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Controllable Fabrication of the Novel pH-, Thermo-, and Light-Responsive Supramolecular Dendronized Copolymers with Dual Self-Assembly Behavior

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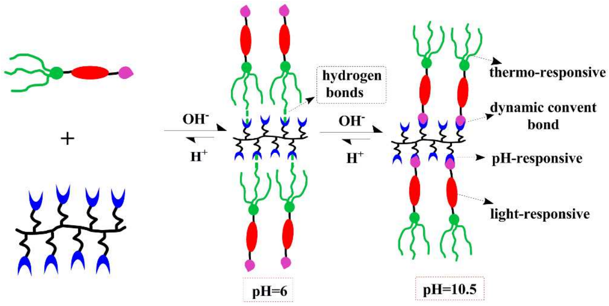
Novel tri-stimulus responsive supramolecular dendronized copolymers are prepared through self-assembly of imine bonds, exhibiting fast and fully reversible phase transitions and *trans-cis* isomerization in alkaline solutions. The lower critical solution temperature (LCST) is controlled with the aldehyde-to-amino molar ratio, and mostly decreases after UV irradiation. As the pH increases, the LCST has an inflection point caused by two different self-assembly behaviors. The aldehyde and amino monomers are assembled by H-bonds in acids, but by dynamic imine bonds in bases. The copolymer concentration plays an essential role in affecting the LCST. The LCST increases with the aldehyde content when the concentration is 5.0 mg mL^{-1} and has an inflection point with the aldehyde content when the concentration is 1.0 mg mL^{-1}. The tri-stimuli-responsive copolymers have three advantages: (1) feasible control via pH-adjusting aldehyde-amino bonds, (2) controllable synthesis, and (3) narrow, tunable phase transition temperature by pH, light and the molar ratio.

Introduction

Multi-responsive polymers, such as dual-[1-3] and tri-responsive [4-10] polymers, are traditionally synthesized by free radical copolymerization, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT). They have tunable chemical structures and physical properties under external stimuli, and have been explored for many prospective multipurpose applications. They are classified into pH-, [11-13] CO_2-, [13-14] temperature-, [15-17] light-[18-19] and redox potential [20-21] responsive polymers, based on the type of stimulus. However, with those synthetic methods, the ratio of each sensitive moiety is not well controlled during the polymerization process, and it is too complicated to synthesize a well-defined stimuli-responsive polymers. [22-27] Nevertheless, multiple responsive properties can be obtained in a single multi-stimuli responsive polymer when different polymeric units are incorporated into one copolymer.

Hydrogen bonding, metal coordination, π-π stacking and ionic interaction [28-33] have been used to construct responsive polymers. Hydrogen bond is a kind of non-covalent bond which can be used to build functional materials in a simple and feasible way. Supramolecular architectures with fascinating stimuli-responsive features can be obtained from the self-assembly based on the dynamic and reversible nature of hydrogen bonding formation-based, which allows us to manipulate the systems for desired functions. On the other hand, dynamic combinatorial chemistry (DCC), a powerful tool for constructing supramolecular architectures with reversible molecular recognition properties, can lead to controlled formation of polymers [34-38] and has become more and more important for many potential applications. Although self-assembly and disassembly are known independently to be able to control he stimuli-responsive behaviors and nanostructure of superamphiphiles, [38-40] however, the synthesis of multi-stimuli responsive polymers with those two kinds of assembly behaviors have been barely reported.



Scheme 1.Self-assembly of G1-Azo-CHO and PVBAHS

Inspired by the successful design of the multi-stimuli responsive homopolymers by combining different functional responsive groups in one polymer backbone, we expect that

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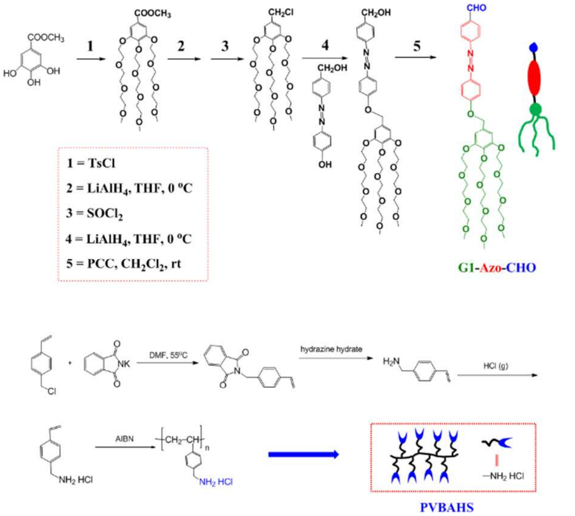
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the introduction of azobenzene and OEG-group into the dendronized monomer can produce a temperature-, pH-, and light-stimulus responsive supramolecular dendronized copolymers via two kinds (hydrogen and dynamic imine bond) of self-assembly behaviors with an amino polymer (Scheme 1). Specifically, the copolymers are synthesized through the hydrogen bonds between OEG-groups and ammonium units in acid, and the imine bonds of the aldehyde and amino in alkaline solution, respectively. According to our previous work,[41-42] the first generation dendron monomer 4-(4'-(3,4,5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzaldehyde (G1-Azo-CHO) and the ammonium polymer poly-(4-vinylbenzylamine hydrochloride) (PVBAHS) are synthesized as shown in Scheme 2. The monomer and the polymer are characterized with proton nuclear magnetic resonance (1H NMR). The pH-, thermo-and light-responsive behaviors of the supramolecular dendronized copolymers are investigated by 1H NMR, ultraviolet-visible (UV-Vis), high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and dynamic light scattering (DLS).



