Temperature/Light Dual-Responsive Inclusion Complexes of α-Cyclodextrins and Azobenzene-Containing Polymers

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Three kinds of photoresponsive copolymers with azobenzene side chains were synthesized by radical polymerization of N-4-phenylazophenylacrylamide (PAPA) with N-isopropylacrylamide (NIPAM), N,N-diethylacrylamide (DEAM) or N,N-dimethylacrylamide (DMAM) respectively. Their structures were characterized by FT-IR, ^{1}H-NMR and UV/Vis spectroscopy. Their reversible photoresponses were studied with or without α-cyclodextrin (α-CD), which showed that both the copolymers and their inclusion complexes with α-CD underwent rapid photoisomerization. The lower critical solution temperature (LCST) of the copolymers and their inclusion complexes with α-CD were investigated by cloud point measurement, which showed that the LCST of three kinds of copolymers increased largely after adding α-CD. After UV irradiation on the solutions of copolymers and their inclusion complexes, the LCST of the copolymers increased slightly with the absence of α-CD, while decreased largely with the presence of α-CD. Furthermore, the LCST reverted to its originality after visible light irradiation. This change of LCST could be reversibly controlled by UV and visible light irradiation alternately. In particular, in the copolymer of PAPA and DMAM, the reversible water solubility of the inclusion complexes could be triggered by alternating UV and visible light irradiation.

Keywords: azo polymers; α-cyclodextrin; inclusion complexes; stimuli-responsive polymers; lower critical solution temperature

1 Introduction

Photoresponsive polymers have attracted considerable interest (1−5) because light as an external stimuli can be controlled remotely, changed rapidly, and it is clean compared with traditional stimuli such as temperature, pH, electric field, and ionic strength (6−9). Azobenzene-containing photoresponsive polymers especially have been widely investigated due to their potential applications (10−13). Azobenzene can undergo reversible photoisomerization upon UV and Vis light irradiation, which leads to the corresponding change in physical and chemical properties (14−17). The photoswitchable properties of the azobenzene polymers can be applied into many fields such as photocontrolled enzymatic bioprocessing, phototriggered targeted drug delivery systems, photocontrolled separation/recovery systems in bioMEMs formats, and photo-driven smart surface (10, 11, 18). By the introduction of azobenzene moiety into temperature-responsive polymers such as poly(N-isopropylacrylamide) (PNIPAM) and poly(N,N-

dimethylacrylamide) (PDEAM), the properties of the polymer solution can be regulated through photoirradiation. Irie (19) first reported a copolymer of NIPAM and N-(4-(phenylazo)-phenyl)-acrylamide with light controlled water solubility. This system works only in a very narrow range of composition and solution temperature. Copolymers with a much wider temperature gap have been obtained by Kroger by copolymerization of DMAM and phenylazophenylacrylat (20). However, the published results have shown that photoisomerization of azobenzne group has slightly affected the solubility of these photoresponsive polymers, which makes it difficult to realize the phase separation through photoirradiation.

α-Cyclodextrin (α-CD) is oligosaccharides consisting of six glucose units which present a toroidal form with a hydrophobic inner cavity and a hydrophilic outer side. This property is in favor of forming inclusion compounds with a large variety of organic molecules that have suitable size, shape and polarity (21, 22). Among them, azobenzene is an excellent guest for inclusion complexation with α-CD (23−28). Based on the inclusion complexation of α-CD and azobenzene, Sol-Gel reversible transition has been obtained by alternately using two kinds of different light irradiation. Therefore, the inclusion complexes of α-CD and azobenzene

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are an ideal system for constructing photoresponsive polymer, of which the solubility properties can be controlled by using the light-controlled molecular recognition of α-CD and azobenzene.

In this paper, we reported three kinds of photoresponsive copolymers with azobenzene side chains. In order to enlarge the window gap of the phase separation, α-CD was introduced into the thermal and photo responsive polymers systems. In the three kinds of photoresponsive copolymers, only poly(N,N-dimethylacrylamide-*co*-N-4-phenylazophenyl acrylamide) (PDMAM-x) showed the reversible light-triggered solubility behavior at present of α-CD via molecular recognition of α-CD and azobenzene moiety. Therefore, we investigated the effect of α-CD on the LCST of the photoresponsive copolymers and the light-controlled solubility behavior of the inclusion complexes, and systematically analyzed the photoisomerization of the inclusion complexes and the mechanism of polymer solubility change upon photoirradiation.

2 Experimental

2.1 Materials

N,N-dimethylacrylamide (DMAM) and 4-aminoazobenze, purchased from Fluka, were used without further purification N-isopropylacrylamide (NIPAM) (Fluka) was recrystallized from toluene and n-hexane, and dried in vacuum at room temperature for 24 h. α-Cyclodextrin (α-CD) (TCI) was recrystallized twice from water and dried in vacuum at 90°C for 24 h. AIBN was purified by recrystallization from ethanol. Acryloyl chloride and propionyl chloride (Fluka) were distilled before use. N,N-diethylacrylamide (DEAM) was synthesized according to the literature (29). All other reagents were used as received from commercial sources.

