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Journal Name

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Photocontrollable Volume Phase Transition of Azobenzene Functionalized Microgel and Its Supramolecular Complex

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A novel photo-responsive microgel (Azo-MG) was successfully prepared by grafting azobenzene moieties onto poly(N-isopropylacrylamide-*co*-acrylic acid) microgel. Azo-MG can form supramolecular complex with α-cyclodextrin (α-CD) through the host-guest interactions between azobenzene pendant groups and α-CD. Both Azo-MG and its supramolecular complex exhibit photocontrollable shifting of volume phase transition temperature (VPTT). After UV irradiation, Azo-MG exhibited an increased VPTT, however, the supramolecular complex (Azo-MG with α-CD) exhibited a decreased VPTT. Near VPTT, the size of Azo-MG and its supramolecular complex can be regulated reversibly with UV and visible light. The as-prepared microgel has great potential as building blocks in the designing of photo-responsive materials.

Introduction

Microgels are solvent containing, cross-linked polymeric colloidal particles. Under external stimuli, the balance between the inside and outside osmotic pressures of the microgel is disrupted and the microgel could swell or contract.[1,2,3] This volume phase transition (VPT) behavior manifests the microgel a useful model system in exploring the physics of soft condensed matter,[4] and also an important building block of smart soft materials, such as drug carriers,[5] sensors,[6,7] catalysts,[8] viscosity modifiers[9] and particular emulsifiers.[10] Among various stimuli, light irradiation is a trigger that can be quickly switched, remotely controlled and focused into specific areas. Therefore, photocontrollable microgels have drawn much attention in recent years but remain a challenge because of the difficulty to functionalize microgel with photo-responsive groups. A few references about photocontrollable microgels have been reported by the incorporation of photothermic nanoparticles,[11] photochromic dyes,[12-18] or photoreactive crosslinkers.[19]

It is well known that azobenzene moiety undergoes *cis*–*trans* isomerization on alternating irradiation with UV and visible light.[20] The isomerization is accompanied by a change in the dipole moment and thus the polarity, causing the light-tunable hydrophilicity of azobenzene-grafted polymers.[21-23] Moreover, *trans*-azobenzene is compatible with α-cyclodextrin (α-CD) while *cis*-azobenzene is not,[24] so the host-guest interaction between α-CD and azobenzene can function as an optical switch in and polymer assemblies.[25, 26] Azobenzene-containing silica gel glass,[27, 28] organogels,[29, 30] hydrogels[31-34] and supramolecular gels[35-37] were successfully prepared. Taking advantage of the photocontrollable isomerization and host-guest interactions, these gels have function such as optical limiting, self-healing, optical actuating, molecular recognition and sol-gel transition. Comparing with their macro-sized counterpart, azobenzene-containing microgels exhibit the merit of fast responsiveness and the ability of assembling into higher order structure. These microgels can contract/swell under light stimuli due to the adsorption/desorption of the azobenzene-containing surfactant[13-17] or the dipole change of the azobenzene-containing cross-linker.[18] Interesting applications such as optical devices based on azobenzene-containing microgels were developed.[18] However, to the best of our knowledge, it remain questions that whether α-CD could form supramolecular complex with azobenzene functionalized microgels and how the volume phase transition of the supramolecular complex is affected by light stimuli.

In this report, a novel photo-responsive microgel with pendant azobenzene moieties was successfully fabricated. The volume phase transition temperature (VPTT) and the size of the azobenzene functionalized microgel (Azo-MG) and its supramolecular complex can be manipulated with light stimulus, which render the material promising candidate for designing various smart devices.

Results and discussion

The synthetic route of Azo-MG is shown in Scheme 1. Firstly, poly(*N*-isopropylacrylamide -*co*-acrylic acid) microgel (AAc-MG) was obtained from copolymerizing of *N*-isopropylacrylamide (NIPAm), acrylic acid (AAc) and *N,N'*-methylenebisacrylamide (BIS), and content of AAc 9.1 mol% according to acid-base titration.[38] Then, Azo-MG was prepared by grafting 4-aminoazobenzene onto the microgel in the

