ARTICLES

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Reversible photoswitching self-assembly of azobenzene-functionalized hyperbranched polyglycerol induced by host-guest chemistry

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Reversible assembly and disassembly of rod-like large complex micelles have been achieved by applying photoswitching of supramolecular inclusion and exclusion of azobenzene-functionalized hyperbranched polyglycerol and α -cyclodextrin as driving force, promising a versatile system for self-assembly switched by light. Hydrogen-nuclear magnetic resonance (¹H NMR) and Fourier transform infrared (FT-IR) spectroscopy were applied to characterize the azobenzene-functionalized hyperbranched polyglycerol. Atomic force microscopy (AFM), transmission electron microscopy (TEM) and dynamic laser light scattering (DLS) were employed to investigate and track the morphology of the rod-like large complex micelles before and after irradiation of UV light.

azobenzene, hyperbranched polyglycerol, reversible self-assembly, host-guest chemistry

1 Introduction

Supramolecular self-assembly of hyperbranched polymers (HBPs) represents a new research direction, and has attracted increasing interest in the past years because of its potential applications in the fields of drug delivery and biomimetics [1–6]. Various topological supramolecular aggregates and hybrids at all scales and dimensions have been generated, such as nano- or micro-micelles, fibers, tubes, and honeycomb films following the pioneering work of Yan *et al.* [4, 5, 7–10].

Up to date, the obtained self-assembly structures of HBPs in solution are generally in static station. However, in life entity or in some other application cases, self-assembling is demanded to be "smart", which means stimuliresponsive and reversible. In this respect, the photoswitched *trans*- and *cis*- transitions of azobenzene are of particular interest, if considering the host-guest chemistry between azobenzene moiety and α -cyclodextrin (α -CD) [11–19]. *Trans* azobenzene can be well recognized by α -CD due to the hydrophobic and van der Waals interactions, whereas the *cis* form cannot be included because of mismatch between the host and α -CD guest [13, 15–18, 20–22]. For instance, Zhang and co-workers used amphiphilic surfactants containing azobenzene and α -CD to fabricate a photo-controlled reversible supramolecular assembly system [23]. Jiang and co-workers reported linear polymer-based amphiphiles containing β -CD had dual reversible self-assembly properties driven by inclusion complexation between azobenzene and β -CD [24]. However photoswitchable self-assembly of HPBs is yet to be reported.

In this article, we attempt to make use of the photoswitchable inclusion and exclusion of azobenzene-functionalized hyperbranched polyglycerol (HPG-azo) with α -CD to obtain a novel kind of "smart" complex mi-

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celles which can undergo reversible assembly and disassembly.

2 Experimental

2.1 Materials

HPG ($M_n = 122$ kDa, PDI = 1.16, DP = 1650), and 4-oxo-4-(prop-2-ynyloxy)butanoic acid (alkyne-COOH) were synthesized according to the previous work [25–28]. CuBr (purified according to ref. [29] before use, 98%) was purchased from Sigma–Aldrich. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, 98%) was purchased from Alfa Aesar. 6-(4-Methoxyazobenzene-4'-oxy)hexyl bromide (azo-Br) was synthesized according to the published protocol [30]. All of the other reagents were purchased from Aldrich and used as recezhaoxiaofen@hotmail.com; ived.

2.2 Characterization

Hydrogen-nuclear magnetic resonance (¹H NMR) measurements were carried out on a Varian Mercury 400 MHz spectrometer using CDCl₃ as the solvent. A PE Paragon 1000 spectrometer was applied to obtain Fourier transform infrared (FTIR) spectra using KBr disks. Dynamic laser light scattering (DLS) measurements were performed using a BI-200SM Dynamic/static Laser Light Scattering, Brookhaven, and the wavelength of the laser was set at 630 nm. AFM images were obtained by using a Digital Instrument (DI) Nanoscope IIIa scanning probe microscope, under the tapping mode. Transmission electron microscopy (TEM) studies were conducted on a JEOL JEM2010 electron microscope at 200 kV. A Varian Cary 100 Bio UV-vis spectrophotometer was applied to obtain UV-vis spectra. Induced circular dichroism (ICD) spectra were recorded on a Biologic MOS-450 spectrometer in DMF with 1 cm quartz cells.