2.2 Preparation of Monomer and Model Compound

N-4-phenylazophenyl acrylamide (PAPA) and the model compound (PAPP: N-4-phenylazophenyl propionamide), illustrated in Scheme 1, were prepared by the condensation of 4-aminoazobenzene with acryloyl chloride or propionyl chloride in THF in the presence of triethylamine (TEA). The crude product was recrystallized from dichloromethane/

petroleum ether mixture and dried in vacuum. PAPA: yield 4.58 g (73%); m.p. 163−165°C; UV (ethanol): $\lambda_{max} = 350$ nm, $\varepsilon = 22083$; FT-IR (KBr, cm^{-1}): 3304 (m, NH), 1666 (vs, C=O), 1635 (m, C=C); ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 7.97−7.87 (m, 4H, azobenzene), 7.79−7.75 (d, 2H, azobenzene), 7.63 (s, 1H, NH), 7.54−7.45 (m, 3H, azobenzene), 6.53−5.80 (m, 3H, CH$_2$=CH-). PAPP: yield 4.93 g (78%); m.p. 166-168°C; UV (ethanol): $\lambda_{max} = 349$ nm, $\varepsilon = 22015$; FT-IR (KBr, cm^{-1}): 3303 (m, NH), 1670 (vs, C=O); ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 7.91 (t, 4H, azobenzene), 7.72−7.68 (d, 2H, azobenzene), 7.54−7.45 (m, 4H, azobenzene and NH), 2.48−2.40 (q, 2H, -CH$_2$-), 1.27 (t, 3H, CH$_3$-).

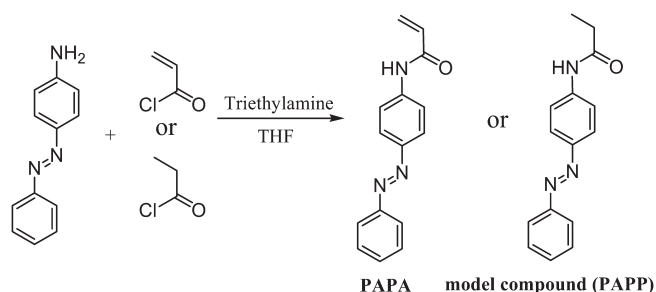### 2.3 Preparation of Photoresponsive Copolymers

A series of photoresponsive copolymers of PNIPAM-x, PDEAM-x, and PDMAM-x (structure shown in Scheme 2), where x denotes the mol% content of azobenzene group in copolymer, were prepared by free radical copolymerization of NIPAM, DEAM or DMAM with PAPA in THF (conc. of monomer = 2 mol/L) using AIBN (1 mol%) as initiator at 65°C for 8 h (Table 1). The polymer was purified by three times' precipitation from THF into diethyl ether, and dried overnight in vacuum at 50°C to give a yellow powder.

2.4 Measurements

All melting points were uncorrected. FT-IR spectra were obtained from KBr pellets with a Nicolet 200SXV-1 Fourier-transform infrared spectrometer. ^{1}H-NMR spectra of the samples were recorded on a Bruker AMX300 NMR spectrometer (300 MHz). GPC measurements were performed at 40°C with a JASCO GPC-900 system equipped with a Ultrastyragel 500 A column in combination with JASCO UV-975 and Waters 410 detectors. THF was used as an eluent with an elution rate of 1.0 mL/min. The molecular weights were calibrated with standard polystyrene. UV-Vis spectra were measured on a VARIAN CARY 100 Conc spectrophotometer using a 1 cm path length quartz cuvette.

Photoirradiation was carried out with a 1 kW high pressure mercury lamp (YMFY, GGZ-1000), employing a band pass filter (SCOG, ZWB2) to obtain light with a wavelength $\lambda = 365$ nm and a cut off filter (SCOG, JB420) for light with

Sch. 1. Synthesis of monomer and model compound.
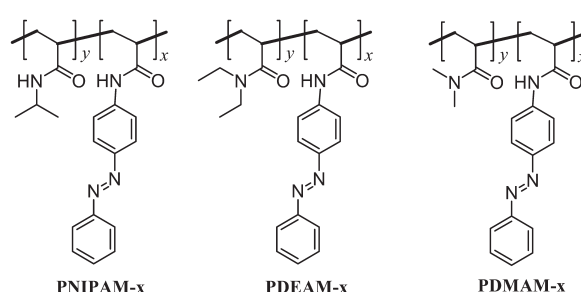
Sch. 2. Chemical structure of the photoresponsive copolymers.

