Light-Triggered Reversible Solubility of α-Cyclodextrin and Azobenzene Moiety Complexes in PDMAA-*co*-PAPA Via Molecular Recognition

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ABSTRACT: Photoresponsive polymer with azobenzene pendant group (PDMAA-*co*-PAPA) was synthesized by radical polymerization of N,N-dimethylacrylamide (DMAA) and N-4-phenylazophenyl acrylamide (PAPA), and the characterization of the inclusion complexes of the PDMAA-*co*-PAPA with α-cyclodextrin (α-CD) were performed by FTIR, GPC, ^{1}H NMR, 2D NOESY, and UV–vis spectroscopy. It was found that the solubility of PDMAA-*co*-PAPA and α-CD inclusion complexes in aqueous solution showed tunable property, which could be triggered by alternating UV–vis light irradiation at a certain temperature due to the effect of molecular recognition of α-CD with azobenzene moiety in the polymer. After UV irradiation, the lower critical solution temperature (LCST) of the polymer aqueous solution increased slightly without α-CD while the LCST decreased sharply at presence of α-CD. Furthermore, UV spectroscopy showed that the photoisomerization of the polymer solution went on rapidly and reversibly, and 2D NOESY data suggested that the inclusion complexation of α-CD with *trans* azobenzene moiety and the decomplexation with *cis* azobenzene resulted in reversible solubility behavior when objected to UV and Vis light irradiation alternately. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2118–2125, 2008

Key words: azo polymers; molecular recognition; stimuli-sensitive polymers; solubility

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] Especially, azobenzene-containing photoresponsive polymers have been widely investigated due to their potential applications.[10–13] Azobenzene can undergo reversible photoisomerization upon UV or Vis light irradiation, which leads to the corresponding change in physical and chemical properties.[14–17] By the introduction of azobenzene moiety into temperature-responsive polymers such as poly(N-isopropylacrylamide) and poly(N,N-dimethylacrylamide), the properties of the polymer solution can be regulated through photoirradiation. Kungwatchakun and Irie[18] first reported a copolymer of N-isopropylacrylamide 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 had been obtained by Kroger et al. by copolymerization of dimethylacrylamide and phenylazophenylacrylat.[19] However, the results showed that photoisomerization of azobenzne group has affected slightly on 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.[20,21] Among them azobenzene is an excellent guest for inclusion complexation with α-CD.[22–27] Based on the inclusion complexation of α-CD with azobenzene, sol–gel reversible transition has been obtained using two kinds of different light irradiation. Therefore, the inclusion complexes of α-CD and azobenzene is 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 with azobenzene.

In this article, we reported the light-triggered solubility change of poly(N,N-dimethylacrylamide-

co-N-4-phenylazophenyl acrylamide)s/α-cyclodextrin complexes (PDMAA-co-PAPA/α-CD) via molecular recognition of α-CD with azobenzene moiety. To enlarge the window gap of the phase separation, α-CD was introduced into the thermal and photo responsive polymers systems. Therefore, we investigated the effect of α-CD on the LCST of the PDMAA-co-PAPA 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.

EXPERIMENTAL

Materials

N, N-dimethylacrylamide (DMAA) and 4-aminoazobenze, purchased from Fluka, were used without further purification. α-Cyclodextrin (α-CD) (TCI) was recrystallized twice from water and dried at 90°C in vacuum. AIBN was purified by recrystallization from ethanol. Acryloyl chloride and propionyl chloride (Fluka) were distilled before use. All other reagents were used as received from commercial sources.

Measurements

All melting points were uncorrected. FTIR 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). The 2D NOESY NMR spectra were recorded on a Bruker Avance NMR (600 MHz) at 25°C. The mixing time before the acquisition of free induction decay was carefully varied and fixed at 500 ms. Sample solution was prepared by using D_2O containing 10 g/L PDMAA-co-PAPA-11.3 and 8.7 g/L α-CD, and irradiated with 365-nm light for 3 h at 25°C. UV–vis spectra were measured on a VARIAN CARY 100 Conc spectrophotometer using a 1-cm path length quartz cuvette. 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.

Photoirradiation was carried out with 1-kW high pressure mercury lamp (YMFY, GGZ-1000), employing a band pass filter (SCOG, ZWB2) to obtain light with a wavelength λ = 365 nm and a cut-off filter (SCOG, JB420) for light with λ > 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.). Irradiated solutions were used after reaching the photostationary state 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 (λ$_{max}$ = 349 nm) of the model compound (PAPP) and the corresponding comonomeric units in the copolymer chain were identical.

