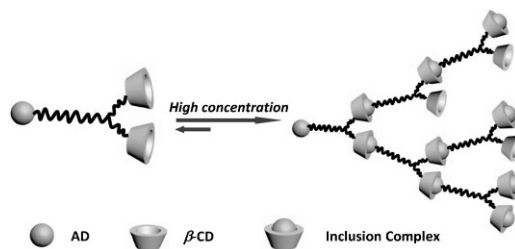


Supramolecular Thermoresponsive Hyperbranched Polymers Constructed from Poly(*N*-Isopropylacrylamide) Containing One Adamantyl and Two β -Cyclodextrin Terminal Moieties^a

Zhishen Ge, Hao Liu, Yanfeng Zhang, Shiyong Liu*

Poly(*N*-isopropylacrylamide) (PNIPAM) oligomer containing one adamantyl (AD) and two β -cyclodextrin (β -CD) moieties at the chain terminals, AD-PNIPAM-(β -CD)₂, was synthesized by atom transfer radical polymerization (ATRP) and successive click reactions. In aqueous solution, AD-PNIPAM-(β -CD)₂ spontaneously forms supramolecular thermoresponsive hyperbranched polymers *via* molecular recognition between AD and β -CD moieties. To the best of our knowledge, this work represents the first report of the construction of supramolecular thermoresponsive hyperbranched polymers from well-defined polymeric AB₂ building units.



Introduction

Representing a special type of soft matter entities, supramolecular polymers are typically built from monomeric units *via* noncovalent interactions including hydrogen bonding, π - π stacking, metal-ligand interactions, and host-guest recognitions, as well as the combination of them.^[1] Compared with conventional polymers, supramolecular polymers show inherent structural reversibility,

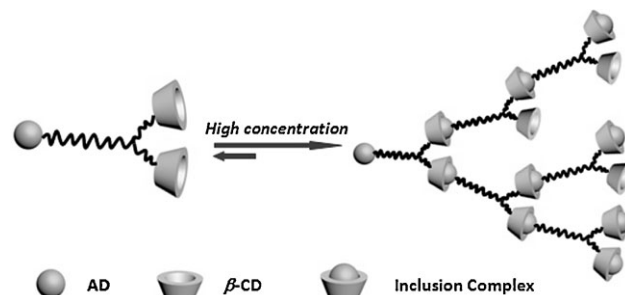
adaptability, and flexibility.^[1,2] Over the past decade, design and synthesis of supramolecular polymers have attracted considerable interests from researchers working in organic chemistry and polymer chemistry. A large variety of supramolecular polymers with varying chain topologies including linear homopolymers and copolymers,^[3] star and branched polymers,^[4] and crosslinked networks^[2a,d,5] have been constructed. Notably, reports concerning supramolecular hyperbranched polymers are relatively rare. Recently, the fabrication of supramolecular hyperbranched polymers from the self-organization of crown ether-based and α -cyclodextrin-based AB₂ small molecule building blocks were reported.^[4f,g] However, to the best of our knowledge, supramolecular hyperbranched polymers constructed from polymeric building blocks, which can endow them with extra properties and functions, have not yet been reported.

Herein, we report on the fabrication of supramolecular thermoresponsive hyperbranched polymer from the self-organization of poly(*N*-isopropylacrylamide) (PNIPAM)

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oligomer, $AD\text{-PNIPAM-(}\beta\text{-CD)}_2$, which contains one adamantyl (AD) and two β -cyclodextrin (β -CD) moieties at the chain terminals, *via* inclusion complexation between AD and β -CD functionalities. The polymeric building block was synthesized *via* the combination of atom transfer radical polymerization (ATRP) and two-step click reactions. At relatively high concentrations, $AD\text{-PNIPAM-(}\beta\text{-CD)}_2$ can form supramolecular hyperbranched polymers in aqueous solution (Scheme 1). 2D NOESY, viscometry, static laser light scattering (SLS), and temperature-dependent optical transmittance were employed to characterize this novel type of supramolecular responsive hyperbranched polymers.



Scheme 1. Schematic illustration of the construction of supramolecular hyperbranched polymers from $AD\text{-PNIPAM-(}\beta\text{-CD)}_2$ in aqueous solution *via* inclusion complexation between adamantyl and β -CD moieties.