Scheme 2. Synthesis route of G1-Azo-CHO and PVBAHS

Results and discussion

Characterization

The chemical structure of G1-Azo-CHO was investigated with ^{1}H NMR (Figure S1a) and ^{13}C NMR. The ^{1}H NMR of the intermediates and ammonium polymer PVBAHS is shown in Figure S1b-d. The characteristic resonance peaks of the vinyl substituent of monomer 4-VBAHS are presented at 6.63, 5.71 and 5.18 ppm (denoted c, b and a, respectively). After polymerization, these signals disappear completely, and the chemical shifts of polymer PVBAHS are quite broad, consistent with the expected polymer structure (Figure S1c and d). From Figure S2a, the absorption peak in 3422 cm^{-1} and 3008 cm^{-1} correspond to N-H and C-H, respectively. The C=C absorption peak is in 1596 cm^{-1}. However, the C=C absorption peak disappear in the FT-IR spectrum of PVBAHS (Figure S2b), and the absorption peak N-H increases. The molecular weight of PVBAHS is M_n, $M_n = 1.2 \times 10^{4}$ g mol^{-1}, which was tested by GPC.

2.1 Stimuli-responsive monomer G1-Azo-CHO

Azobenzene compounds exhibit a photo isomerization behavior with a reversible conversion between the *trans*- and *cis*-forms under the UV–Vis irradiation. The light-responsive behavior was monitored with UV–Vis absorption spectra on the transformation of the azobenzene group, when the monomer G1-Azo-CHO was irradiated by UV or visible light. In absorption spectrum of monomer G1-Azo-CHO, the absorption peak in 358 nm due to the π–π* electron transition of the *trans*-azobenzene obviously decreases when the solution is exposed to UV-light (Figure 1a). But the band intensity at about 450 nm from the n–π* transition of cis-form azobenzene increases slightly, indicating the transformation from *trans*- to *cis*-form after the UV irradiation. cis-form azobenzene returns to *trans*-form under the visible light irradiation, and the absorption peak of *trans*- and *cis*-form is restored to the original state (Figure 1b), exhibiting an excellent reversible photoisomerization property. Additionally, when the UV irradiation time is elongated to more than 5 min, the absorption spectra are almost constant, suggesting a photo stable state is reached within a certain range of time.

For the amphiphiles monomer containing azobenzene and OEG-groups, after the UV irradiation, the LCST changes with the isomerization of *trans*- and *cis*-forms. Before the UV irradiation the LCST of monomer is 39.8 °C, but after the UV irradiation for 2 h, the LCST decreases to 39.5 °C , it was slightly changed (Figure 1c). The phase transition is easily observed by the visual method (Figure S3a). The LCST dependence on the pH of the monomer G1-Azo-CHO is shown in Figure 1d. The plot suggests that the pH has a slightly influence on the LCSTs of the G1-Azo-CHO. The LCSTs increase from 39.5 °C to 40.8 °C with the increase of the pH from 1 to 10. Furthermore, the LCSTs of monomer have a slight change with the increase of G1-Azo-CHO concentration from 1.0 to 20.0 mg ml^{-1}. The LCSTs decreases from 39.5 °C to 36.4 °C (Figure S4).

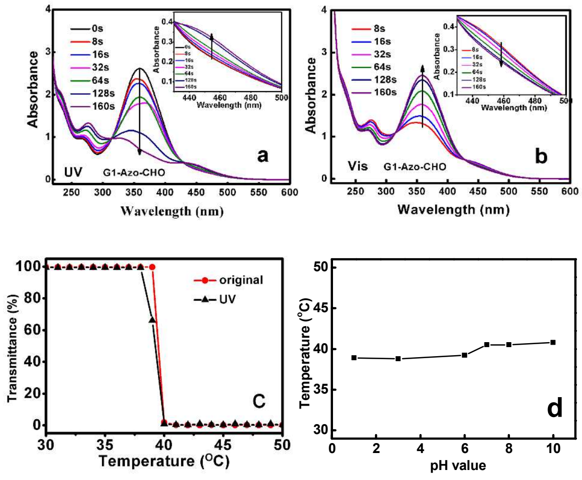


Figure 1. Time-dependent UV-*Vis* absorption spectra recorded at room temperature for the aqueous solution of G1-Azo-CHO upon (a) UV irradiation (365nm) and (b) *Vis* irradiation (470nm) for varying time durations (0–160s); (c) transmittance-dependent temperature plot of aqueous solution of G1-Azo-CHO before (round plot) and after (triangle plot) UV irradiation; (d) pH effects on the LCST of monomer.