Synthesis of monomer and model compound

N-4-phenylazophenyl acrylamide (PAPA) and N-4-phenylazophenyl propionamide (PAPP), depicted 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) according to the procedure of Moniruzzaman et al.[28] In brief, 4-aminoazobenzene (5 g, 25 mmol) was dissolved in 50 mL of THF in a 100 mL flask, to which TEA (2.53 g, 25 mmol) was added. Acryloyl chloride (3 mL, 32 mmol) was charged dropwise via a glass syringe, whereas the solution was maintained in an ice-cooled water bath with continuous stirring. After completion the reaction mixture was allowed to come to room temperature and stirred for 24 h. The resulting precipitate was filtered off; the solution was concentrated and then poured into ice-water to form yellow precipitate which was collected by filtration. The crude product was dried at 30°C in vacuum, then recrystallized from dichloromethane/ petroleum ether mixture and dried in vacuum. PAPA: yield 4.58 g (73%); m.p. 163–165 °C; FTIR (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—); UV (ethanol): λ$_{max}$ = 350 nm, ε = 22,083. PAPP: yield 4.93 g (78%); m.p. 166–168°C; FTIR (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,
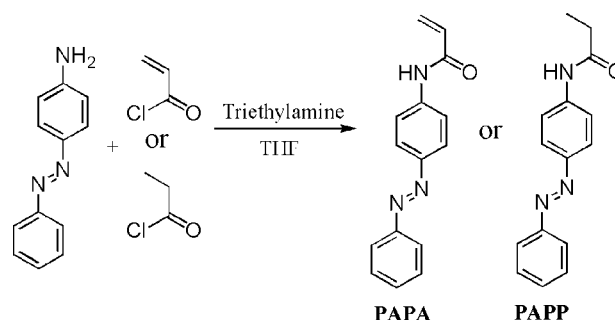
Scheme 1 Synthesis of PAPA and PAPP and structure of PDMAA-co-PAPA-x.
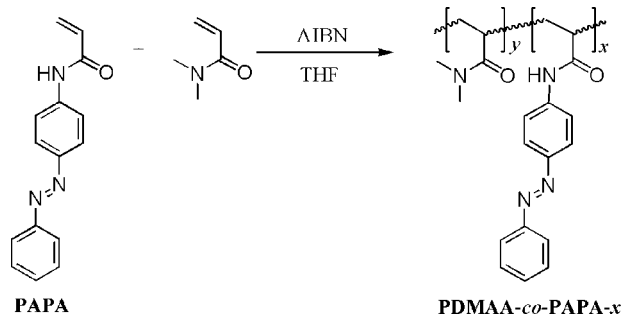
Scheme 2 Synthesis of PDMAA-*co*-PAPA-*x*.

azobenzene), 7.54–7.45 (m, 4H, azobenzene and NH), 2.48–2.40 (q, 2H, —CH$_2$—), 1.27 (t, 3H, CH$_3$—); UV (ethanol): λ_{max} = 349 nm, ε = 22,015.

Synthesis of copolymers

A series of PDMAA-*co*-PAPA-*x* copolymers (as shown in Scheme 2), where *x* denotes the mol % content of azobenzene group in copolymer, were prepared by varying the content of azobenzene comonomer (PAPA) from 3 to 15 mol % in the feed through free radical copolymerization of DMAA with PAPA in THF (conc. of monomer = 2 mol/L) using AIBN (1 mol %) as initiator at 65°C for 8 h (as shown in Table I). The polymer was purified by three times precipitation in diethyl ether and dried overnight in vacuum at 50°C. FTIR (KBr, cm^{-1}): 3310 (m, NH), 3118, 3037 (w, Ar—H), 2928 (s, C—H), 1636 (vs, C=O), 1534 (m, NH), 1401(s, C—N), 846 (m, 1,4-disubstituted benzene), 765, 687 (m, monosubstituted benzene). ^{1}H NMR (300 MHz, D$_2$O, δ in ppm): 8.22 (br, NH), 7.00–8.00 (br, azobenzene), 3.42–2.05 (br, (CH$_3$)$_2$N— and —CH—C=O), 1.46–0.87 (br, —CH$_2$—).