Table 1. Polymerization conditions and results of NIPAM, DEAM or DMAM with PAPA

Sample code	Molar feed ratio of PAPA (%)	Molar content of PAPA in copolymer (%)	Yield in %	Molecular weight	
				Mn	Mw/Mn
PNIPAM	0	0	85	4365	1.90
PNIPAM-0.63	0.6	0.63	43	5271	2.04
PNIPAM-2.3	1.5	2.3	39	5116	1.48
PNIPAM-3.0	2	3.0	37	6729	1.43
PNIPAM-3.5	3	3.5	33	7815	1.59
PNIPAM-4.7	4	4.7	30	8131	1.52
PNIPAM-7.7	6	7.7	25	8979	1.63
PNIPAM-10.8	7.5	10.8	27	12359	1.80
PNIPAM-14.2	9	14.2	21	9565	1.65
PDEAM	0	0	75	4586	2.67
PDEAM-1.2	1	1.2	55	6293	2.51
PDEAM-2.4	1.5	2.4	38	5852	3.16
PDEAM-3.0	2	3.0	32	9078	1.76
PDEAM-7.2	5	7.2	29	6095	4.30
PDEAM-13.3	8	13.3	25	5807	3.90
PDMAM-3.5	3	3.5	29	2684	1.68
PDMAM-5.6	5	5.6	26	2136	1.68
PDMAM-9.6	7	9.6	21	1828	1.94
PDMAM-11.3	9	11.3	24	3647	1.83
PDMAM-12.5	11	12.5	25	3830	3.47
PDMAM-14.3	13	14.3	18	2679	2.35
PDMAM-15.7	15	15.7	20	3425	3.80

$\lambda > 420$ nm. Cloud point, at which 50% of the overall transmittance change had taken place, was determined by measuring the transmittance of a 0.5% aqueous solution of the copolymer at 650 nm at the heating rate of 0.5°C/min (VARIAN CARY 100 Conc). To measure the LCST of *cis* copolymers with or without α-CD, the copolymers solutions were first objected to 365 nm light irradiation for 40 min, and the light irradiation was hold on in the heating process. The LCST of *trans* copolymers with or without α-CD were determined after visible light irradiation for 40 min without further irradiation. The molar content of azobenzene group in the copolymer was determined according to Beer's law. It was assumed that the absorption coefficients ($\lambda_{max} = 349$ nm) of the model compound (PAPP) and the corresponding comonomeric units in the copolymer chain were identical.

3   Results and Discussion

3.1   Synthesis and Characterization of the Copolymers with Azobenzene Side Chains

Three kinds of photoresponsive copolymers, PNIPAM-x, PDEAM-x, and PDMAM-x (structure shown in Scheme 2), were prepared by radical polymerization varying the content of azobenzene comonomer (PAPA) in the feed. Table 1 shows that the content of azobenzene in the three kinds of copolymers is more than that in the feed. The yield of copolymer decreases when the feed ratio of PAPA increases, which resulted from the inhabitation of azobenzene (20). Their