Experimental Part

Materials

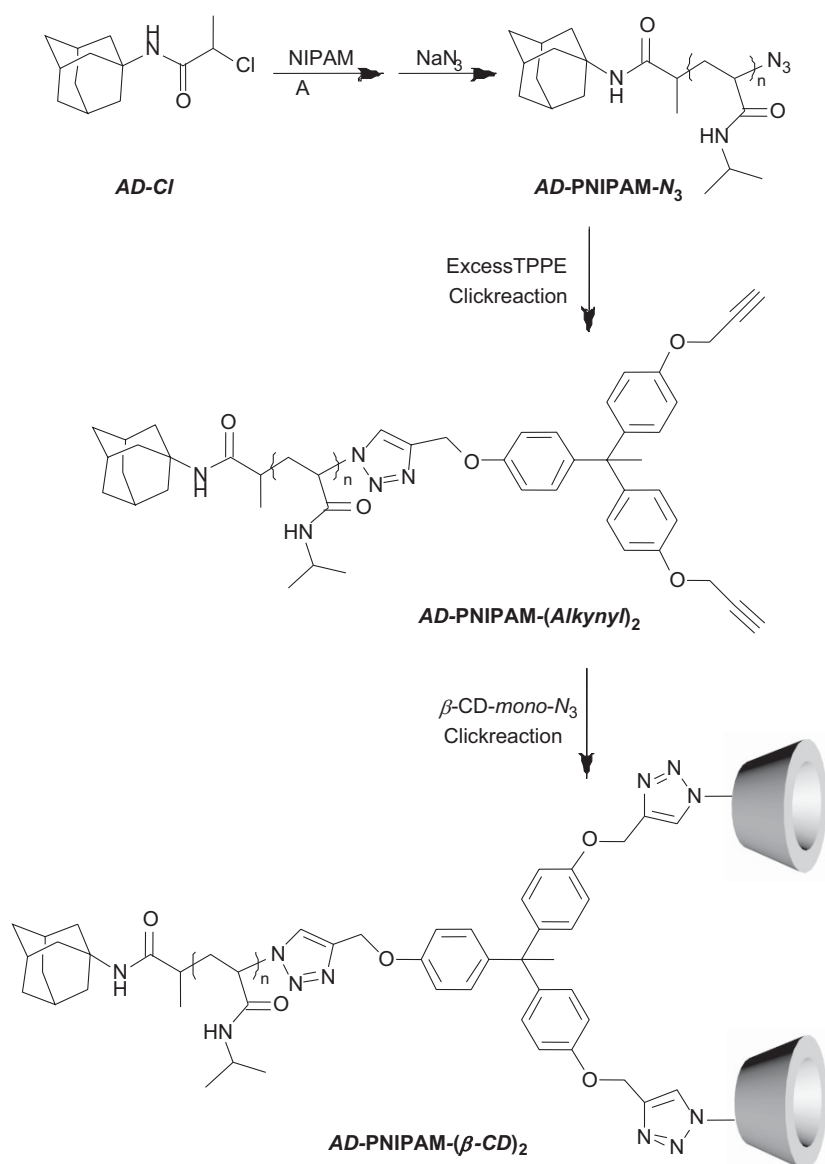
β -Cyclodextrin and *N*-isopropylacrylamide (NIPAM) (97%, Tokyo Kasei Kagyo Co.) were purified by recrystallization from water and a benzene/*n*-hexane mixture, respectively. Dichloromethane (CH_2Cl_2) and triethylamine (TEA) were dried over CaH_2 and distilled just prior to use. 1-Adamantanamine (Aldrich), copper (I) chloride (CuCl , 98%, Aldrich), copper (II) chloride (CuCl_2 , 99.9%, Sinopharm Chemical Reagent Co. Ltd.), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), 2-chloropropionyl chloride ($\geq 95\%$, Fluka), sodium azide (NaN_3 , Aldrich), sodium hydride (NaH , 57–63% oil dispersion, Alfa Aesar), propargyl bromide (80% in toluene stabilized with MgO , Alfa Aesar), and other reagents were used as received. Alkynyl-functionalized Wang resin,^[6a] β -CD-*mono-N}_3*,^[6b] 1,1,1-tris(4-(prop-2-ynyloxy)phenyl)ethane (TPPE),^[6c] and tris(2-(dimethylamino)ethyl)amine (Me_6TREN)^[6d,e] were synthesized according to literature procedures.