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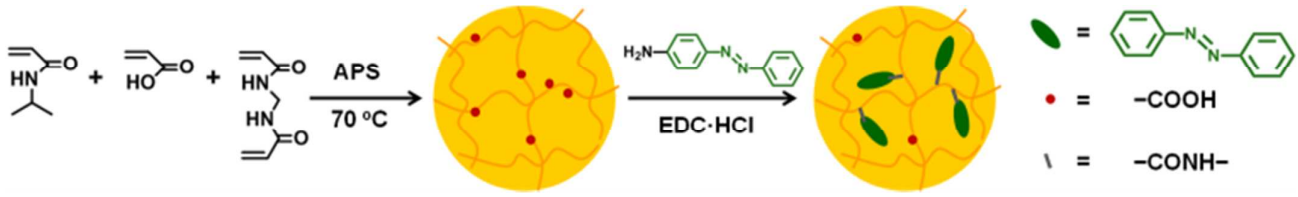
Electronic Supplementary Information (ESI) available: UV-Vis spectrum of Azo-MG with different irradiating time. See DOI: 10.1039/x0xx00000x

presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride



Scheme 1 The synthetic route of Azo-MG.

(EDC·HCl). As shown in Fig. 1, the AAc-MG displays a strong amide I band (C=O stretching) at 1641 cm^{-1}, a strong amide II band at 1548 cm^{-1}, and a weak amide III band at 1264 cm^{-1}.[32] The doublet at 1387 and 1362 cm^{-1}, are characteristic bands of the isopropyl groups in the NIPAM units. The peak at 1715 cm^{-1} is assigned to the stretching of the undissociated carboxylic group of the AAc units. After the reaction, this peak is weakened, as denoted by the dotted line. Meanwhile, a new shoulder peak at 1427 cm^{-1} appears, assigning to C-C stretching in the phenyl rings. The FTIR results suggest that 4-aminoazobenzene groups are successfully introduced via EDC coupling. ^{1}HNMR spectra of the AAc-MG and Azo-MG are shown in Fig. 2. After the reaction, new peaks appear from appear from 7.4 – 7.9 ppm, corresponding to the phenyl protons of the azobenzene moities.[39] The ^{1}HNMR results confirm the incorporation of the azobenzene moieties onto the microgel. On the basis of acid-base titration, the contents of unreacted AAc and pedant azobenzene are determined to be 3.3 mol% and 5.8 mol%, respectively. Therefore, the resulted Azo-MG microgel contains temperature-responsive PNIPAm chain segments, pH-responsive AAc groups, and light-responsive azobenzene moieties.

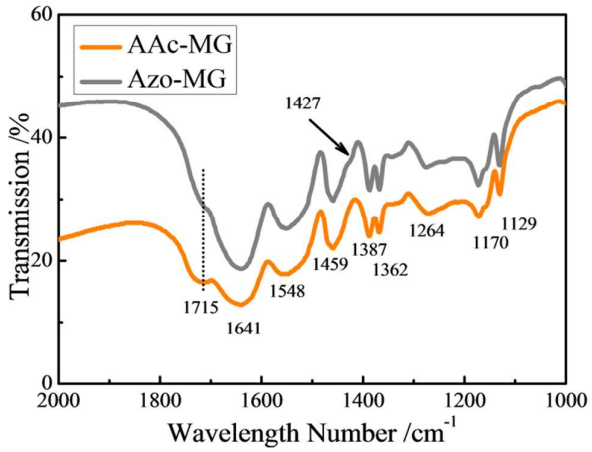


Fig.1 FTIR spectra of AAc-MG and Azo-MG.

UV-vis spectroscopy was applied to investigate the photoisomerization of azobenzene moieties on the Azo-MG and its supramolecular complex with α-CD. As shown in Fig. 3a, after irradiation with UV light (λ = 360 nm), the absorbance at 349 nm decreases remarkably and another peak at 433 nm appears, which are ascribed to π-π* and n-π* transitions, respectively.[32] The change of the spectrum indicates the isomerization of azobenzene moieties from *trans*- to *cis*- state. After irradiation with visible light (λ = 450 nm), the peak at 349 nm arises and the peak at 433 nm disappears, suggesting that the photoisomerization of azobenzene moieties is reversible. Both the *trans*- to *cis*- and the *cis*- to *trans*- isomerization can be finished within 1 min (Fig. S1). In addition, the photoisomerization of azobenzene moieties on the supramolecular complexes of Azo-MG was also investigated. As shown in Fig. 3b, a red shift of π-π* absorbance band from 349 nm to 356 nm is observed in the presence of α-CD, which implies that host-guest complexes are formed between α-CD and trans-azobenzene.[41] It is worth to note that the n-π* absorbance band is not affected by the addition of α-CD, indicating the weak association between α-CD and cis-azobenzene.[42]