RESULTS AND DISCUSSION

Synthesis and characterization of the copolymer and its inclusion complexes

A number of PDMAA-*co*-PAPA-*x* copolymers were prepared by radical polymerization (Table I). The azobenzene content in the copolymer was determined by the UV–vis absorption of the azobenzene moiety, assuming that its absorption coefficient is identical to that of the model compound (PAPP). The molecular weights of the polymers were measured by GPC. The structure of the copolymer and its inclusion complexes was confirmed by ^{1}H NMR and FTIR spectroscopy. Figure 1(b) illustrates the typical FTIR spectrum of the copolymer PDMAA-*co*-PAPA-11.3. The absorption band at about 3200 cm^{-1} is attributed to the secondary bonded amide group of CO—NH. Because of the overlap of N—H bending and C=O stretching vibrations of a secondary amide, the absorption bands of these groups occur widely at about 1630 cm^{-1}. Multiple bands in the region 1348–1500 cm^{-1} are due to stretching vibration of aromatic C—C. The bands at 766 and 687 cm^{-1} are due to in-plane and out-of-plane C—H bending vibrations of aromatic ring of azobenzene.[29] The band at 2927 cm^{-1} is attributed to C—H stretching of CH$_2$ and CH groups. As shown in Figure 1(c), the inclusion complexes of PDMAA-*co*-PAPA-11.3/α-CD exhibit the absorption bands which occur both in PDMAA-*co*-PAPA-11.3 and α-CD.

Figure 2 shows the ^{1}H NMR spectra of α-CD, PDMAA-*co*-PAPA-11.3, and PDMAA-*co*-PAPA-11.3/α-CD in D$_2$O. As shown in Figure 2(b), the resonance band at 2.8 ppm is assigned to *N,N*-dimethyl group in the side chain of the copolymer, and the bands at 2.5 ppm and 1.2–1.7 ppm are assigned to —CH$_2$—CH— group in the main chain of the copolymer. The integrated signals of —CH$_2$=CH— from DMAA and PAPA are disappeared. Compared with the spectra of α-CD, PDMAA-*co*-PAPA-11.3, and PDMAA-*co*-PAPA-11.3/α-CD, the resonance signals between 7 and 8 ppm assigned to azobenzene moiety and NH group in the copolymer becomes sharp and shifts downfield after the addition of α-CD, and the resonance bands assigned to C$_1$, C$_3$, C$_5$, and C$_6$ protons of α-CD also exhibit considerable upfield shifts in PDMAA-*co*-PAPA-11.3/α-CD system. These downfield shifts of azobenzene protons and upfield shifts of α-CD protons may be caused by the interaction of the inner protons of α-CD and the ring

TABLE I
Copolymerization of DMAA with PAPA

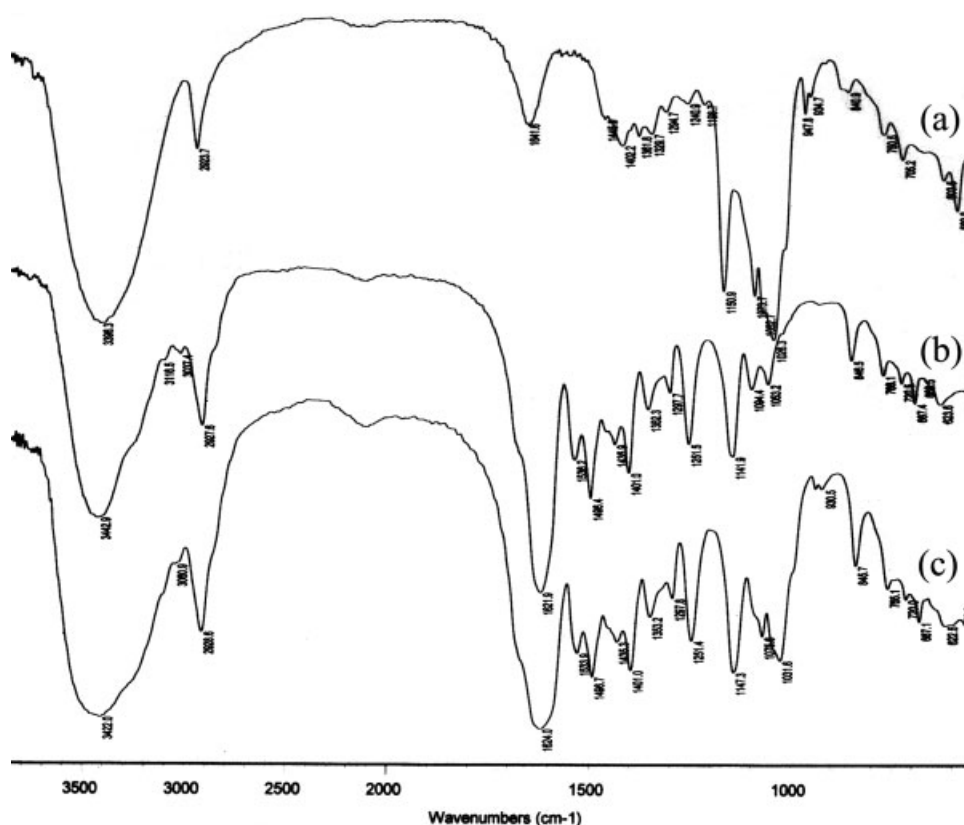| Sample code	Molar feed ratio of PAPA (%)	Conversion in %	Molar content of PAPA in copolymer (%)	Molecular weight	
				M_n	M_w/M_n
PDMAA-*co*-PAPA-3.5	3	29	3.5	2684	1.68
PDMAA-*co*-PAPA-5.6	5	26	5.6	2136	1.68
PDMAA-*co*-PAPA-9.6	7	21	9.6	1828	1.94
PDMAA-*co*-PAPA-11.3	9	24	11.3	3647	1.83
PDMAA-*co*-PAPA-12.5	11	25	12.5	3830	3.47
PDMAA-*co*-PAPA-14.3	13	18	14.3	2679	2.35
PDMAA-*co*-PAPA-15.7	15	20	15.7	3425	3.80