Sample Synthesis

The synthetic routes employed for the preparation of $AD\text{-PNIPAM-(}\beta\text{-CD)}_2$ were shown in Scheme 2.

Preparation of Adamantyl-Containing ATRP Initiator (AD-Cl)

A 100-mL round-bottom flask was charged with 1-adamantanamine (6.05 g, 40 mmol), TEA (4.15 g, 41 mmol), and dry CH_2Cl_2 (50 mL). The mixture was cooled to 0°C in an ice-water bath, 2-chloropropionyl chloride (5.21 g, 41 mmol) in dry CH_2Cl_2 (10 mL) was then added dropwise over 1.5 h. After the addition was completed, the reaction mixture was stirred at 0°C for another



Scheme 2. Synthetic routes employed for the preparation of $AD\text{-PNIPAM-(}\beta\text{-CD)}_2$ building block containing one AD and two β -CD moieties at the chain terminal *via* two-step click reactions.

1 h and then at room temperature for 12 h. After removing the insoluble salts by suction filtration, the filtrate was concentrated and further purified by silica gel column chromatography using petroleum ether/ethyl acetate (1:1 v/v) as the eluent. After removing the solvents by a rotary evaporator, the final product, *AD-Cl*, was obtained as a white solid (8.83 g, yield: 91.3%). $^1\text{H NMR}$ (CDCl_3 , δ , ppm, TMS): 1.56–2.01 (15H, ADH), 4.20–4.38 (1H, BrCH CH_3), 6.16–6.35 (1H, NHCO) (Figure S1a).

Synthesis of AD-PNIPAM-Cl

The general procedure employed for the preparation of *AD-PNIPAM-Cl* was as follows. A reaction flask equipped with a magnetic stirring bar and a rubber septum was charged with *AD-Cl* (0.725 g, 3 mmol), NIPAM (5.09 g, 45 mmol), Me $_6$ TREN (0.346 g, 1.5 mmol), and *tert*-butyl alcohol (15 ml). The flask was degassed by three freeze–pump–thaw cycles, back-filled with N_2 , and then placed in an oil bath thermostated at 25 °C. After ~5 min, CuCl (0.149 g, 1.5 mmol) was introduced to start the polymerization under the protection of N_2 flow. The reaction solution became dark green and more viscous as polymerization proceeded. After about 3 h, the conversion is higher than 70% indicated by $^1\text{H NMR}$. The reaction was terminated using CuCl $_2$, diluted with 30 mL THF, and then exposed to air. The reaction mixture was passed through a silica gel column to remove the copper catalyst. After removing the solvents by a rotary evaporator, the residues were dissolved in THF and precipitated into an excess of the mixture of anhydrous diethyl ether and petroleum ether (1:2 v/v) to remove residual monomers. The above dissolution–precipitation cycle was repeated twice. The final product was dried in a vacuum oven, yielding a white solid (3.83 g, 65.9% yield: $\overline{M}_n = 1\ 300$, $\overline{M}_w/\overline{M}_n = 1.10$). The actual DP of *AD-PNIPAM-Cl* was determined to be 11 by $^1\text{H NMR}$ analysis in CDCl_3 (Figure S1b). Thus, the polymer was denoted as *AD-PNIPAM* $_{11}$ -Cl.

Preparation of AD-PNIPAM $_{11}$ -N $_3$

A 100-mL round-bottom flask was charged with *AD-PNIPAM* $_{11}$ -Cl (3.72 g, 2.5 mmol), DMF (20 mL), and NaN $_3$ (0.65 g, 10 mmol). The reaction mixture was allowed to stir at 45 °C for 48 h. After removing most of the solvents at reduced pressure, the remaining portion was diluted with THF, and then precipitated into an excess of *n*-hexane. The sediments were re-dissolved in THF and passed through a neutral alumina column to remove residual sodium salts, and then precipitated into an excess of the mixture of anhydrous diethyl ether and petroleum ether (1:2 v/v). The obtained product was dried in a vacuum oven, yielding a white solid (3.6 g, yield: 96.4%, $\overline{M}_{n,\text{GPC}} = 1\ 300$ kDa, $\overline{M}_w/\overline{M}_n = 1.10$).