2.3 Synthesis of alkyne-modified HPG

As shown in Scheme 1, HPG (1.170 g, 15.82 mmol hydroxyl) and N,N-dimethylformamide (DMF, 4 mL) were added into a Schlenk flask under nitrogen flow and stirred until the HPG was totally dissolved and the flask was immerged into the ice-water bath. Then N,N-dicyclohexylcarbodimide (DCC,



Scheme 1 Synthetic protocol for HPG-azo.

3.300 g, 16.01 mmol), alkyne-COOH (2.540 g, 16.29 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.195 g, 1.58 mmol) were added into the reaction system and the Schlenk was sealed with a rubber plug. The reaction was carried out in dark for 24 h at room temperature. During the reaction, a small amount of dichloromethane could be added if the system became too viscous. Then the mixture was filtered and the residual dichloromethane was removed by a rotary evaporator under reduced pressure. After that, the mixture was precipitated in de-ionized water followed by solubilizing the precipitate with acetone as little as possible and then filtered. The solution was precipitated in de-ionized water twice. The final product was obtained after drying in a vacuum oven overnight at 30 °C (0.382 g, yield 38.2%). The final product was light yellow and sticky, and should be stored in darkness [31].

2.4 Synthesis of azo-N₃

6-(4-Methoxyazobenzene-4'-oxy) hexyl azide (azo-N₃) was synthesized from the substitution reaction of NaN₃ and azo-Br. To a 200 mL three-neck round-bottom flask equipped with a condenser were added a solution of sodium azide (0.781 g, 12 mmol) in DMF (10 mL) and azo-Br (2.35 g, 6 mmol). The flask was immersed in an oil bath at 75–80 °C and kept stirring for 5 days (caution: the azide is quite explosively sensitive to friction during feeding and when the temperature is higher than 80 °C). The mixture was precipitated in de-ionized water followed by filtering and washing by 100 mL de-ionized water. The precipitation was dissolved in acetone and then precipitated in de-ionized water. The precipitation was filtered and dried in vacuum at room temperature overnight. Yield: 1.512 g, 71.4%.

2.5 Synthesis of HPG-azo

To the Schlenk flask, HPG-alkyne (75 mg, 0.276 mmol of alkyne groups calculated by the ¹H NMR spectrum), azo-N₃ (195 mg, 0.552 mmol), dichloromethane (4 mL) were added and the flask was deoxygenated by bubbling nitrogen for 10 min. Then CuBr (8 mg, 0.055 mmol) and PMDETA (11.8 μ L, 0.055 mmol) were added to the flask under nitrogen flow. The reaction was carried out under room temperature and lasted 12 h in darkness. After the reaction, the mixture was precipitated in ether for three times. The final product of HPG-azo was obtained after drying in a vacuum oven at room temperature overnight [32, 33].

2.6 Self-assembly and disassembly of the complex micelles constructed by HPG-azo and α-CD

In order to test the self-assembly properties of HPG-azo and α -CD system, we prepared 0.167 mg mL⁻¹ HPG-azo solution in DMF followed by dissolving excess α -CD (25 times the amount of azobenzene groups of HPG-azo). Then a cer-

tain amount of water was added dropwise into the solution until the solution became opalescence indicating the self-assembly had occurred. The cloudy dispersion was then irradiated by UV light at 365 nm for 30 min, affording a transparent solution again which might indicate the disassembly of the complexation between HPG-azo and α -CD. DLS was used to track the micelles' size variation during the process of adding water. Before and after UV light irradiation, DLS, AFM and TEM were applied to characterize the assembled morphology. UV-vis spectra were also conducted to record transmittance of the solution at 600 nm. AFM samples were made by the spin-coating method on freshly-peeled mica substrates before and after irradiation. TEM samples were made by dropping onto 200 mesh holey lacey carbon grids on a copper support.

3 Results and discussion

3.1 Synthesis of alkyne-modified HPG

Similar to our previous work, alkyne-modified HPG was synthesized by DCC condensation. Figure 1 shows the ¹H NMR and FTIR spectra of HGP-alkyne. All the peaks in the ¹H NMR spectrum were coded by letters associated to the protons of the products. As shown in the ¹H NMR spectrum of HPG-alkyne, two newly appearing peaks: peak b (OCH₂CCH) at 5.18 ppm and peak c (CH₂CH₂COO) at 2.67 ppm demonstrated the successful linkage of alkyne to HPG. Because CDCl₃ is a poor solvent for HPG (addition with the shielding effect of the terminal chains), the signal from the