2.2 pH triggered two kinds of assembly behaviors of copolymers

To investigate the pH-responsive properties, a series of solutions of copolymer with different pH value are prepared to monitor the assembly behavior using ^{1}H NMR. From Figure 2a, when the pH is changed from 1.34 to 6.20, the aldehyde signal in 9.5 ppm can be observed. When the pH is adjusted to 8.15, the peak of aldehyde disappears. However, from the results above, we can′t define the assembly behavior of G1-Azo-CHO and ammonium polymer PVBAHS. Here, we will use the system of benzylamine and G1-Azo-CHO as the model to illustrate the self-assembly behaviors. Figure S5a shows the 1H NMR spectra of benzylamine in acidic and alkaline solutions. The chemical shift of methylene of benzylamine is 4.067 ppm in acid and is 3.794 ppm in alkaline solution. The 1H NMR spectra of benzylamine and G1-Azo-CHO in different pHs are shown in Figure S5b-e. From Figure S5b and c, we can find when the solution of benzylamine and G1-Azo-CHO is acidic, the chemical shift of methylene of benzylamine is 4.067 ppm, and the peak area ratio of the proton of Ar-H to that of methylene ($–CH_2$-$NH^{3+}Cl^-$) is 1:0.18. This suggests no imine bonds are formed. When the pH is adjusted to 7.2, the peak area ratio of the proton of Ar-H to that of methylene ($–CH_2$-$NH^{3+}Cl^-$) is changed into 1:0.13 (Figure S5d). This indicates that ammonium is partially hydrolyzed to amino. In alkaline solution, the peak of methylene ($–CH_2$-$NH^{3+}Cl^-$) disappear completely and the chemical shift of methylene ($–CH_2$-NH_2) is found at 3.794 ppm (Figure S5f), suggesting that imine bonds are formed. In Figure 2b, the peak of methoxy (-O-CH_3) is moved to the high-field when the pH of the solution changes from 1.34 to 6.20. This phenomenon also is observed in the ether bond (-O-CH_2-) of the OEG group. The slight move of those chemical shifts confirms the formation of hydrogen bonds.

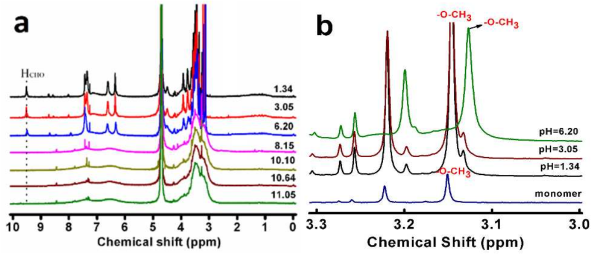


Figure 2. ^{1}H NMR spectrum of the mixture solutions with different pH values in D_2O (a); the removed chemical shifts of copolymers in acid condition compared with the monomer (b).

The self-assembly behaviors are further investigated by FT-IR analysis. In acidic condition, the peak representing aldehyde -CH=O stretch (ν = 1696 cm^{-1}) is retained and that of imine C=N stretch (ν = 1647 cm^{-1}) is not observed. However, in alkaline condition, the absence of the free aldehyde -CH=O stretch (ν = 1696 cm^{-1}) and the appearance of imine C=N stretch (ν = 1647 cm^{-1}) indicate that the aldehyde groups of G1-Azo-CHO have completely reacted with $–NH_2$ groups of the benzylamine and the self-assembly product is synthesized by dynamic convalent bonds of the aldehyde and amino (Figure S6). The similar results can be observed from the self-assembly of G1-Azo-CHO and ammonium polymer PVBAHS in different pH (Figure 3a). The appearance of imine C=N stretch (ν = 1647 cm^{-1}) also indicates the copolymers are synthesized by dynamic covalent bonds of the aldehyde and amino in alkaline solution (Figure 3a).

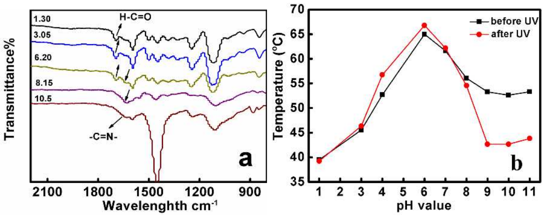


Figure 3. (a) The FT-IR absorption spectrum of copolymer in different pHs; (b) pH effect on the LCST value of the mixture solution.