Preparation of AD-PNIPAM $_{11}$ -(Alkynyl) $_2$

To a Schlenk tube equipped with a magnetic stirring bar, *AD-PNIPAM* $_{11}$ -N $_3$ (1.49 g, 1 mmol), PMDETA (0.87 g, 5 mmol), TPPE (8.41 g, 20 mmol), and 10 mL DMF were added. After one brief freeze–thaw cycle, CuBr (0.72 g, 5 mmol) was introduced under protection of N_2 flow. The reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 60 °C. After 12 h, the tube was broken and the mixture was diluted with THF. The copper catalysts were removed by passing through a basic alumina column. After removing most of the solvents, the remaining portion was diluted with THF, and then precipitated into an excess of anhydrous diethyl

ether/petroleum ether mixture (1:2 v/v). The above dissolution–precipitation cycle was repeated for six times to remove the excess TPPE. After drying in a vacuum oven overnight at room temperature, *AD-PNIPAM* $_{11}$ -(alkynyl) $_2$ was obtained as a white solid (1.58 g, yield: 82.7%, $\overline{M}_{n,\text{GPC}} = 1\ 900$, $\overline{M}_w/\overline{M}_n = 1.11$).

Preparation of AD-PNIPAM $_{11}$ -(β -CD) $_2$

To a Schlenk tube equipped with a magnetic stirring bar, *AD-PNIPAM* $_{11}$ -(alkynyl) $_2$ (0.96 g, 0.5 mmol), β -CD-*mono-N* $_3$ (1.39 g, 1.2 mmol), PMDETA (87 mg, 0.5 mmol), and 10 mL DMF were added. After one brief freeze–thaw cycle, CuBr (72 mg, 0.5 mmol) was introduced under protection of N_2 flow. The reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 80 °C. After 8 h, the tube was frozen in liquid N_2 and broken followed by addition of excess alkynyl-functionalized Wang resin. Then the reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 80 °C. After 8 h, the tube was broken and the mixture was diluted with hot DMF. Wang resin was then removed by hot filtration. The copper catalysts were removed by passing through a basic alumina column. After removing most of the solvents, the remaining portion was diluted with DMF, and then precipitated into an excess of into an excess of acetone. After drying in a vacuum oven overnight at room temperature, *AD-PNIPAM* $_{11}$ -(β -CD) $_2$ was obtained as a white solid (1.68 g, yield: 79.4%, $\overline{M}_{n,\text{GPC}} = 5\ 600$, $\overline{M}_w/\overline{M}_n = 1.11$).

Fabrication of Supramolecular Hyperbranched Polymer From AD-PNIPAM $_{11}$ -(β -CD) $_2$

Typically, *AD-PNIPAM* $_{11}$ -(β -CD) $_2$ (0.1 g) was dispersed in 10 mL deionized water directly. After sonication for 10 min, the aqueous solution of *AD-PNIPAM* $_{11}$ -(β -CD) $_2$ was allowed to stand for 2 h under stirring.

Characterization

All $^1\text{H NMR}$ spectra were performed at 25 °C on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for ^1H) operating in the Fourier transform mode. CDCl_3 and DMSO-*d* $_6$ was used as the solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 32 scans with a spectral resolution of 4 cm^{-1} . Molecular weights and molecular weight distributions of *AD-PNIPAM* $_{11}$ -(alkynyl) $_2$ and *AD-PNIPAM* $_{11}$ -Cl were determined by gel permeation chromatography (GPC) with a Waters 1515 pump and a Waters 2414 differential refractive index detector (set at 30 °C). It used a series of three linear Styragel columns (HT2, HT4, and HT5) at an oven temperature of 45 °C. The eluent was THF at a flow rate of 1.0 mL min^{-1} . A series of low polydispersity polystyrene standards were employed for the GPC calibration. The MALDI-TOF mass spectrum was recorded in the reflector mode on a Bruker BIFLEXe III mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. α -Cyano-4-hydroxycinnamic acid (CHCA) was used as the matrix and a strong cation-exchange resin DOWEX 50W-X8 was used to improve the ionization. The 2D NMR (NOESY) experiment was recorded at 400 MHz in D $_2$ O on a VARIAN UNITY plus NMR spectrometer at 20 °C. The polymer concentration

was fixed at $10.0 \text{ mg} \cdot \text{mL}^{-1}$. Measurements of the reduced viscosities, η_{sp}/C , of the aqueous solutions of $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ and the mixture of $AD\text{-PNIPAM}_{111}$ and $\beta\text{-CD}$ (1:2 molar ratio) as a function of total polymer concentrations were conducted using an Ubbelohde viscometer at $20 \pm 0.05 \text{ }^\circ\text{C}$. The optical transmittance of the aqueous solution was acquired on a Unicou UV-Vis 2802PCS spectrophotometer and measured at a wavelength of 500 nm using a thermostatically controlled cuvette. SLS was employed to estimate the weight-average molar mass (\overline{M}_w) of the supramolecular hyperbranched polymers self-organized from $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ in aqueous solution at varying concentrations. A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632 \text{ nm}$) as the light source was used.