Figure 1 (A) ¹H NMR spectrum of alkyne-modified HPG; (B) FT-IR spectrum of alkyne-modified HPG.

core of HPG was slightly weakened. The reaction degree can be roughly calculated by the following formula in which A_c , A_e , A_d and A_f represent the peak area of peaks c, e, d and f respectively.

$$R = 5/8 \cdot [A_{\rm c}/(A_{\rm e} + A_{\rm d} + A_{\rm f})]$$

From the integration of the signals from the ¹H NMR spectrum, ~ 56% hydroxyl groups of HPG were transferred into alkyne groups. The absorption peaks in the FTIR spectrum also confirmed the formation of the expected structure. The peaks at 2100 and 3280 cm⁻¹ were associated with alkyne groups and the peak at around 1740 cm⁻¹ was assigned to carbonyl groups.

3.2 Synthesis of azo-N₃

As shown in Figure 2(A), all the peaks were labeled in ¹H NMR spectrum, and the peak e (CH_2N_3) was shifted from 3.44 ppm to around 3.30 ppm compared with azo-Br. This could also be confirmed by the FTIR spectra as shown in Figure 2(B). The newly appeared sharp peak at 2100 cm⁻¹ was assigned to azido groups in azo-N₃.

3.3 Synthesis and photoisomerization behaviors of HPG-azo

HPG-azo was synthesized by Cu(I)-catalyzed azide-alkyne click chemistry between alkyne-modified HPG and azo-N₃. As shown in Figure 3(A), the alkyne peak at 2100 cm⁻¹ disappeared completely showing that the click reaction was almost 100%. As mentioned above, ~ 56% hydroxyl groups



Figure 2 (A) ¹H NMR spectrum of azo-N₃; (B) FTIR spectra for (1) azo-Br and (2) azo-N3

of HPG were transferred into alkyne groups, and all of them reacted with azo- N_3 groups during the step of "click" reaction. The molecular weight of the HPG was 122 kDa, which meant there were 1649 hydroxyl groups for a single HPG molecule on average. Therefore, we calculated that on average one HPG-azo macromolecule possesses around 924 azo-arms.

Figure 4 shows the photoisomerization behaviors of HPG-azo examined by UV-vis spectra in DMF. Upon irradiation with UV light at 365 nm, the absorption band of HPG-azo at around 359 nm (ascribed to π - π * transition) decreased significantly, and simultaneously the absorption at 448 nm (ascribed to n- π * transition) increased slightly (Figure 4(A)), indicating that the azobenzene groups of HPG-azo changed from *trans* to *cis* state. By contrast, when the DMF solution of HPG-azo was put in dark, the absorption at 359 nm increased gradually again and the absorption at 448 nm decreased, suggesting that the azobenzene groups of HPG-azo recovered from *cis* to *trans* state [34–36]. The whole recovering process took about one day at room temperature in dark.

3.4 Self-assembly and disassembly of the complex micelles constructed by HPG-azo and α-CD

In order to test the self-assembly properties of HPG-azo and α -CD system, we prepared 0.167 mg mL⁻¹ HPG-azo solu-



Figure 3 (A) FTIR spectrum of HPG-azo; (B) ¹H NMR spectrum of HPG-azo.



Figure 4 (A) Absorption spectra of HPG-azo in DMF solution, observed (a) before and after (b) 20 s, (c) 40 s, (d) 120 s and (e) 600 s of 365 nm light irradiation at 365 nm. (B) The recovery absorption spectra of HPG-azo in DMF solution which was irradiated for 15 min by UV light at 365 nm, observed after (f) 24 min, (g) 77 min, (h) 234 min, (i) 974 min and (j) 24 h of stirring in the darkness.