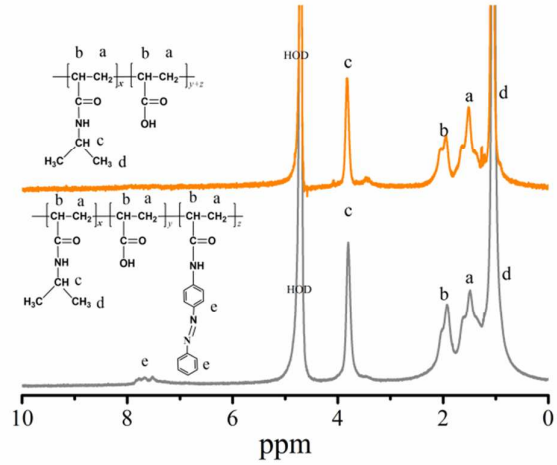


Fig. 2 ^{1}HNMR spectra of AAc-MG and Azo-MG in D_2O.

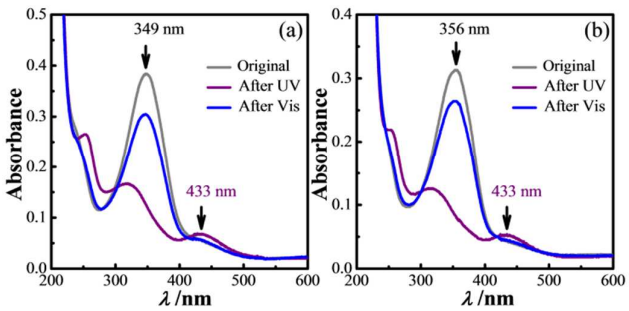


Fig. 3 UV-Vis spectra of Azo-MG (3.3 mol% AAc and 5.8 mol% Azo) in the absence (a) and presence (b) of α-CD (5.0 mM).

NOESY spectra were carried out to investigate how the Azo-MG interacts with α-CD. As denoted by the squares in Fig. 4a, the NOESY spectrum for the mixture of Azo-MG and α-CD before UV irradiation shows correlation peaks between inner protons in the α-CD cavities and protons on the phenyl rings of azobenzene moieties.[39] After UV irradiation, the correlations peaks becomes very weak (Fig. 4b), indicating the disassociation of host-guest complex formed by α-CD with the pendant azobenzene moieties.

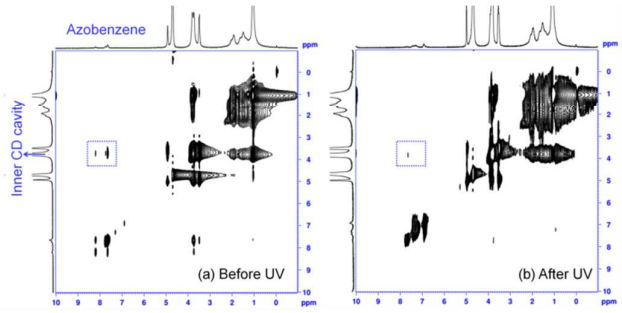


Fig.4 2D-NOESY spectra of the supramolecular complex of Azo-MG and α-CD before and after UV-irridiation.