Results and Discussion

Synthetic routes employed for the preparation of $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ are shown in Scheme 2. The PNIPAM precursor, $AD\text{-PNIPAM}_{111}\text{-N}_3$, was prepared via ATRP using $AD\text{-Cl}$ as the initiator in the presence of $\text{CuCl}/\text{Me}_6\text{TREN}$ catalyst, followed by the nucleophilic substitution reaction with sodium azide. In order to obtain well-defined PNIPAM precursor, the ATRP of NIPAM was carried out at a monomer concentration of 0.34 g mL^{-1} with a feed ratio of $[\text{monomer}]:[\text{initiator}]:[\text{CuCl}]:[\text{Me}_6\text{TREN}] = 15:2:1:1$.^[7] The dialkynyl functionalized polymer, $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$, was obtained via the click reaction of $AD\text{-PNIPAM}_{111}\text{-N}_3$ with a large excess of TPPE.^[8] The residual TPPE was removed completely by precipitation into a mixture of anhydrous diethyl ether and petroleum ether (1:2 v/v). From the $^1\text{H NMR}$ spectrum of $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ (Figure S1), the peak integral ratio of methylene protons ($\delta = 4.69 \text{ ppm}$) adjacent to alkynyl moiety to those of methylene protons ($\delta = 5.15 \text{ ppm}$) neighboring to the 1,2,3-triazole moiety is 2:1, indicating a successful end group modification. From THF GPC traces obtained before and after click reaction (Figure S2), it is evident that the elution peak of $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ is mono-modal and quite symmetric, indicating that there exists essentially no chain coupling reactions. From FT-IR spectrum of $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ (Figure S3d), we can observe that the characteristic azide absorbance peak at $\approx 2108 \text{ cm}^{-1}$ completely disappeared, accompanied with the appearance of a new absorbance band at $\approx 2118 \text{ cm}^{-1}$ characteristic of alkynyl moieties.

The final product, $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$, was obtained by the click reaction of $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ with a slightly excess of $\beta\text{-CD-}mono\text{-N}_3$. Then, the *alky-*

nyl-functionalized Wang resin was added to the reaction mixture to remove excess $\beta\text{-CD-}mono\text{-N}_3$ via click reaction followed by hot filtration. $^1\text{H NMR}$ and FT-IR were employed to characterize the polymeric AB_2 building block, $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ (Figures S4 and S5). From Figure S4c, we can observe the appearance of signals at $\delta = 5.8\text{--}5.5$, $4.9\text{--}4.7$, $4.5\text{--}4.2$, and $3.8\text{--}3.4 \text{ ppm}$ characteristic of $\beta\text{-CD}$ protons. FT-IR results revealed that absorbance bands at 2108 and 2118 cm^{-1} disappeared completely for the final product (Figure S5c), as compared to those of $\beta\text{-CD-}mono\text{-N}_3$ (Figure S5a) and $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ (Figure S5b), indicating that all alkynyl functionalities of $AD\text{-PNIPAM}_{111}\text{-(alkynyl)}_2$ have been consumed and the absence of any $\beta\text{-CD-}mono\text{-N}_3$ starting material. Moreover, MALDI-TOF MS analysis and DMF GPC were also employed to characterize the AB_2 macromonomer, $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$. In Figure 1a, the signal ($m/z = 4254.3$) can be assigned to sodium adducts of $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$, and other peaks can be assigned to $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ with varying degree of polymerizations (DPs). Moreover, the isotope pattern of representative peaks agrees quite well with the simulated one (see Figure 6S). The DMF GPC analysis of $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ reveals a relatively narrow and symmetric elution peak (Figure 1b). No tailing or shoulder at the lower or higher molecular weight side can be discerned.