tion in DMF followed by dissolving excess a-CD. Because DMF is a good solvent for both HPG-azo and α -CD, the solution was transparent. After addition of water into the DMF solution, the solution became opalescence due to the efficient complexation between the azobenzene moiety and α -CD in the presence of water. The process was monitored by DLS (Figure 5(A)). A peak around 800 nm appeared after 0.5 mL of deionized water was added into 6 mL of the DMF solution, indicating the self-assembly of HPG-azo and α-CD. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to observe the corresponding self-assembly morphology, as shown in Figure 6. Rod-like assembled structures were found. Estimated from AFM images, the rods have length of around 540 nm and a diameter of 127 nm on average. In addition, some short rods fused with two to three dots with in diameter 100 nm were also observed. From the TEM image, the typical rods are 280 nm in length and 63 nm in width. The rod size measured by TEM was almost half of that measured by AFM. The reason is likely attributed to the stained TEM samples with tungstophosphoric acid hydrate. As the HPG core binds with tungstophosphoric acid hydrate more tightly, the colour of the core part would be much darker, which makes the periphery part of HPG hardly seen under TEM bright field. Furthermore, as shown in Figure 6(E), we can clearly distinguish that the rod-like structures are aggregated linearly from three or more smaller dots (labeled by red cycles) that could be unimolecular micelles of α -CD/HPG-azo complex [37, 38]. This morphology is in agreement with that observed by AFM. In order to demonstrate that the rod-like micelles resulted from the complexation of HPGazo and α -CD, we prepared control samples without α -CD or in the absence of water. No similar self-assembly morphology was found in those samples. The formation of complexation between HPG-azo and a-CD was also con-



Figure 5 DLS charts of HPG-azo and α-CD complex after adding water (A) before UV irradiation and (B) after UV irradiation.



Figure 6 AFM images of (A) rod-like micelles before irradiation and (B) its phase image. AFM images of (C) rod-like micelles before irradiation for the fourth cycle and (D) its phase images. TEM images of (E) rod-like micelles before irradiation and (F) unimolecular micelle after the irradiation.

firmed by induced circular dichroism spectra (ICD) measurements (Figure 7). The peak appearing at around 353 nm was associated to the complexation between HPG-azo and α -CD. Therefore host-guest inclusion of azobenzene group and α -CD is the inducing factor for the self-assembly of HPG-azo in our system [32, 39, 40].

To demonstrate the photoswitching behaviors of selfassembly of HPG-azo, the cloudy dispersion was then irradiated by UV light at 365 nm for 30 min, affording a transparent solution again. DLS measurements show that the peak at around 800 nm disappeared as expected, and the peak around 200 nm appeared again, which corresponds to the micelles assembled by several HPG-azo molecules. (figure 5(B)). It is noteworthy that there was also a peak around 50 nm in Figure 5(B), which corresponds to the unimolecular micelle of HPG-azo. Because HPG-azo molecules were amphiphilic with the hydrophilic core and hydrophobic arms, they tend to form multi-molecular micelles when a certain amount of water is added into the system. The photoswitching behavior could be explained as follows. During the irradiation process, most of the trans-azobenzene units transform into cis-ones, making the guest of a-CD released from the host of azobenzene because of the mismatch between the host and guest. The TEM image after irradiation shows that the rod-like structures disassembled into unimolecular micelles and multi-molecular micelles of HPG-azo (Figure 6(F)). The ICD spectrum further proved that the azo moiety was excluded by α -CD because the signal at around 353 nm disappeared (see in Figure 7) [39, 41]. Therefore, the exclusion of α -CD caused by UV irradiation was the main reason for the disassembly of rod-like micelles.

Moreover, the clear solution became opalescence again after being stirred by a magnetic bar for one day in dark, and the peak around 800 nm in DLS also appeared. Because DLS is more sensitive to larger particles, the signal from the unimolecular micelles was sometime much weaker than the larger one. Therefore we used the peaks around 200 nm which correspond to the multi-molecular micelles to indicate the disassembly of rod-like micelles for convenience. With alternating irradiation of the solution with UV light and stirring in dark for one day, this assembly and disas-



Figure 7 ICD spectra of (1) HPG-azo and α -CD complex and (2) after 30 min of UV irradiation.

sembly process could be recycled for many times. As shown in the AFM images in Figure 6(C), for the fourth cycle, the rod-like aggregates could be again clearly distinguished. The rods' size was around 670 nm in length and 200 nm in width, which was quite similar to the first cycle case. Considering the morphology errors came from irradiation and magnetic stirring, we conclude that the self-assembled morphology kept almost the same in different cycles. The particle size and transmittance at 600 nm were tracked for five cycles and the results are depicted in Figure 8(A), showing the reversible self-assembly and disassembly for the HPG-azo and α -CD systems through photoswitching. In fact, the transparency difference before and after irradiation could be observed by naked eyes and the comparison photo is shown in Figure 8(B) [42].