structures were characterized by FT-IR, UV-Vis and ¹H-NMR spectroscopy. Figure 1 shows the FT-IR spectra of PNIPAM homopolymer, PNIPAM-7.7, PDEAM homopolymer, PDEAM-13.3, and PDMAM-11.3. The characteristic peaks of azobenzene group, multiple bands in the region 1348–1500 cm^{-1} assigned to stretching vibration of aromatic C-C and the bands at 766 and 687 cm^{-1} assigned to in-plane and out-of-plane C-H bending vibrations of aromatic ring of azobenzene (30), all appear in the three kinds of polymers with azobenzene side chains. In the three kinds of copolymers, the absorption band at about 3200 cm^{-1} is attributed to the secondary bonded amide group of CO-NH, and the wide absorption bands at about 1630 cm^{-1} are attributed to the N-H bending and C=O stretching vibrations of a secondary amide. The characteristic peaks of isopropyl at 1385 cm^{-1} and 1366 cm^{-1}, ethyl at 1379 cm^{-1} and 1360 cm^{-1} and methyl groups at 1351 cm^{-1}, appear in the spectra of PNIPAM-7.7, PDEAM-13.3, and PDMAM-11.3, separately. UV-Vis spectra of these copolymers with azobenzene side chains shows two absorption peaks at $\lambda_{max} = 349$ nm and $\lambda = 425$ nm corresponding to the π-π^* and n-π^* transitions of *trans*-azobenzene, respectively (Figure 2). Furthermore, ¹H-NMR spectra confirmed azobenzene group in the three kinds of polymers. As shown in Figure 3, the resonance peaks in the region 7.3–8.0 ppm are attributed to the protons of the azobenzene group, and the wide weak band between 8.3–10 ppm is assigned to NH group attached to azobenzene. The resonance band of NH group in N-isopropylacrylamide appears in the region 6.0–7.0 ppm (Figure 3a).
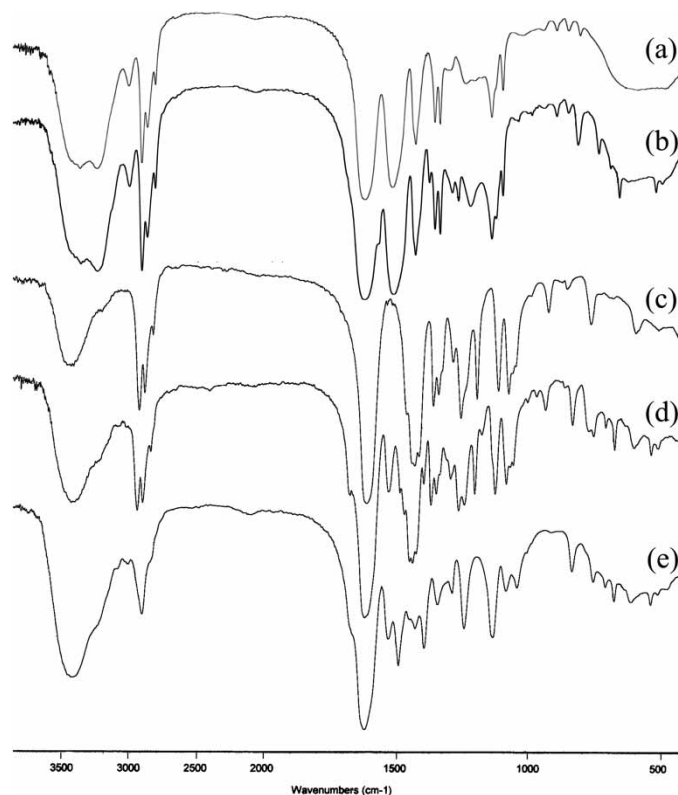
Fig. 1. FT-IR spectra of (a) PNIPAM, (b) PNIPAM-7.7, (c) PDEAM, (d) PDEAM-13.3, and (e) PDMAM-11.3.

3.2 Photoresponses of the Copolymers and their Inclusion Complexes with α-CD

In order to study the photoresponses of the copolymers and their inclusion complexes with α-CD, UV-Vis absorption spectra of the photoresponsive copolymers were measured in aqueous solution in the presence of equimolecular α-CD or not. As shown in Figure 4, the maximum absorption band of all of three photoresponsive copolymers increases to 351.5 nm from 348.5 nm and the intensity also increases slightly after the addition of equimolecular α-CD, which indicates the formation of the inclusion complexes between the azobenzene-containing copolymers and α-CD. It is known that α-CD can stably form 1:1 inclusion complexes with *trans*-azobenzene and the association constant for α-CD and *trans*-azobenzene is 1.0×10^4 M^{-1} (27). Furthermore, the reversible photoresponses of the copolymers and their inclusion complexes with α-CD were investigated as a function of irradiation time. Figure 5 shows rapid photoisomerization of the inclusion complexes which only needs 3 min to reach the photostationary state. With increasing UV irradiation time, the absorption peak of the photoresponsive inclusion complexes at 351.5 nm decreases sharply and blueshifts, and they reaches the photostationary state (*cis*-azobenzene) after 3 min. The opposite change of the inclusion complexes also could be achieved after using >420 nm light irradiation. In the *cis* to *trans* photoisomerization of the PNIPAM-2.3 and PDEAM-1.2 systems, the only

difference is that UV-Vis absorption intensity in all scan scope increases with increasing the visible light irradiation time, which resulted from a slight phase transition when the temperature rises due to the thermal effect of visual light. The reversible photoisomerization of three photoresponsive copolymers without α-CD is also investigated and shows the same results. The *trans* to *cis* and *cis* to *trans* photoisomerization of three inclusion complexes undergoes rapidly,
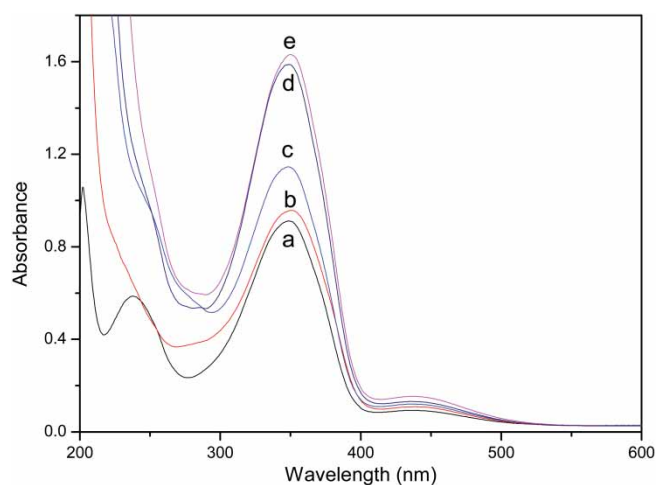