In aqueous solution, AD derivatives can form stable complexes with $\beta\text{-CD}$ moieties due to the inclusion complexation with high association constant,^[9] which have been widely used to construct supramolecular polymers.^[3g,h,5b,10] Presumably, $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ can self-assemble into supramolecular hyperbranched polymers in aqueous solution at relatively high concentration via the inclusion complexation between AD and $\beta\text{-CD}$ moieties. Nuclear overhauser effect (NOE) technique is very sensitive to the interproton distance, thus it can provide direct evidence for the molecular recognition event.^[2b,4g,10a] Figure S7 shows the 400 MHz 2D NOESY spectrum of $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$ in D_2O at $20 \text{ }^\circ\text{C}$ and

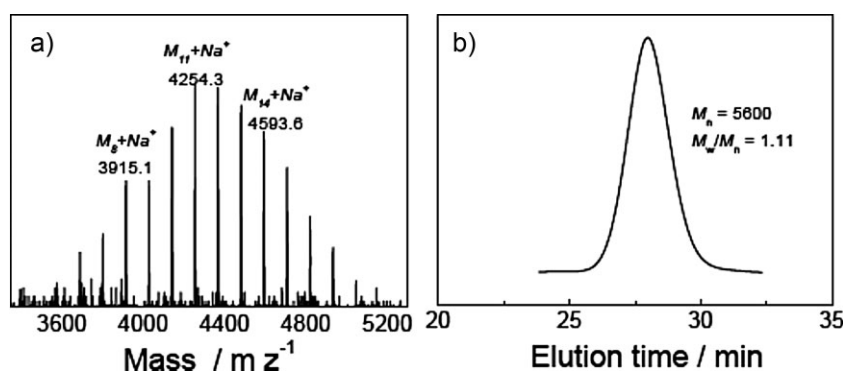


Figure 1. (a) MALDI-TOF mass spectrum and (b) DMF GPC trace obtained for $AD\text{-PNIPAM}_{111}\text{-(}\beta\text{-CD)}_2$.

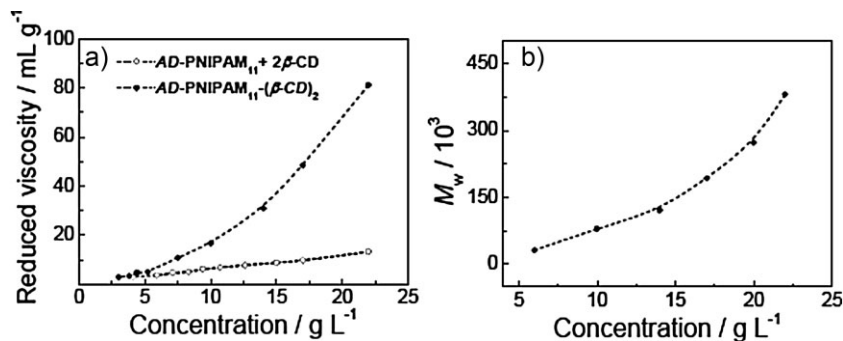


Figure 2. Concentration dependence of (a) the reduced viscosity and (b) apparent weight-average molecular weight (\bar{M}_w) obtained for aqueous solutions (20 °C) of AD-PNIPAM₁₁-(β-CD)₂ and AD-PNIPAM₁₁/β-CD mixture ([AD]/[β-CD]=1/2), respectively.

10 g L. The peaks at δ = 2.2, 2.1, and 1.7 ppm are ascribed to the protons of AD functionality, and the signals at δ = 3.9 and 3.6 ppm are attributed to the inner protons C(3)-H (H₃) of β-CD overlapped with the resonance signals of methine (d) (NCH) of PNIPAM and C(5)-H (H₅) proton of β-CD, respectively. The peak of methylene proton (H_c) in the AD group is correlating well with inner protons (H₃) of β-CD, and the peaks of methine (H_a) and methylene protons (H_b) are correlating with inner protons (H₃, H₅) of β-CD. These results indicated that the AD moiety has been inserted into the cavity of β-CD. Moreover, there are crosspeaks between H_b/H_c and H₃, indicating that the AD moiety is deeply included in the cavity of β-CD.