The dynamic photoswitching process could be explained by Scheme 2. Before irradiation, the azobenzene moiety in the peripheral part is included by α -CD due to the hydrophobic interaction. We roughly calculated the ratio of inclusion. The solution before irradiation was precipitated and washed by water and dried in vacuum. The weight difference between the precipitate and the original HPG-azo reflects the amount of α -CD nesting the azobenzene moiety. As a result, every azo-arm was included by 0.51 α -CD (i.e., about half of azo units were included by α -CD). The low inclusion ratio is mainly caused by the high density of azo groups and the simultaneous self-assembly of HPG-azo during the inclusion of α -CD that might lead to the decrease of effective azobenzene units. With increasing the inclusion of α -CD, the interactions between CDs (e.g., hydrogen bonding and crystallization), drive HPG-azo unimolecular and multi-molecular micelles to self-assemble into larger micelles such as rods. When irradiated by UV-light, the trans-azobenzene units of HPG-azo transform into cis-ones, and α -CD guests drop from the azo-arms, inducing the disassembly of rod-like micelles. Because the host-guest inclusion of HPG-azo and α -CD can be switched by light, the self-assembly and disassembly of HPG-azo can be reversibly tuned readily [43].



Figure 8 (A) Changes of R_h of the micelles (triangle line) formed by HPG-azo and α -CD and transmittance at 600 nm (circle line) of the solution upon alternating irradiation with UV for 30 min and stirred in darkness for one day. Five cycles are shown in the figure; (B) the comparison photo of solution of HPG-azo and α -CD before (right) and after (left) irradiation.



Scheme 2 The structure of HPG-azo and illustration of the photoswitching of self-assembly and disassembly of HPG-azo and α -CD complexation.

4 Conclusions

An azobenzene-functionalized hyperbranched polymer was readily prepared by efficient Cu(I)-catalyzed alkyne/azide click chemistry [44, 45]. This polymer showed host-guest interaction induced assembly and disassembly behaviors switched by light. Our work provids a novel smart system which combines photo-chemistry, host-guest chemistry and self-assembly of HBPs. The "smart" reversible assembly and disassembly transitions would have potential applications in intelligent materials and biomimetics [19, 46–49].

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- 1 Guo B, Sun XY, Zhou YF, Yan DY. Supramolecular self-assembly and controllable drug release of thermosensitive hyperbranched multiarm copolymers. *Sci China Chem*, 2010, 53(3): 487–494
- 2 Han J, Gao C. Host-Guest Supramolecular Chemistry of Dendritic Macromolecules. Curr Org Chem, 2011, 15(1): 2–26
- 3 Adeli M, Haag R. Multiarm star nanocarriers containing a poly(ethylene imine) core and polylactide arms. *J Polym Sci Pol Chem*, 2006, 44(19): 5740–5749
- 4 Gao C, Yan DY. Hyperbranched polymers: From synthesis to applications. *Prog Polym Sci*, 2004, 29(3): 183–275
- 5 Zhou YF, Yan DY. Supramolecular self-assembly of amphiphilic hyperbranched polymers at all scales and dimensions: Progress,