To further verify the self-assembly behaviors of the hydrogen and imine bonds, the relationships of the LCST and UV irradiation in different pH are investigated. When the pH of the solution is 1.34, the LCST of the mixture is 39.2 °C (Figure 3b and Figure S7) and slightly decreases after UV irradiation. The same phenomenon is observed for the monomer G1-Azo-CHO. These indicate that no self-assembled copolymer is formed. In acidic condition, the LCSTs sharply increase from 39.2 °C to 67.0 °C with the increase of pH. This indicates that more and more ammonium groups of PVBAHS combine with H^+ ions in the solution and form hydrogen bonds with OEG-groups of G1-Azo-CHO. Compared to the LCSTs before UV irradiation, the LCSTs of the mixture increase after UV irradiation. This phenomenon is consistent with that reported by Jochum et al.[43] where the azobenzene moiety is attached to the end of the polymer and the LCST of polymer increases after UV irradiation. The above results determine that the copolymer is formed via the self-assembly of hydrogen bonding between the OEG-group in G1-Azo-CHO and the ammonium unit in the ammonium polymer PVBAHS. This conclusion agrees well with FT-IR and ^{1}H NMR results. In alkaline solution, the LCSTs of the copolymer obviously decrease after UV irradiation in different pH. This trend is consistent with our previous observation,[41] where the azobenzene group is in the middle of the polymer main-chain and OEG-group, and the LCST decreases after UV irradiation.

Combined with the results of ^{1}HNMR, FT-IR and UV irradiation experiments, we can conclude that the copolymers are synthesized through hydrogen bonds between the OEG-group of G1-Azo-CHO and the ammonium units of PVBAHS in acid, and through imine bonds of the aldehyde and amino in alkaline solution, respectively. The bond forming-breaking process is reversible and the reversible character can be used to trigger the self-assembly process by changing the pH of the solution. The mixing of the ammonium polymer PVBAHS with the stimuli-responsive monomer leads to the formation of the tri-stimuli responsive copolymers through self-assembly of hydrogen or imine bonds.

2.3 Photo-isomerization of copolymers

Azobenzene compounds exhibit a photo-isomerization behavior which undergoes a reversible conversion between the *trans* and cis-forms under the irradiation of UV and visible light. The UV-Vis absorption spectra of the copolymer $P_{0.6}$ in water solution are recorded at different time intervals of UV and Vis irradiation. The absorption spectrums are recorded after UV (Figure 4a) and Vis irradiation (Figure 4b) for different times, respectively. Furthermore, the same tests are taken on the copolymers $P_{1.0}$-$P_{0.2}$ (Figure S8a-d). In order to further investigate the *trans-cis* isomerization process, the *trans-cis* transition of azobenzene moiety is monitored with HPLC. From Figure 4c and 4d, when the solutions of the monomer

G1-Azo-CHO and copolymer $P_{1.0}$ are irradiated by UV light for 30 min, the peak of trans-isomers disappears and the peak of cis-isomers appears. Furthermore, the other copolymers ($P_{0.2}$ and $P_{0.4}$) also show the same changes in HPLC tests (Figure S9a and 9b). All results suggest that the rapid photo-isomerization of the self-assembly copolymers is reversible between the UV and visible light irradiations, showing an appealing application as light stimuli-responsive materials.

Table1. The effect of UV-light on polymers with different molar ratio of CHO/NH_2

Samples	Molar ratio of CHO/NH_2	Mw (g/mol)	Concentration (mg/mL)	LCST (°C)	
				initial	After UV
1	1:1	7.1×10^4	1.0	46.4	45.4
2	0.8:1	5.9×10^4	1.0	49.4	47.3
3	0.6:1	4.7×10^4	1.0	53.1	48.3
4	0.4:1	3.5×10^4	1.0	56.5	50.9
5	0.3:1	2.9×10^4	1.0	48.8	43.7
6	0.2:1	2.4×10^4	1.0	39.4	41.5

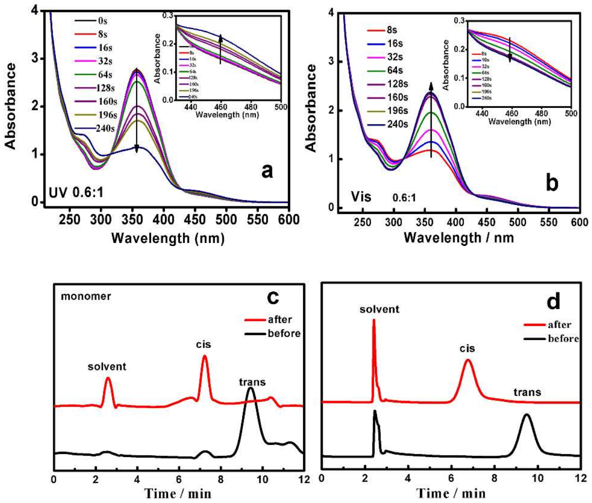


Figure 4. Absorption spectrums of the supramolecular dendronized copolymer $P_{0.6}$ of (a)UV and (b) *Vis* irradiation with different times; HPLC outflow curve of (c) monomer G1-Azo-CHO and (d)the copolymer $P_{1.0}$ solution (CH_3OH/H_2O: 80/20).