Fig. 2. UV-Vis absorption spectra of (a) model compound (PAPP), (b) PAPA, (c) PNIPAM-7.7, (d) PDEAM-13.3, and (e) PDMAM-11.3 in ethanol solution.
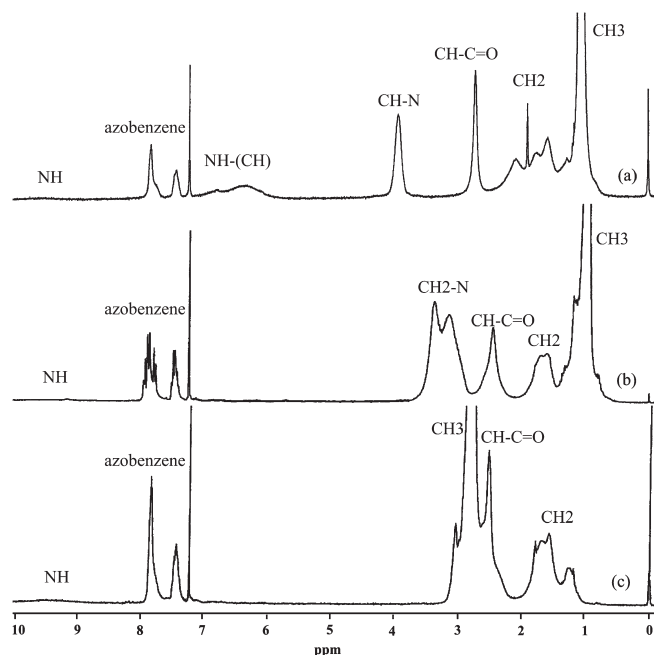
Fig. 3. ^{1}H-NMR spectra of (a) PNIPAM-7.7, (b) PDEAM-13.3, and (c) PDMAM-11.3 in CDCl$_3$.

which indicates that the photoisomerization of azobenzene group is much stronger than the incusion complexation of α-CD and azobenzene group. Therefore, the photoisomerization of the copolymers with azobenzene side chains has not been hindered by α-CD.

3.3 LCST of the Photoresponsive Copolymers and their Inclusion Complexes with α-CD

To investigate the effect of α-CD on the solution properties of the photoresponsive copolymer, the LCST of three kinds of copolymers was examined by monitoring the changes of turbidity before and after UV irradiation whether α-CD was present or not. As shown in Figure 6, The LCST of three

kinds of photoresponsive copolymers decreases with increasing the azobenzene content in the polymer, and high azobenzene content in the polymer makes the copolymer insoluble such as PNIPAM-7.7, PNIPAM-10.8, PNIPAM-14.2, PDEAM-7.2, PDEAM-13.3, PDMAM-14.3, and PDMAM-15.7. After adding equimolecular α-CD, the LCST increases sharply, and the insoluble copolymer becomes soluble such as PNIPAM-7.7, PDMAM-14.3, and PDMAM-15.7. However, even adding excess α-CD, PNIPAM-10.8, PNIPAM-14.2, PDEAM-7.2, and PDEAM-13.3 can not dissolve in water because of strong hydrophobicity of the copolymers. When these copolymers solution is objected to UV irradiation, the LCST increases slightly in the absence of α-CD, while the LCST decreases considerably in the presence of an equivalent α-CD. The change of LCST is larger with a higher content of azobenzene in the presence of equivalent α-CD. However, there is no effect of α-CD on the LCST of the homopolymers of PNIPAM and PDEAM (data not shown). It is well known that the phase separation depends on the subtle balance between the hydrogen bond formation ability of the polymer with water and the intermolecular hydrophobic forces (19). Through introduction of azobenzene moiety into the polymer, the intra- and intermolecular hydrophobic interaction is enforced and the polymer becomes less soluble to precipitate at lower temperature. The photogenerated *cis* forms to increase the solubility of the polymer due to the less hydrophobic property, which results in an increase of LCST. But photoisomerization of azobenzene moiety slightly affects the LCST of the copolymers without α-CD because of a little change of polarity. α-CD can form 1:1 inclusion complexes with *trans* azobenzene and cannot with *cis* azobenzene (23−28). In the presence of equimolecular α-CD, the copolymer becomes soluble due to the outer hydrophilic essence of α-CD binding equimolecular *trans* azobenzene moiety of the copolymer, which results in a large increase of the LCST, especially in the copolymer with a high azobenzene content. After UV irradiation, *trans* azobenzene moiety
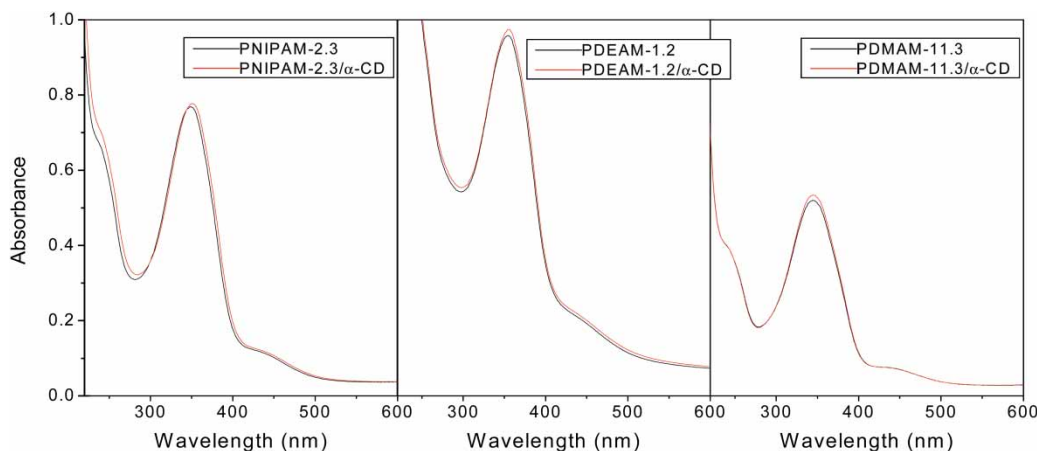

