 2009, **30**, 632
22 C. Y. Hong, Y. Z. You, D. C. Wu, Y. Liu, C. Y. Pan, *J. Am. Chem. Soc*., 2007, **129**, 5354.
23 L. Chen, X. Y. Zhu, D. Y. Yan, Y. Chen, Q. Chen, Y. F. Yao, *Angew. Chem.*, 2006, **45**, 87.
24 Q. Yan, J. Y. Yuan, Y. Kang, Y. W. Yin, *Polym. Chem*., 2010, **1**, 423.
25 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2001, **40**, 2004.
26 A. T. ten Cate, H. Kooijman, A. L. Spek, R. P. Sijbesma, E. W. Meijer, *J. Am. Chem. Soc*., 2004, **126**, 3801.
27 (a)W. Tao, Y. Liu, B. B. Jiang, S. R. Yu, W. Huang, Y. F. Zhou, D. Y. Yan, *J. Am. Chem. Soc*., 2012, **134**, 762. (b) X. Y. Huan, D. L. Wang, R. J. Dong, C. L. Tu, B. S. Zhu, D. Y. Yan, X. Y. Zhu, *Macromolecules*, 2012, **45**, 5941-5947.
28 Y. Bai, X. D. Fan, W. Tian, H. Yao, L. H. Zhuo, H. T. Zhang, W. W. Fan, Z. Yang, W. B. Zhang, *Polymer*, 2013, **54**, 3566.
29 C. G. Mu, X. D. Fan, W. Tian, Y. Bai, X. Zhou, *Polym. Chem*., 2012, **3**, 1137.