2.4 Dual thermo- and light-responsive behavior

The dendritic monomer moiety provides the polymer with thermo-responsive properties, which are dominated by OEG-based dendron units with their large sizes and shielding effect.[41] The LCST-type soluble-to-insoluble phase transition is observed in each case (Figure S2b shows the phase transition of the copolymer), and is related to the different molar ratio of CHO/NH_2. The triple relationships of LCST, UV irradiation and the molar ratio of CHO/NH_2 are summarized in Table 1. The dual thermo- and light-responsive behaviors of the copolymers in alkaline condition are investigated by UV/Vis spectroscopy. Figures 5a shows how the UV light and the molar ratio of CHO/NH_2 affect the LCSTs of the copolymers. From Figure 5, we can observe that the copolymers show a sensitive phase change before (Figure 5a) and after (Figure 5b) UV irradiate, and the change of the LCSTs has a large hill-like dependence on the molar ratio of aldehyde and amino (Figure 5c). For example, when the molar ratio is 0.2:1, the LCST is 39.4 °C. When the molar ratio is increased to 0.4:1, the highest LCST of 56.5 °C can be obtained. With the further increase of the molar ratio, however, the LCST decreases to 46.4 °C. Similar trend is observed for the LCSTs after UV irradiation. In addition, when the solutions of copolymer are exposed to UV light of 365 nm for 2 h, the LCSTs of most copolymers decrease compared to those initials, except the $P_{0.2}$. To reveal the reversible thermo-responsiveness under the light-irradiation, the solutions are subjected to a couple of UV-Vis irradiation cycles (Figure 5d). When the original solution of copolymer is irradiated by UV light, the LCST decreases, but it can recover to the initial state after irradiated by visible light for 2 h. This cycle can be repeated multiple times without macroscopic retrogression.

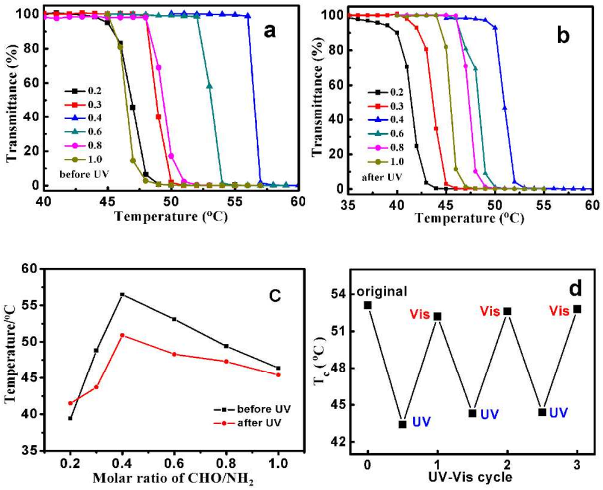


Figure 5. Temperature-dependent transmittance of different self-assembly polymer aqueous solutions (a) before and (b) after UV irradiation; (c) UV-Vis irradiation effect on polymers cloud point, before (black line) and after (red line) UV irradiation; (d) UV and *Vis* light-induced reversible change of LCST of $P_{0.6}$ in aqueous solution, the LCST were measured at 600nm;

In addition, the concentration of copolymer also plays an essential role in affecting the LCST. Figure 6 shows the temperature-dependent transmittance of aqueous solution of 5.0 mg mL^{-1} supramolecular dendronized copolymers with the molar ratio of CHO/NH_2 changing from 0.2:1 to 1:1. When the number of the monomer G1-Azo-CHO increases, the LCSTs of the supramolecular dendronized copolymers increase from 45.6 °C to 54.4 °C during the heating process (details in Figure S10 and Table S1). However, when the concentration of the copolymers is 1.0 mg mL^{-1}, the LCSTs of copolymers firstly increases then decreases with the increase of the molar ratio of CHO/NH_2.

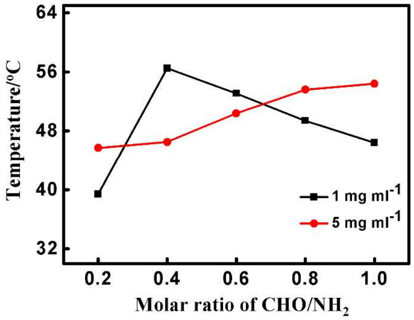


Figure 6. Thermo-responsive of self-assembly copolymers with different CHO/NH$_2$ ratio in concentration 1.0 mg mL^{-1} and 5.0 mg mL^{-1} during the heating process, respectively.

Based on all the above results, three conclusions can be obtained. Firstly, the LCST of the supramolecular dendronized copolymer is related to the number of aldehyde moiety. In a high concentration addition the LCST increases with the increased number of aldehyde, and it has an inflection point in a low concentration. Secondly, the copolymers have a shape response to the thermo-stimuli, no matter in the heating or cooling process. Thirdly, the concentration of solution has a great effect on the LCSTs of the copolymers.