Fig. 4. Effect of equimolecular α-CD on the UV-Vis absorption band of the photoresponsive copolymers. Left: PNIPAM-2.3 0.19 g/L; middle: PDEAM-1.2 0.45 g/L; right: PDMAM-11.3 0.026 g/L.
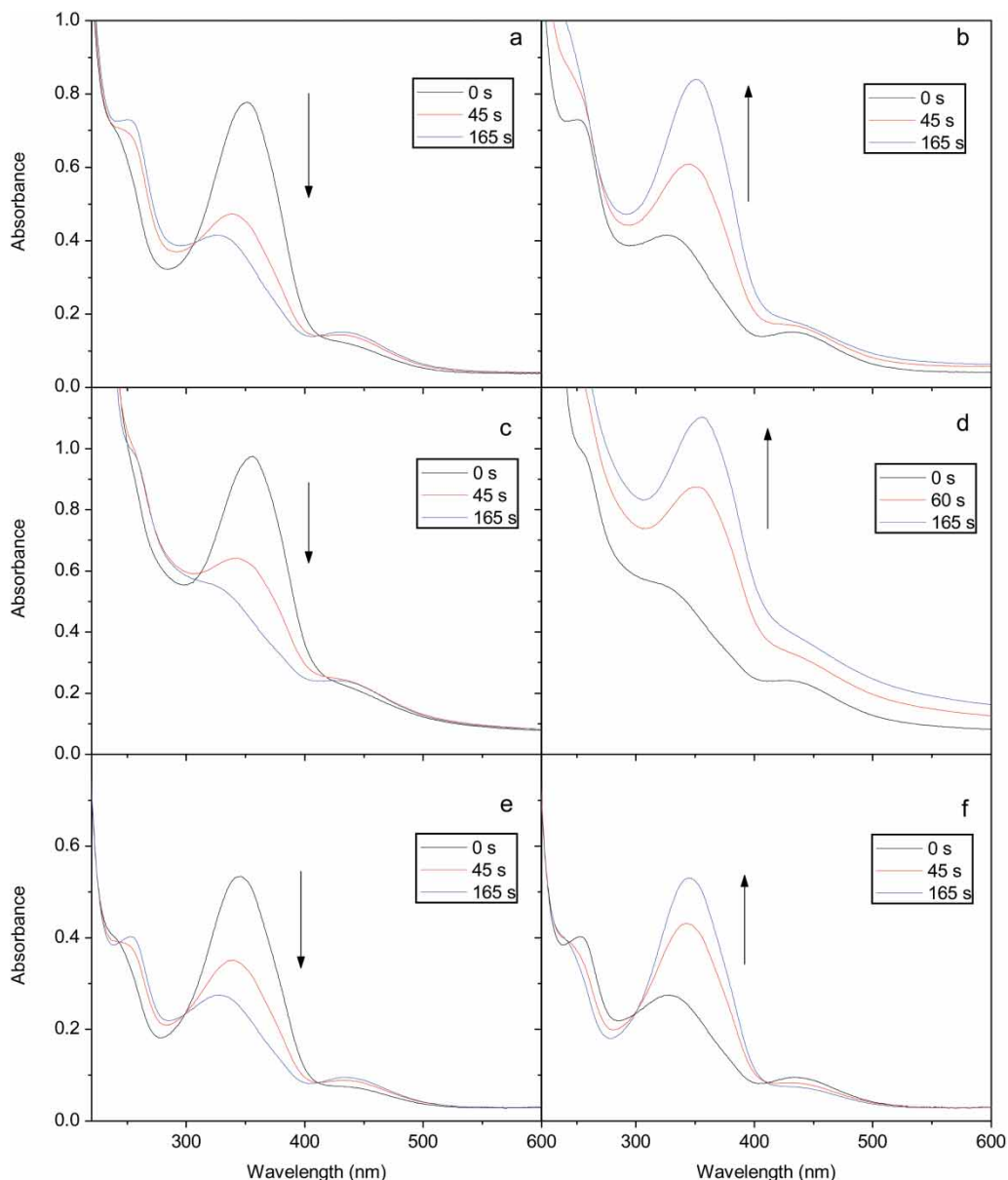
Fig. 5. UV-Vis absorption as a function of irradiation time in water in the presence equimolecular α-CD. a and b: PNIPAM-2.3 0.19 g/L; c and d: PDEAM-1.2 0.45 g/L; e and f: PDMAM-11.3 0.026 g/L; a, c, and e: 365 nm light irradiation; b, d, and f: > 420 nm light irradiation.