characteristics and perspectives. *Chem Commun*, 2009(10): 1172–1188

- 6 Yan DY, Gao C, Frey H. Hyperbranched Polymers: Synthesis, Properties, and Applications. New York: Wiley, 2011
- 7 Yan DY, Zhou YF, Hou J. Supramolecular self-assembly of macroscopic tubes. *Science*, 2004, 303: 65–67
- 8 Gao C, Zheng X. Facile synthesis and self-assembly of multihetero-arm hyperbranched polymer brushes. *Soft Matter*, 2009, 5(23): 4788–4796
- 9 Liu C, Gao C, Yan DY. Honeycomb-patterned photoluminescent films fabricated by self-assembly of hyperbranched polymers. *Angew Chem Int Ed*, 2007, 46(22): 4128–4131
- 10 Whitesides GM, Grzybowski B. Self-assembly at all scales. Science, 2002, 295(5564): 2418–2421
- 11 Asakawa M, Ashton PR, Balzani V, Brown CL, Credi A, Matthews OA, Newton SP, Raymo FM, Shipway AN, Spencer N, Quick A, Stoddart JF, White AJP, Williams DJ. Photoactive azobenzene-containing supramolecular complexes and related interlocked molecular compounds. *Chem-Eur J*, 1999, 5(3): 860–875
- 12 Chen L, Zhu XY, Yan DY, Chen Y, Chen Q, Yao YF. Controlling polymer architecture through host-guest interactions. *Angew Chem Int Ed*, 2006, 45(1): 87–90
- 13 Guo MY, Jiang M. Macromolecular self-assembly based on inclusion complexation of cyclodextrins. *Prog Chem*, 2007, 19(4): 557–566
- 14 Harada A, Hashidzume A, Yamaguchi H, Takashima Y. Polymeric rotaxanes. *Chem Rev*, 2009, 109(11): 5974–6023
- 15 Callari F, Petralia S, Sortino S. Highly photoresponsive monolayerprotected gold clusters by self- assembly of a cyclodextrinazobenzene-derived supramolecular complex. *Chem Commun*, 2006(9): 1009-1011
- 16 Chen X, Hong L, You X, Wang YL, Zou G, Su W, Zhang QJ. Photo-controlled molecular recognition of alpha-cyclodextrin with azobenzene containing polydiacetylene vesicles. *Chem Commun*, 2009, 11: 1356–1358
- 17 Luo CH, Zuo F, Ding XB, Zheng ZH, Cheng X, Peng YX. Lighttriggered reversible solubility of alpha-cyclodextrin and azobenzene moiety complexes in PDMAA-co-PAPA via molecular recognition. J Appl Polym Sci, 2008, 107(4): 2118–2125
- 18 Luo CH, Zuo F, Zheng ZH, Cheng X, Ding XB, Peng YX. Tunable smart surface of gold nanoparticles achieved by light-controlled molecular recognition effection. *Macromol Rapid Commun*, 2008, 29(2): 149–154
- 19 Liu Z, Jiang M. Reversible aggregation of gold nanoparticles driven by inclusion complexation. *J Mater Chem*, 2007, 17(40): 4249–4254
- 20 Fujimoto T, Nakamura A, Inoue Y, Sakata Y, Kaneda T. Photoswitching of the association of a permethylated alphayclodextrin-zobenzene dyad forming a Janus 2 pseudorotaxane. *Tetrahedron Lett*, 2001, 42(45): 7987–7989
- 21 Zheng PJ, Hu X, Zhao XY, Li L, Tam KC, Gan LH. Photoregulated sol-gel transition of novel azobenzene-functionalized hydroxypropyl methylcellulose and its alpha-cyclodextrin complexes. *Macromol Rapid Comm*, 2004, 25(5): 678–682
- 22 Luo CH, Zuo F, Zheng ZH, Ding XB, Peng YX. Temperature/ ight dual-responsive inclusion complexes of alpha-cyclodextrins and azobenzene-containing polymers. *J Macromol Sci Pure*, 2008, 45(5): 364–371
- 23 Wang YP, Ma N, Wang ZQ, Zhang X. Photocontrolled reversible supramolecular assemblies of an azobenzene-containing surfactant with alpha-cyclodextrin. *Angew Chem Int Ed*, 2007, 46(16): 2823–2826
- 24 Zou J, Guan B, Liao XJ, Jiang M, Tao FG. Dual reversible self-assembly of pnipam-based amphiphiles formed by inclusion complexation. *Macromolecules*, 2009, 42(19): 7465–7473
- 25 Zhou L, Gao C, Xu WJ. Efficient grafting of hyperbranched polyglycerol from hydroxyl-functionalized multiwalled carbon nanotubes by surface-initiated anionic ring-opening polymerization. *Macromol Chem Phys*, 2009, 210(12): 1011–1018
- 26 Zhang Y, He H, Gao C. Clickable macroinitiator strategy to build amphiphilic polymer brushes on carbon nanotubes. *Macromolecules*,