Figure 1 FTIR spectra of (a) α-CD, (b) PDMAA-*co*-PAPA-11.3 and (c) PDMAA-*co*-PAPA-11.3/α-CD.

current of the aromatic rings in azobenzene moiety, indicative of the formation of inclusion complexes.

Photoresponses of the inclusion complexes

The photoisomerization of the inclusion complexes of azobenzene and α-CD in diluted solution was investigated by UV absorption spectra as a function of irradiation time. As shown in Figure 3(a,c), both PAPA/α-CD and PDMAA-*co*-PAPA-11.3/α-CD show two absorption peaks at $\lambda_{max} = 350$ nm and $\lambda = 425$ nm corresponding to the π–π* and n–π* transitions of *trans*-azobenzene, respectively. The absorption peak at 350 nm decreases sharply with increasing 365 nm UV irradiation time, while the absorption peak at 425 nm increases slightly with increasing 365 nm UV irradiation time. It takes UV irradiation 3 min to reach the photostationary state (*cis*-azobenzene). The opposite change also can be observed after using photoirradiation with >420 nm light on the PAPA/α-CD or PDMAA-*co*-PAPA-11.3/α-CD in the photostationary state (*cis*-azobenzene), as shown in Figure 3(b,d). The photoisomerization of PAPA and PDMAA-*co*-PAPA-11.3 at absence of α-CD was also investigated and showed the same results. The *trans* to *cis* and *cis* to *trans* photoisomerization undergoes rapidly both in monomer and copolymer whether α-CD is present or

not. Therefore, there is no effect of α-CD on the photoisomerization of azobenzene monomer and azobenzene-containing polymer in diluted solution, and no effect of the introduction of azobenzene into the polymer pendant on the photoisomerization of azobenzene moiety.