becomes *cis* form and decomplexes from the inner of α-CD due to large steric hindrance. α-CD is only detached from polymer side chain because there is no long spacer between the azobenzene group and main polymer chain. The polymer precipitates due to the larger hydrophobicity of *cis* azobenzene moiety compared with the inclusion state, which results in a corresponding large decrease of the LCST.

Figure 7 shows the reversibility of the LCST of PNIPAM-7.7 and PDMAM-14.3 systems using UV and visible light irradiation alternately. Due to the small change of the LCST between *trans* and *cis* copolymers in the absence of α-CD, it is difficult to evaluate the reversibility of the

LCST of the copolymers without α-CD. For the same reason, the reversibility of the LCST is also barely characterized in PNIPAM-x (x < 5), PDEAM-x, PDMAM-x (x < 10) in the presence of α-CD. The reversibility of the LCST is achieved by using photoirradiation only in PNIPAM-7.7, PDMAM-9.6, PDMAM-11.3, PDMAM-12.5, PDMAM-14.3, and PDMAM-15.7 with α-CD. As mentioned above, high azobenzene content enlarges the difference between hydrophilic complexation and hydrophobic decomplexation, which enlarges the difference between the LCST of the complexation state and the LCST of the decomplexation state. Therefore, it is easy to characterize the reversible change of LCST.
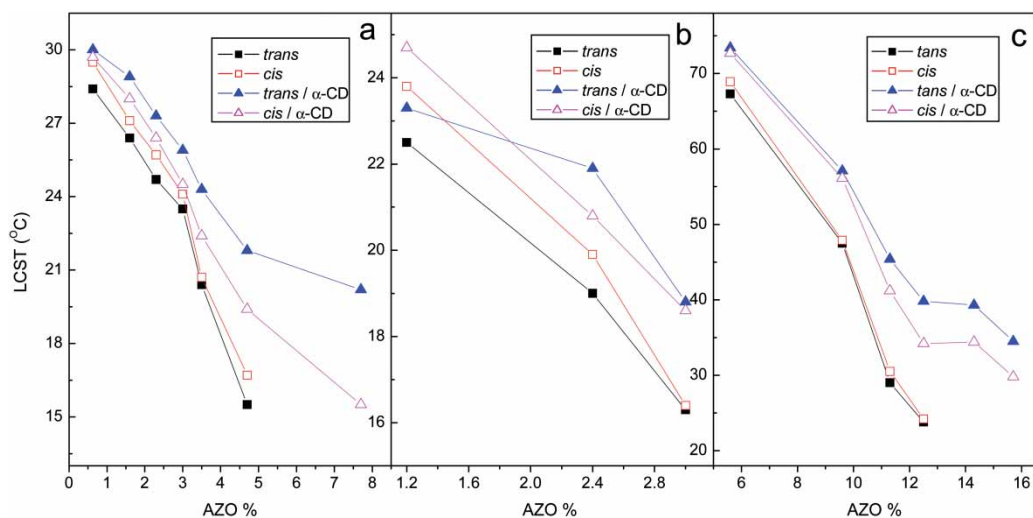
Fig. 6. Influence of equivalent α-CD on the LCST of the photoresponsive copolymers with different azobenzene content before (■ and ▲) and after (□ and △) UV irradiation. (a) PNIPAM-x, 5 g/L; (b) PDEAM-x, 5 g/L; (c) PDMAM-x, 5 g/L.