Viscometry was further employed to characterize the growth of supramolecular hyperbranched polymers with increasing polymer concentrations (Scheme 1). The variation of reduced viscosities of AD-PNIPAM₁₁-(β-CD)₂ in aqueous solution as a function of the concentrations at 20 °C is shown in Figure 2a. For comparison, the variation of reduced viscosity of the solution mixture of AD-PNIPAM and β-CD at a [AD]/[β-CD] molar ratio of 1:2 is also presented. The reduced viscosities of AD-PNIPAM₁₁/β-CD solution mixture increased almost linearly with polymer concentrations in the range of 2.8–22 g · L⁻¹. However, for the aqueous solution of AD-PNIPAM₁₁-(β-CD)₂, when the concentrations are higher than ~6 g · L⁻¹, the reduced viscosities increase exponentially with polymer concentrations, clearly indicating the increase of molecular weight of the obtained supramolecular hyperbranched polymer. Moreover, SLS was employed to estimate \bar{M}_w of the supramolecular hyperbranched polymers self-organized from AD-PNIPAM₁₁-(β-CD)₂ in aqueous solution (20 °C) at varying concentrations (Figure 2b). The measured \bar{M}_w dramatically increases with polymer concentrations, which is similar to the concentration dependence of reduced viscosities (Figure 2a). The average aggregation

number, N_{agg} , of the supramolecular hyperbranched polymer was also calculated by comparing \bar{M}_w of the supramolecular polymer with that of the building block, AD-PNIPAM₁₁-(β-CD)₂. N_{agg} increased from ~5 to ~61 in the polymer concentration range of 6–22 g · L⁻¹. Combined with the structure of the AB₂ building block and the results obtained from 2D NOESY, viscometry, and SLS analysis, we can conclude that the macromonomer, AD-PNIPAM₁₁-(β-CD)₂, self-organizes to form supramolecular hyperbranched polymers in aqueous solution at relatively high concentrations according to the Flory theory concerning branched polymers (Scheme 1).^[11]

Figure 3 shows the temperature dependence of transmittance at 500 nm of the aqueous solutions of AD-PNIPAM₁₁ and AD-PNIPAM₁₁-(β-CD)₂ at 10 g · L⁻¹, respectively. For AD-PNIPAM₁₁, the transmittance decreases rapidly above 10 °C. Compared to the cloud point (CP) of PNIPAM homopolymers (at ~32 °C),^[12] the remarkably low CP of AD-PNIPAM₁₁ suggested that the CP of low molecular weight PNIPAM oligomer is strongly affected by the hydrophobic AD end group. In marked contrast, the optical transmittance of AD-PNIPAM₁₁-(β-CD)₂ solution only exhibits a decrease above ~35 °C, accompanied with the appearance of bluish tinge, which is characteristic of microscopic aggregates. Presumably, hydrophobic AD moieties were embedded into the hydrophilic β-CD cavities within the supramolecular hyperbranched polymer constructed from AD-PNIPAM₁₁-(β-CD)₂, and this will considerably elevate its CP, as compared to the AD-PNIPAM₁₁ precursor.^[13]

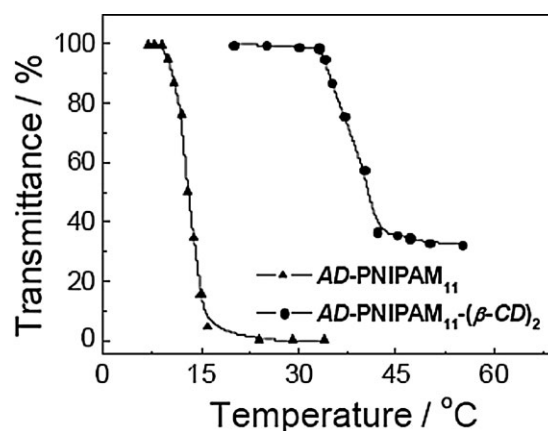


Figure 3. Temperature dependence of transmittance at 500 nm recorded for aqueous solutions of AD-PNIPAM₁₁ and AD-PNIPAM₁₁-(β-CD)₂, respectively. The polymer concentrations are fixed at 10.0 g · L⁻¹.

Conclusion

In summary, well-defined AB₂ polymeric building block, AD-PNIPAM₁₁-(β-CD)₂, was successfully synthesized via the combination of ATRP and two-step click reactions, which was characterized by FT-IR, ¹H NMR, GPC, and MALDI-TOF MS. In aqueous solution, AD-PNIPAM₁₁-(β-CD)₂ spontaneously self-organizes to form supramolecular thermo-responsive hyperbranched polymers with elevated CP via inclusion complexation between AD and β-CD moieties. To the best of our knowledge, this work represents the first report of the construction of supramolecular thermo-responsive hyperbranched polymers from well-defined polymeric AB₂ building units.

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