To further investigate the unique change of the LCST when the concentration is 1.0 mg mL^{-1}, we prepare a serial of solutions in 1.0 mg mL^{-1} to study the light- and thermo-responsive behaviors, and examine the nanostructure of superamolecular dendronized copolymers with TEM and DLS experiments. Here, we will use three copolymers ($P_{0.2}$, $P_{0.4}$ and $P_{1.0}$) examples to illustrate the self-assembly behaviors. Figure 7 shows the nanostructures of the copolymers ($P_{0.2}$, $P_{0.4}$ and $P_{1.0}$). Before the UV-irradiation, $P_{0.2}$ are smooth cubes with the size of about 200-300 nm in diameter (Figure 7a). After UV-irradiation, it grows to 2500 nm and becomes irregular agglomerates of small domains (Figure 7d). $P_{0.4}$ has a nanowire structure with the diameter around 10 nm and the length of tens of micrometers (Figure 7b); some large cube-like blocks with size of 700 nm appear after UV irradiation for 2 h (Figure 7e). $P_{1.0}$ has a broken-cell-like structure with sizes 1500 nm (Figure 7c), and its shape become almost spherical with sizes 1000 nm after exposed to the UV-light (Figure 7f). Figure 8 shows the average size changes of those copolymers based on DLS measurements. After irradiated by UV light, the Z-average diameter of $P_{0.2}$ polymer increases from 280 to 1818 nm (Figure 8a), the diameter of $P_{0.4}$ decreases from 2156 to 1179 nm (Figure 8b), and the diameter of $P_{1.0}$ decreases from 1553 to 1046 nm (Figure 8c). At the same time, the LCST of each copolymers aqueous solution also changes as the size of copolymer changes. After irradiated under UV-light (365 nm) for 2h, the LCST of P0.2 increases from 39.4 to 41.4 °C (ΔT = 2 °C) because of the increase of the diameter size. When $P_{0.4}$ and $P_{1.0}$ are exposed to UV light, the Z-average diameter both decrease, causing the decrease of the LCST. It is likely that the nanostructural changes of the copolymer have a great influence on its LCST. These results match well the LCST results. The observation of the LCST affected by size change is consistent with our previous research.[41]

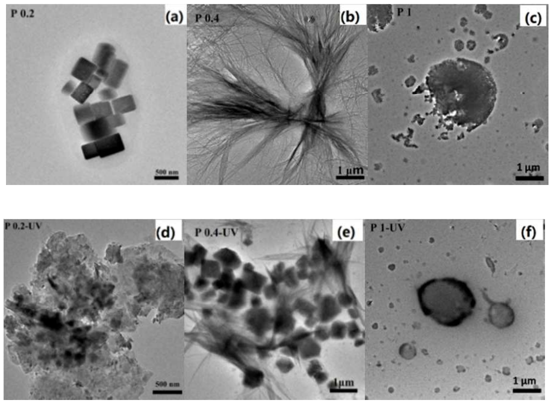


Figure 7. TEM images of the polymer $P_{0.2}$, $P_{0.4}$, $P_{1.0}$ micelle solution (1 mg mL^{-1}) at 60^{o}C before and after UV irradiation for 2h (a, b, c are represent $P_{0.2}$, $P_{0.4}$, $P_{1.0}$ in original state, respectively; d, e, f are represent $P_{0.2}$, $P_{0.4}$, $P_{1.0}$ after UV-irradiation for 2h, respectively).

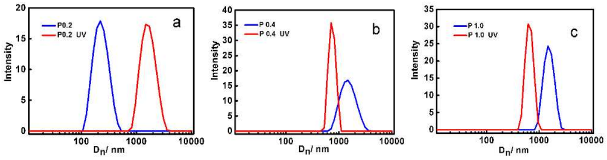


Figure 8. Z-average diameter of $P_{0.2}$, $P_{0.4}$, $P_{1.0}$ in original and after UV irradiation, respectively (plot (a) is $P_{0.2}$, plot (b) is $P_{0.4}$, plot (c) is $P_{1.0}$).

Experimental

3.1 Materials

4-(4'-hydroxy)-azobenzene and 3,4,5-tris (2- (2- (2-methoxyethoxy) ethoxy) ethoxy) benzyl chloride were synthesized by our lab. Pyridinium chlorochromate (PCC) (>98%) and hydrazine monohydrate (98%) were purchased from Aladdin. 2,2′-Dimethyl-2,2′-azodipropionitrile (AIBN, >99%, Tianjin Chemical Company, China) was recrystallized from ethanol. 4-vinylbenzyl chloride (>90%) was purchased from Sigma-Aldrich. Diethyl ether (99.5%) was purchased from Tansoole. Other chemical reagents were commercially available. Deionized water was obtained from a reagent water system (Aquapro) with a specific resistivity of 18.25 MΩ cm^{-1}.