3.4 Light-Triggered Reversible Solubility Behavior of the Inclusion Complexes

Furthermore, light-triggered reversible solubility behavior of the inclusion complexes was observed. Figure 8 shows the reversible change of transmittance of the PDMAM-14.3 inclusion complexes when objected to UV and visible light irradiation at 36°C alternately. After UV irradiation on the PDMAM-14.3 inclusion complexes at 36°C, the polymer solution becomes opaque. Meanwhile, it recovers the transparent state by visible light irradiation at the same temperature again. However, only in the PDMAM-x (x > 11) inclusion complexes solution, the transparent-opaque reversible transition can be observed obviously. Two conditions are required to obtain transparent-opaque reversible transition: One is steep change around the LCST, another is a wide

temperature gap between two photostationary states (20). The former requires uniform polymer composition, which can be obtained through controlling low conversion of polymerization. The latter requires the large hydrophility-hydrophobicity change between two photostationary states, which is resolved by the inclusion complexation between α-CD and azobenzene containing polymer. After UV irradiation at a certain temperature between two LCST, the *cis* polymers form and α-CD is detached from the copolymers side chains. The hydrophobicity of the copolymers is improved greatly compared with the state of inclusion complexes, which makes the polymer solution opaque. Also by visible light irradiation, α-CD forms inclusion complexes with azobenzene side chain again, resulting in a recovery of transparent properties of polymer solution at the same
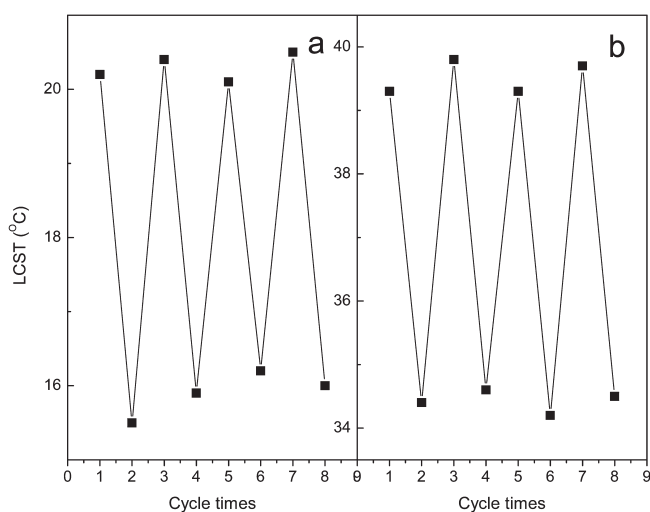

Fig. 7. Reversible change of the LCST of (a) PNIPAM-7.7 and (b) PDMAM-14.3 in the presence of the equivalent α-CD using UV and visual light irradiation alternately.
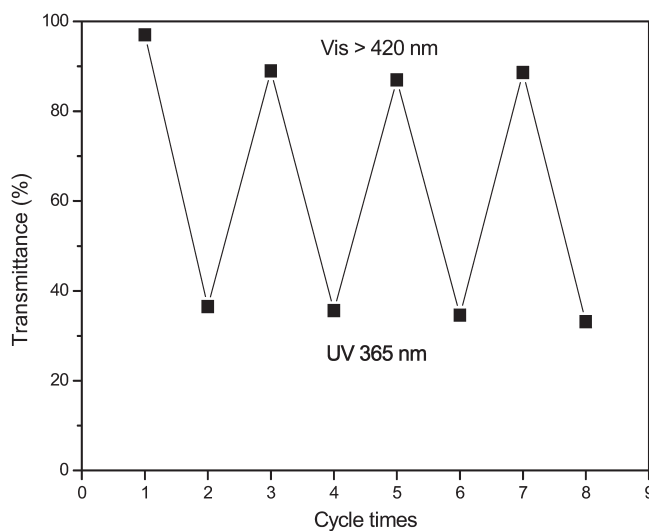

Fig. 8. Transparent-opaque reversible recycles of PDMAM-14.3 inclusion complexes at 36°C using UV and visual light irradiation alternately.

temperature. Therefore, the addition of α-CD enlarges the photo-induced phase separation window gap and makes it easy to control photoswitchable solubility of the polymer, which is almost impossible without α-CD.

4 Conclusions

By the introduction of α-CD into the photoresponsive copolymers with azobenzene side chain, we have successfully changed the LSCT of the photoresponsive copolymers and obtained the photoresponsive inclusion complexes in which photoreversible solubility change takes place after photoirradiation. After UV irradiation, α-CD is detached from polymer side chain and the polymer precipitates due to the larger hydrophobicity of *cis* azobenzene moiety compared with the inclusion state, while it attaches a azobenzene side chain again using visible light irradiation and the polymer redissolves again. This reversible large change of side chain polarity results in the reversibility of the LCST and the transmittance. The addition of α-CD into polymer systems enlarges the photo-induced phase separation window gap and makes it easy to control photoswitchable solubility of the polymers. This photoswitchable system may be applied to construct the smart materials especially in the light-controlled drug delivery.

5 Acknowledgments

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