Effect of α-CD on the LCST of the copolymer upon photoirradiation

To investigate the effect of α-CD on the solubility of the azobenzene-functionalized polymer, the LCST of the PDMAA-*co*-PAPA in aqueous solution at absence or presence of equivalent α-CD was examined by monitoring the changes of turbidity before and after 365-nm UV irradiation. Figure 4(a) shows the transmittance as a function of temperature for 0.5% aqueous solution of the PDMAA-*co*-PAPA-11.3 and its complexes with α-CD. The LCST of the PDMAA-*co*-PAPA-11.3 increases slightly after UV irradiation; while the LCST increases to 45.5°C from 29°C after adding α-CD and decreases to 41°C sharply after UV irradiation in the presence of equivalent α-CD. The same tendency occurs in the other polymer systems with a different azbenzene content [Fig. 4(b)]. Meanwhile the LCST of the copolymer decreases fast with increasing content of azobenzene moiety
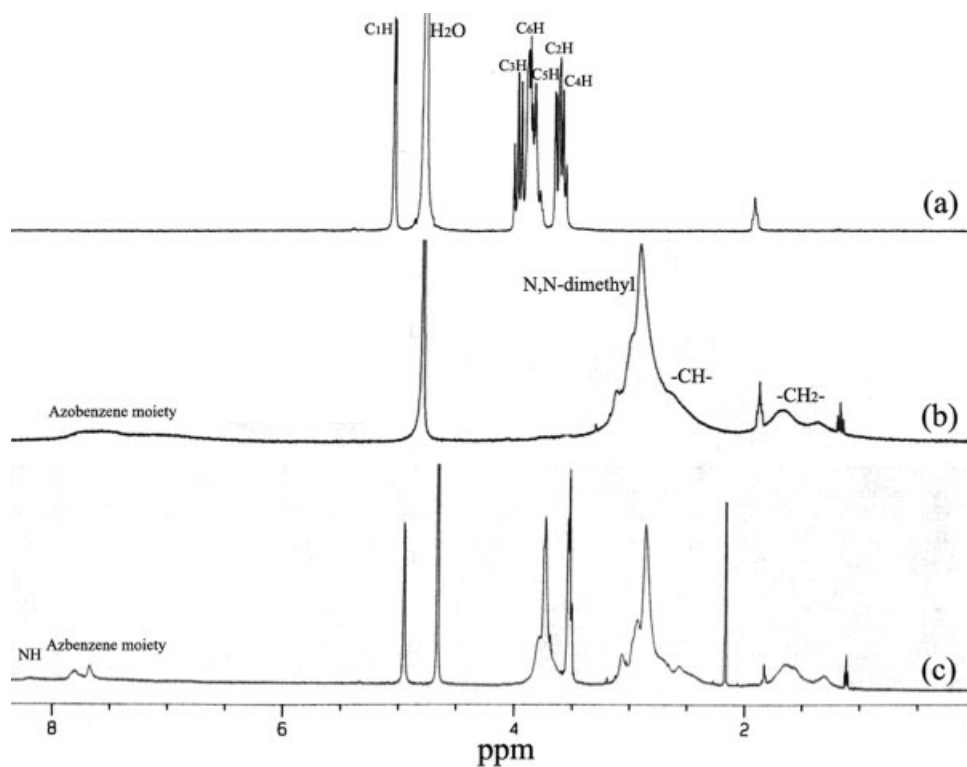
Figure 2 ^{1}H NMR spectra of (a) α-CD, (b) PDMAA-*co*-PAPA-11.3 and (c) PDMAA-*co*-PAPA-11.3/α-CD in D$_2$O.
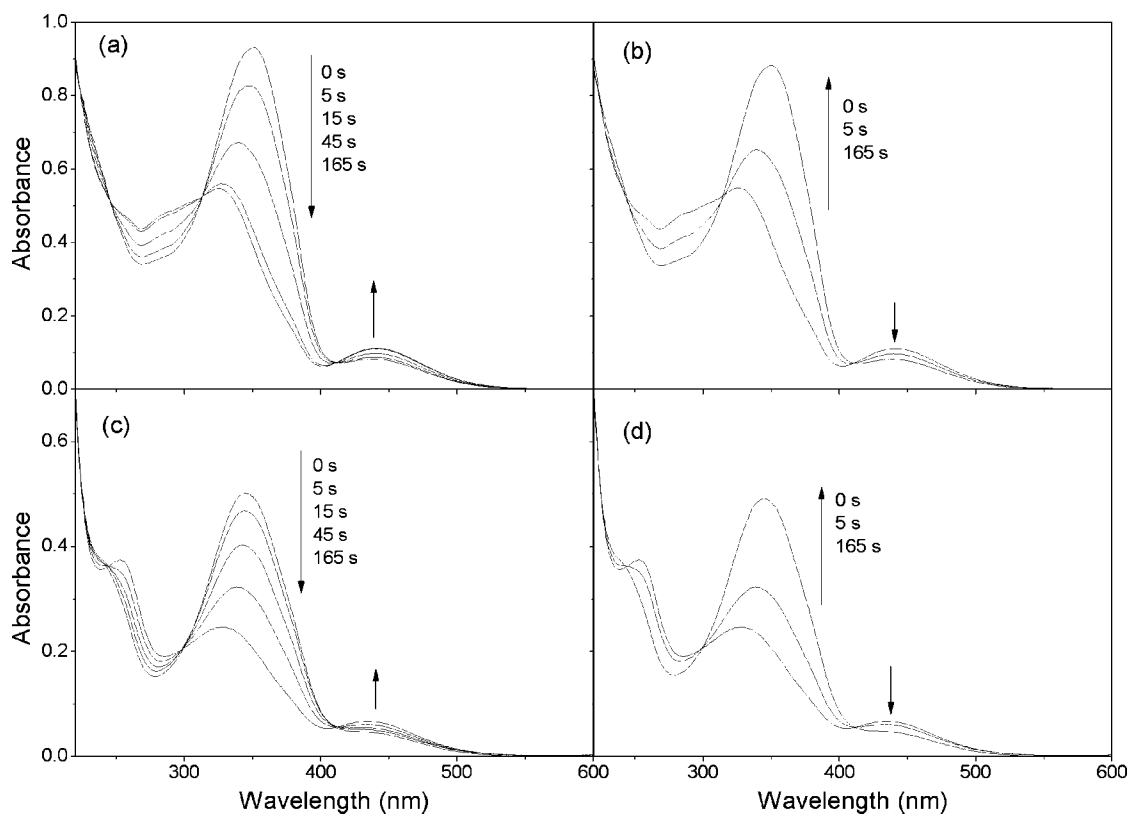