2008, 41(24): 9581–9594

- 27 Kainthan RK, Muliawan EB, Hatzikiriakos SG, Brooks DE. Synthesis, characterization, and viscoelastic properties of high molecular weight hyperbranched polyglycerols. *Macromolecules*, 2006, 39(22): 7708–7717
- 28 Gao C, He H, Zhou L, Zheng X, Zhang Y. Scalable functional group engineering of carbon nanotubes by improved one-step nitrene chemistry. *Chem Mater*, 2008, 21(2): 360–370
- 29 Gao HF, Matyjaszewski K. Synthesis of star polymers by a combination of ATRP and the "click" coupling method. *Macromolecules*, 2006, 39(15): 4960–4965
- 30 He X, Zhang H, Yan D, Wang X. Synthesis of side-chain liquid-crystalline homopolymers and triblock copolymers with p-methoxyazobenzene moieties and poly(ethylene glycol) as coil segments by atom transfer radical polymerization and their thermotropic phase behavior. *J Polym Sci Pol Chem*, 2003, 41(18): 2854–2864
- 31 Han Y, Gao C. Miktoarms hyperbranched polymer brushes: One-step fast synthesis by parallel click chemistry and hierarchical self-assembly. *Sci China Chem*, 2010, 53(12): 2461–2471
- 32 Wu J, He H, Gao C. β-Cyclodextrin-capped polyrotaxanes: One-pot facile synthesis via click chemistry and use as templates for platinum nanowires. *Macromolecules*, 2010, 43(5): 2252–2260
- 33 Lutz JF. 1,3-Dipolar cycloadditions of azides and alkynes: A universal ligation tool in polymer and materials science. *Angew Chem Int Ed*, 2007, 46(7): 1018–1025
- 34 Kumar GS, Neckers DC. Photochemistry of azobenzene-containing polymers. *Chem Rev*, 1989, 89(8): 1915–1925
- 35 Zimmerman G, Chow LY, Paik UJ. The photochemical isomerization of azobenzene. *J Am Chem Soc*, 1958, 80(14): 3528–3531
- 36 Hartley GS. 113 The *cis*-form of azobenzene and the velocity of the thermal cis -> *trans*-conversion of azobenzene and some derivatives. *J Chem Soc*, 1938, 633–642
- 37 Cheng F, Zhang KK, Chen DY, Zhu L, Jiang M. Self-assembly of heteroarms core-shell polymeric nanoparticles (HCPNs) and templated synthesis of gold nanoparticles within HCPNs and the superparticles. *Macromolecules*, 2009, 42(18): 7108–7113
- 38 Cheng L, Hou GL, Miao JJ, Chen DY, Jiang M, Zhu L. Efficient

synthesis of unimolecular polymeric janus nanoparticles and their unique self-assembly behavior in a common solvent. *Macromolecules*, 2008, 41(21): 8159–8166

- 39 Kodaka M. A general rule for circular dichroism induced by a chiral macrocycle. *J Am Chem Soc*, 1993, 115(9): 3702–3705
- 40 Zhu XY, Chen L, Yan DY, Chen Q, Yao YF, Xiao Y, Hou J, Li JY. Supramolecular self-assembly of inclusion complexes of a multiarm hyperbranched polyether with cyclodextrins. *Langmuir*, 2004, 20(2): 484–490
- 41 Zhao YL, Stoddart JF. Azobenzene-based light-responsive hydrogel system. *Langmuir*, 2009, 25(15): 8442–8446
- 42 Pang Y, Liu JY, Su Y, Zhu BS, Huang W, Zhou YF, Zhu XY, Yan DY. Bioreducible unimolecular micelles based on amphiphilic multiarm hyperbranched copolymers for triggered drug release. *Sci China Chem*, 2010, 53(12): 2497–2508
- 43 Yagai S, Kitamura A. Recent advances in photoresponsive supramolecular self-assemblies. *Chem Soc Rev*, 2008, 37(8): 1520–1529
- 44 Kolb HC, Finn MG, Sharpless KB. Click chemistry: Diverse chemical function from a few good reactions. *Angew Chem Int Ed*, 2001, 40(11): 2004–2021
- 45 Ladmiral V, Legge TM, Zhao YL, Perrier S. "Click" chemistry and radical polymerization: Potential loss of orthogonality. *Macromolecules*, 2008, 41(18): 6728–6732
- 46 Zhai S, Hong HY, Zhou YF, Yan DY. Synthesis of cationic hyperbranched multiarm copolymer and its application in self-reducing and stabilizing gold nanoparticles. *Sci China Chem*, 2010, 53(5): 1114–1121
- 47 Zhang JX, Ma PX. Polymeric core-shell assemblies mediated by host-guest interactions: Versatile nanocarriers for drug delivery. *Angew Chem Int Ed*, 2009, 48(5): 964–968
- 48 Wang YP, Zhang M, Moers C, Chen SL, Xu HP, Wang ZQ, Zhang X, Li ZB. Block copolymer aggregates with photo-responsive switches: Towards a controllable supramolecular container. *Polymer*, 2009, 50(20): 4821–4828
- 49 Sun XY, Zhou YF, Yan DY. Drug release property of a pH-responsive double-hydrophilic hyperbranched graft copolymer. *Sci China Ser B Chem*, 2009, 52(10): 1703–1710