The influences of functionalization of azobenzene and the photoisomerization on the VPT of Azo-MG and its complex with α-CD were studied by dynamic light scattering (DLS). Since Azo-MG is triple-responsive, the DLS measurements were performed at different pH, different photo-history and varying temperature. The size of AAc-MG was also measured as the comparison. A single peak of hydrodynamic radius (R_h) distribution function (Fig. 5a) and a single relaxation mode (Fig. S2) of scattering intensity autocorrelation function are observed, indicating the absence of microgel aggregating. As shown in Fig. 5a, in deionized water (pH 6.0), the R_h peak of AAc-MG is about 295 nm while the R_h peak of Azo-MG and its supramolecular complex are about 240 nm. As shown in Fig. 5b, with temperature increasing from 20°C to 50°C, the averaged hydrodynamic radius (<R_h>) of AAc-MG decreases from 295 nm to 240 nm while the <R_h> of Azo-MG decreases from 260 nm to 200 nm. After the functionalization of azobenzene, the content of ionic AAc moieties is reduced and the content of hydrophobic azobenzene groups is increased, which is evidenced by the ζ potential measurements (Table 1). Therefore, the <R_h> of Azo-MG is smaller than that of AAc-MG. Moreover, due to the random distribution of AAc moieties in the microgel and the low ionic strength of the solvent, the lower critical solution temperature (LCST) of each subchain of the microgel is polydispersed, resulting the smooth VPT of both AAc-MG and Azo-MG.[43] As shown in Fig. 5b, there is no significant difference in VPT curves before and after the UV irradiation whether in the presence or the absence of α-CD. The insensitivity to light stimuli of Azo-MG and its supramolecular complex is possibly due to the ionization of AAc groups. At pH 6.0, the microgel is highly charged (Table 1) and the Coulomb force drive the microgel to swell even at high temperature,[44] so the hydrophilicity change induced by the photoisomerization of azobenzene and association with α-CD is negligible. Therefore, the irradiation of UV and the addition of α-CD do not affect the size of the Azo-MG.

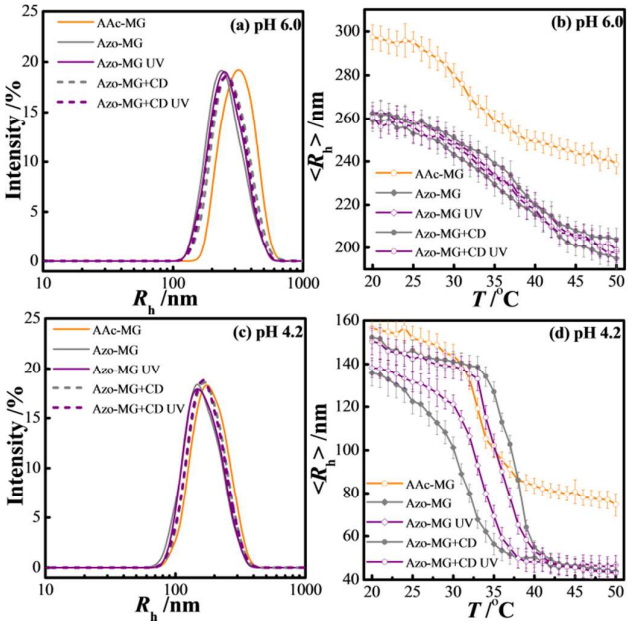


Fig.5 R_h distribution functions and temperature dependence of <R_h> of AAc-MG (9.1 mol% AAc) and Azo-MG (3.3 mol% AAc and 5.8 mol% Azo) before and after UV radiation in the absence and presence (5.0 mM) of α-CD at pH = 6.0 or 4.2. Error bars are generated by 3 repeating measurement. (Attention: the four VPT curves of Azo-MG and its supramolecular complex in Fig. 3b almost overlap each other, indicating the insensitivity to light stimuli)

Table 1 ζ potential (mV) of AAc-MG and Azo-MG at different pH.[a]

	pH 6.0	pH 4.2
AAc-MG	-40.2±2.9	-6.5±1.5
Azo-MG	-23.9±1.2	-1.6±0.1

a. 9.1 mol% AAc for AAc-MG, and 3.3 mol% AAc and 5.8 mol% azobenene for Azo-MG.

What occurs if the charge of AAc-MG and Azo-MG is neutralized? As shown in Fig. 5c, at pH 4.2, AAc-MG, Azo-MG and its supramolecular complex exhibit R_h peak at about 140nm, smaller than those at pH 6.0. Also faster relaxation time can be seen from scattering intensity autocorrelation function at pH 4.2. These facts indicate pH sensitivity of the microgels. However, light responsiveness is not observed. As shown in Fig. 5d, with temperature increases from 20°C to 50°C, the <R_h> of the AAc-MG decreases from 160 nm to 75 nm, while the <R_h> of the Azo-MG decreases from 140 nm to 50 nm. The deswelling ratio (<R_h(20°C)>/ <R_h(50°C)>) at pH 4.2 is larger than that of pH 6.0, as a result of the neutralization of the ionic acrylic acid groups. The irradiation of of UV and the addition of α-CD do not influence the size of the microgel significantly at low temperature (<30°C) or high temperature (>40°C), suggesting that the change of hydrophilicity induced by the photoisomerization of azobenzene and association with