3.2 Methods

The NMR measurements were performed on a Bruker ARX400 MHz spectrometer. The chemical structures were analyzed by Fourier transform infrared spectroscopy (FT-IR, Vector-22, Switzerland) in the range of 400–4000 cm^{-1}.The apparent number-average Mn was measured on a Gel Permeation Chromatography (GPC) (PL-GPC120) instrument. Cloud point temperature (Tc) was measured on a Shimadzu UV-2600 equipped with a temperature controller (+0.1 °C) at 600 nm with the rate of 1 °C min^{-1} during the heating/cooling test. The photo-isomerization of azobenzene was obtained with a 365 nm UV LED (FUWO, FUV-6BK, 160 mW cm^{-2}) or a 470 nm Vis LED (FUWO, F7B-B20, 160 mW cm^{-2}). The *cis –trans* isomerism was investigated with HPLC, Agilent C18 was used as the analytical column; the detection wavelength was set as 356 nm; the mobile phase was CH_3OH/H_2O (20:80, v/v), and the flow rate was 1.0 mL min^{-1}.

DLS test was carried on a Malvern Zetasizer Nano ZS equipped with a 4 mW He-Ne laser (633nm) to obtain the Z-average size (apparent average hydrodynamic diameter, Rh) and PDI. The microstructure was observed using a Tencial 2.0 TEM operating at 200 kV. The concentration of the samples for DLS and TEM measurement was set at 1.0 mg mL^{-1} except those specified.

3.3 Synthesis of monomer G1-Azo-CHO and polymer PVBAHS

3.3.1 4-(4′-(3,4,5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzylalcohol (G1-Azo-CH_2OH). The synthesis route of 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl chloride was referred to an article.[41] A mixture of 3, 4, 5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyl chloride (19.00g, 31mmol), 4-((4′-hydroxy) phenylazo) benzyl alcohol (6.84g, 30mmol), KI (0.5g), and K_2CO_3 (8.28g, 60mmol) in dry acetone (200mL) was stirred at 65 °C for 24h. After removal of acetone in vacuo, the crude product was subsequently purified by flash column chromatography using ethyl acetate as the eluent. The resulting purified product was an orange liquid (18.40 g), yield: 76.2%. ^1H NMR (δ, ppm, $CDCl_3$): 7.95-7.85 (m, 4H, Ar-H); 7.51-7.49 (m, 2H, Ar-H); 7.09-7.07 (m, 2H, Ar-H); 6.69 (s, 2H, Ar-H); 5.03 (s, 2H, $ArCH_2O$-); 4.78 (s, 2H, $ArCH_2OH$-); 4.18-4.16 (t, 6H, -OCH_2-); 3.87-3.79 (t, 6H, -OCH_2-); 3.73-3.71 (t, 6H, -OCH_2-); 3.66-3.64 (t, 12H, -OCH_2-); 3.55-3.53 (t, 6H, -OCH_2-); 3.37 (s, 9H, -OCH_3).

3.3.2 4-(4'-(3,4,5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzaldehyde (G1-Azo-CHO). PCC (0.957g, 0.0045mol) was stirred in 40 mL followed by adding the solution of 4-(4'-(3,4,5-tris (2-(2-(2-methoxyethoxy) ethoxy) ethoxy) benzyloxy) phenylazo) benzalcohol (G1-Azo-CH_2OH) (2.3g, 0.0028mol) in CH_2Cl_2 (10mL). Then the reaction was stirred at room temperature for 10h. The reaction was monitored by thin-layer chromatography (TLC) using pet. Ethyl acetate was the mobile phase. The mixture was evaporated to remove CH_2Cl_2. The crude product was purified through column chromatography with ethyl acetate to give G1-Azo-CHO (1.7g, 74.2%). ^1H NMR 400 MHz (δ, ppm, D_2O):δ9.48 (s, H, Ar-CHO), 7.38-7.30 (m, 2H, Ar-H), 7.28 (s, 2H, Ar-H), 6.56 (s, 2H, Ar-H), 6.34 (s, 2H, Ar-H), 4.68-4.67 (m, 2H, Ar-H), 4.45-4.26 (m, 2H, Ar-H), 3.90-3.78 (t, 6H, -OCH_2-), 3.62-3.55 (t, 6H, -OCH_2-), 3.50-3.49 (t, 6H, -OCH_2-), 3.45-3.43 (t, 6H, -OCH_2-), 3.36-3.26(t, 6H, -OCH_2-), 3.22-3.18 (t, 6H, -OCH_2-), 3.15 (s, 9H, -OCH_3).^{13}C NMR 101 MHz (δ, ppm, D_2O): δ192.12 (Ar-CHO), 161.57, 146.21, 125.15, 125.15, 114.79, 114.79 (-N=N-Ar-OR), 154.89, 142.61, 131.65, 130.31, 122.63, 122.63 (-Ar-N=N-), 152.28, 152.28, 136.46, 108.84, 106.19, 136.78 (-R-Ar-$_3$OR), 72.18(Ar-CH_2-O-Ar-), 57.98 (-OCH_3), 71.09, 70.97, 70.18, 69.81, 69.71, 69.58 (-OCH_2-).