α-CD is covered by some other effect. At low temperature, the hydration of PNIPAm segments dominate the swelling of the microgel. While at high temperature, it is the intra-molecular hydrogen bonds and hydrophobic force drive the mirogel to contract.[10] However, the volume phase transition temperature (VPTT, the temperature at which the $<R_h>$ decreases fastest) shifts with the irradiation of UV and the addition of α-CD (Scheme 2). It is 32°C and 33°C for dark-adapted Azo-MG and UV-irradiated Azo-MG in the absence of α-CD, and 37°C and 35°C for dark-adapted Azo-MG and UV-irradiated Azo-MG in the presence of α-CD (5.0 mM), respectively. It is reported that azobenzene functionalized polymers have similar variation tendency of LCST,[32, 45] indicating the shifting of VPTT of Azo-MG may be caused by change of the LCST of its subchains. When α-CD is absent, the *trans*- to *cis*- photoisomerization leads to an increase in the polarity of the subchains and hence delays the VPTT of the Azo-MG. When α-CD is present, the hydrophobic *trans*-azobenzene moieties are included into the hydrophobic cavity of α-CD and the hydrophilic exterior of α-CD enhanced the hydrophilicity of the microgel, so the VPTT is elevated to 37°C. When the supramolecular complex of Azo-MG and α-CD is irradiated by UV, α-CD is disassociated and the VPTT is reduced to 35°C.

The thermal responsiveness of the Azo-MG can be regulated by tuning the azobenzene content or α-CD concentration. Azo-MG with different azobenzene content was prepared, and their VPTT in different α-CD concentration was measured. As shown in Table 2, Azo-MG1, which has a low AAc content, precipitates after grafting azobenzene, which implies that a certain amount of residual AAc groups is necessary to stabilize the microgel. At the same concentration of α-CD, Azo-MG3 shows lower VPTT than Azo-MG2, as a result of the higher content of hydrophobic azobenzene moieties. Both Azo-MG2 and Azo-MG3 exhibits higher VPTT with increasing α-CD concentration and lower VPTT after UV irradiation. These facts are consequences of the dynamic equilibrium of host-guest interaction. With higher α-CD content, more azobenzene moieties are included into the cavity of α-CD, resulting better hydrophilicity and higher VPTT. After UV irradiation, more azobenzene moieties are in the *cis*-state that cannot associate with α-CD, leading to the decrease of VPTT.

Table 2. VPTT of Azo-MG and its suparmolecular complex[a]

	Content (mol%)		[α-CD]	VPTT (°C)	
	AAc	Azo	(mM)	Original	After UV
Azo-MG1	0.5	3.6	Precipitated		
Azo-MG2	3.3	5.8	0	32	33
			1.0	34	33
			5.0	37	35
Azo-MG3	4.3	7.8	0	29	30
			5.0	34	32

a. Measured at pH 4.2.

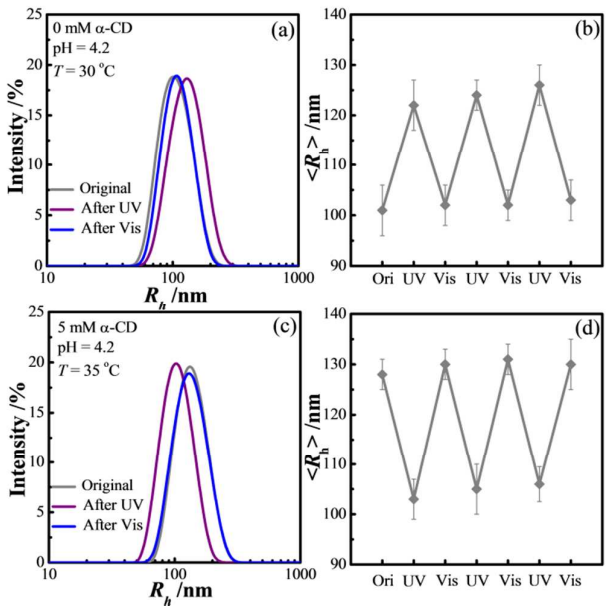
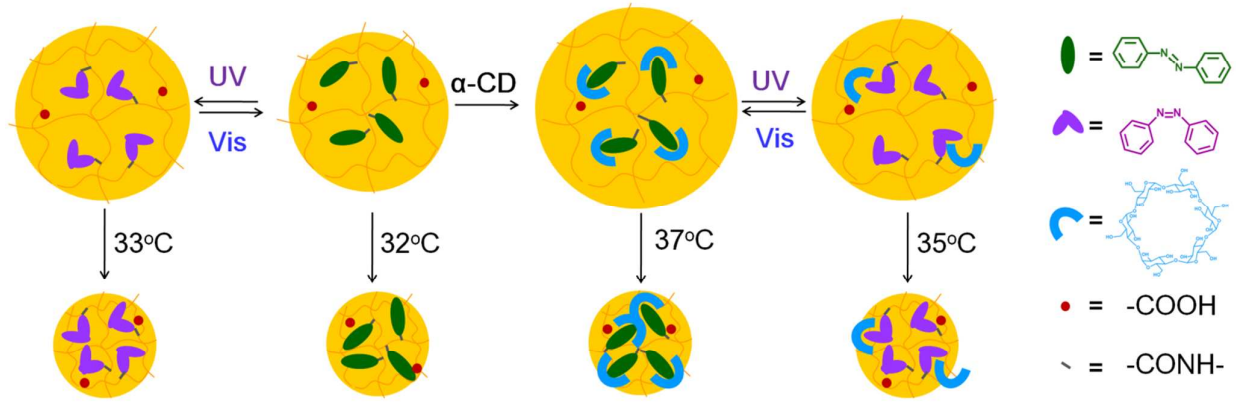


Fig. 6 Distribution of R_h (a and c) and reversibility (b and d) of the photocontrollable swelling/deswelling of Azo-MG (3.3 mol% AAc and 5.8 mol% Azo): (a) (b) pH = 4.2, T = 30°C and in the absence of α-CD, (c)(d) at pH = 4.2, T = 35°C and in the presence of 5.0 mM α-CD. Error bars are generated by 3 repeating measurement.



Scheme 2 Schematic illustration on the photocontrolled VPTT of Azo-MG and its supramolecular complex with α-CD.

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Near the VPTT, there is a temperature "window" to manipulate the size of the Azo-MG and its supramolecular complex with light. As shown in Fig. 6a, at pH = 4.2, T = 30 °C and in the absence of α-CD, the $\langle R_h \rangle$ of the Azo-MG increases from 102±5 nm to 122±5 nm after UV irradiation, while decreases *vice versa* after visible light irradiation, and the reversible size change can be repeated for at least 3 times (Fig. 6b). Moreover, at pH = 4.2, T = 35°C and in the presence of α-CD, the $\langle R_h \rangle$ of the complex of Azo-MG and α-CD decreases from 127±5 nm to 103±4 nm after UV irradiation (Fig. 6c), while increases *vice versa* after visible light irradiation, and the size change is also reversible (Fig. 6d). The change of the R_h is corresponding to the shifting of relaxation curves of scattering intensity autocorrelation function. At temperature around VPTT, the driving forces of swelling (the hydration of the PNIPAm segments) and shrinking (the intra-molecular hydrogen bonds and the hydrophobic interactions) are assumed to have equivalent strength, and the hydrophilicity change caused by photoisomeration of azobenzene moieties and association with α-CD become significant. Therefore, the photocontrollable size-manipulation can be achieved at temperature near the VPTT.

Conclusions

In conclusion, azobenzene functionalized microgel with photo-responsive azobenzene pendant moieties, temperature-responsive PNIPAM chain segments and pH-responsive acrylic acid groups were successfully prepared. In comparison with other reported light-responsive microgel, the Azo-MG shows two unique properties. Firstly, the light-responsiveness can be switched to on or off with pH and temperature, and also be tuned with azobenzene content or α-CD concentration. Secondly, the Azo-MG and its supramolecular complex have contrary change of particle size under the stimuli of UV or visible light. These properties render the Azo-MG an promising candidate in the intelligent materials based on photo-responsive microgel, such as drug delivery, catalyst carriers, and optical devices.