3.3.3 N-(4-Vinylpheny) phthalimide. Potassium phthalimide (30.6g, 0.166mol) was added to dry DMF (25mL) and stirred at room temperature for 1.5 h, the DMF (10mL) solution of 4-vinylbenzyl chloride (20g, 0.131mol) was added drop by drop. After the reaction was completed, the solvent was poured in ice water, the crude solid was precipitated, then crystallized from methanol for three time, and the white flakes were obtained (25.69g, 74.46%). ^1H NMR (δ, ppm, $CDCl_3$): 7.84 (dd, 2H, Ar-H), 7.71 (dd, 2H, Ar-H), 7.43 – 7.30 (m, 4H, Ar-H), 6.67 (dd, 1H, ArCH=), 5.71 (dd, 1H, ArCH=CH-), 5.22 (dd, 1H, ArCH=CH-), 4.83 (s, 2H, $ArCH_2$-).

3.3.4 4-vinylbenzylamine (4-VBA). N-(4-vinylpheny) phthalimide (10.0g, 0.038mol) was dissolved in ethanol (50mL) and treated with a solution of hydrazine hydrate (2.85g, 0.057mol) in ethanol (5mL), and the mixture were stirred for 4h up to the disappearance of phthalimide (TLC, eluent CH_2Cl_2). After the removal of the solvent at reduced pressure, the solid residue was taken with chloroform (50mL) and treated with 20% NaOH (50mL). The aqueous was separated, extracted with chloroform (3×50mL) and the extracts combined and dried over Na_2SO_4. Then the removal the chloroform gave the free bases 4-VBAHS (4.8g, 95%).

3.3.5 4-vinylbenzylamine hydrochloride (4-VBAHS). A solution of 4-VBA (4.8g) in dry diethyl ether (100mL) was stirred at room temperature with dry gaseous hydrochloric acid. The white precipitate was filtered, washed with fresh ether, dried and crystallized to produce the hydrochlide derivative (4.2g, 70%).^1H NMR (δ, ppm, D_2O): 7.42-7.35 (m, 2H, Ar-H); 7.30-7.14 (m, 2H, Ar-H); 6.63 (dd, 1H, ArCH=); 5.71 (dd, 1H, ArCH=CH-), 5.18 (dd, 1H, ArCH=CH-), 3.99 (s, 2H, $ArCH_2$-).

3.3.6 Polymerization (PVBAHS). The monomer 4-VBAHS (2.000g), initiator of AIBN (0.0973g) and solvent were introduced in the desired ratios under nitrogen in a clear flask and magnetically stirred. After a suitable period the mixture was poured into acetone and the polymer was filtered, submitted to three dissolution/precipitation cycles with methanol/acetone and vacuum-dried. The poly-(4-VBAHS) were obtained (0.6302g, 31.6%). ^1H NMR 400 MHz (δ, ppm, D2O): 7.43-6.90 (m, 2H, Ar-H), 6.90-6.60 (m, 2H, Ar-H), 4.13-4.03 (m, 2H, $ArCH_2$-), 1.80-1.20 (m, 3H, -CH_2CH-).

3.3.7 Self-assembly experiment. To prepare the self-assembly dendronized copolymers, the aqueous solutions of G1-Azo-CHO and PVBAHS are mixed at the desired ratio. The copolymers with different molar ratio of aldehyde/amino are named as $P_{1.0}$, $P_{0.8}$, $P_{0.6}$, $P_{0.4}$, $P_{0.3}$ and $P_{0.2}$, respectively (Table S1). All copolymers were synthesized at the same condition. After the self-assembly, the thermo-, light-and pH-responsive properties were investigated by UV-Vis, ^1H NMR, FT-IR and HPLC.

Conclusions

In summary, pH, temperature and light tri-stimuli responsive supramolecular dendronized copolymers have been successfully synthesized by self-assembly through hydrogen or imine bonds. The supramolecular dendronized copolymers are fabricated by changing the molar ratio of amino and aldehyde. In normal case, the LCSTs of the copolymers increase with the increased number of OEG groups. However, the LCSTs of the supramolecular dendronized copolymers in different pHs have an inflection point that is caused by two different self-assembly behaviors. Hydrogen bonds are formed in acidic solution and imine bonds are formed in alkaline solution. Besides pH, the concentration and the nanostructure of copolymers are essential for the changes of LCST. The copolymer $P_{0.2}$ appears as smooth cubes with the diameter size around 280 nm which increases to 1820 nm after the UV irradiation, resulting in the increase of the LCST of the copolymer $P_{0.2}$. When $P_{0.4}$ and $P_{1.0}$ are exposed to the UV light, the Z-average diameters both decrease, causing the decrease of the LCST. As multi-stimuli-responsive polymers have a great potential for future applications, and are mainly synthesized via RAFT or other complicated polymerization, our finding demonstrates a facile way to fabricate stimuli-responsive polymers and therefore may display a bright future.

Conflicts of interest

There are no conflicts to declare.

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