Experimental section

Materials. *N,N'*-methylenebis (acrylamide) (BIS), acrylic acid (AAc), ammonium persulfate (APS), acetic acid (HAc) and alpha cyclodextrin (α-CD) were purchased from Aladdin. *N*-Isopropylacrylamide (NIPAM), *N*-(3-dimethylaminopropyl)-*N'*-ethyl-carbodiimide hydrochloride (EDC·HCl) and 4-aminoazobenzene were obtained from TCI. Sodium dodecylsulfate (SDS), sodium acetate (NaAc) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent co., Ltd. NIPAM was purified by recrystallization from hexane and dried in vacuum. AAc was distilled under reduced pressure.

Synthesis of AAc-MG. The P(NIPAM-co-AAc) microgel (AAc-MG) was synthesized by free radical precipitation polymerization.[46] Briefly, 1.400 g of NIPAM, 0.100g of AAc, 0.033 g of BIS, and 0.057 g of SDS were dissolved in 100 mL of water. The solution was filtered to remove any possible precipitates. Then the reaction mixture was transferred to a three-necked round-bottom flask equipped with a condenser and a nitrogen inlet and heated to 70 °C under a gentle stream of nitrogen. After 1 h, 5.0 mL of 0.06 M APS solution was added to initiate the reaction. The reaction was allowed to proceed for 5 h. The resultant pink-blue dispersion was purified by dialysis (cutoff 3500) against water with frequent water change for at least one week. The solid content of AAc-MG dispersion is 11 mg/mL. The AAc content is 9.1 mol% according to the acid-base titration. Microgels with AAc content of 4.1 mol% and 12.1 mol% were synthesized using same procedure but different feeding amounts of AAc (0.050g and 0.150g, respectively).

Synthesis of Azo-MG. 0.164 g 4-aminoazobenzene was dissolved in 20 mL of the hot aqueous solution of α-CD (35mM). After cooling to room temperature, 20 mL of AAc-MG dispersion (AAc content = 9.1 mol%) were mixed with the 4-aminoazobenzene solution. The mixture was kept in darkness and stirred for 12 h. Then 0.107g of EDC·HCl was added. The mixture was kept under darkness and stirred for another 48 h. The resultant dark-green dispersion was purified by dialysis (cutoff 3500) against deionized water with frequent water change for two weeks to remove α-CD and residual reactants. The resulted Azo-MG is denoted as Azo-MG2 (Table 2). Azo-MG1 and Azo-MG3 were synthesized following same procedure but different amounts of reactants. As for Azo-MG1, microgel of 4.1 mol% AAc content, 0.073 g 4-aminoazobenzene and 0.047 g EDC·HCl were used. As for Azo-MG3, microgel of 12.1 mol% AAc content, 0.221g 4-aminoazobenzene and 0.141g EDC·HCl were used. The content of azobenzene and unreacted AAc and was determined by acid-base titration.

Complex of Azo-MG and α-CD. 0.049 g of α-CD was dissolved in 10 mL of deionized water (pH 6.0) or HAc-NaAc buffer (20mM, pH 4.2), respectively. Then 0.10 mL of Azo-MG dispersion was added to the two solutions, respectively. All the solutions were stirred in darkness for 48 h.

Methods. The AAc contents in the AAc-MG and Azo-MG were determined by acid-base titration using 10 mM NaOH aqueous solution and 10 mM HCl aqueous solution as the standard

solutions, and phenothalin and methyl orange as the indicators. FTIR spectra were measured with a NICOLET 6700 Infrared Spectroscopy, using KBr as the sample holder. Samples used for the UV-vis spectroscopy and DLS measurement were kept in darkness for 48 h as the dark-adapted sample. UV-irradiation (365 nm, 500 mW/cm^2) and visible light-irradiation (450 nm, 500 mW/cm^2) were conducted with LED pointolites (Shanghai Uvata). UV-Vis spectra were measured by a TU-1901 spectrophotometer. The NMR spectra were recorded in D_2O at room temperature on a Bruker AVANCE III 400 MHz NMR spectrometer. Dynamic light scattering measurements were performed with a Zetasizer Nano ZS90 (Malvern Instruments Ltd.), with scattering angle at 90^o and wavelength at 633 nm. The temperature dependence of size was collected after equilibrating at each temperature for 5 min. Before measurements, solutions were filtered with syringe filters.

Acknowledgments

Funding from the Natural Science Foundation of Zhejiang Province (LQ14E030002), Natural Science Foundation of Ningbo (2015A610020), K. C. Wong Magna Fund in Ningbo University and Ningbo Key Laboratory of Specialty Polymers (2014A22001) are gratefully acknowledged.

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