Figure 3 UV–vis absorption as a function of irradiation time; PAPA/α-CD 4.0 × 10^{-5} mol/L ethanol solution using (a) 365 nm light irradiation and (b) >420 nm light irradiation; PDMAA-*co*-PAPA-11.3/α-CD 2.45 × 10^{-2} g/L aqueous solution using (c) 365-nm light irradiation, and (d) >420 nm light irradiation.
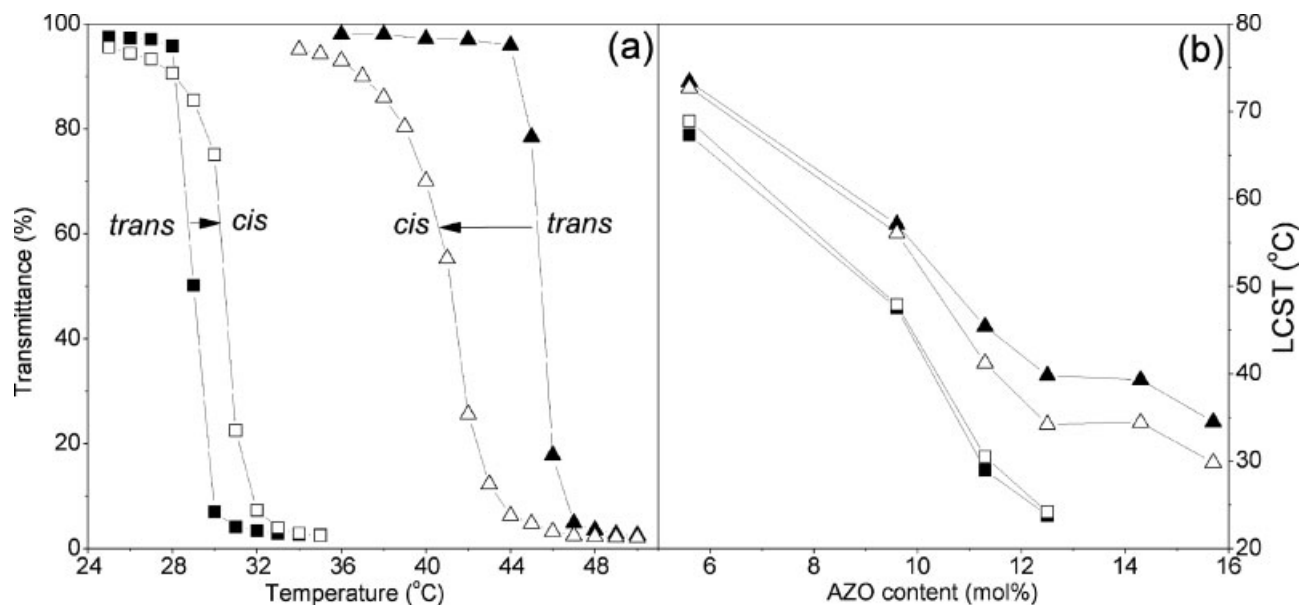
Figure 4 (a) Influence of UV irradiation on the phase transition profiles of PDMAA-*co*-PAPA-11.3 (5 g/L) (before, ■; after, □) and PDMAA-*co*-PAPA-11.3 (5 g/L)/α-CD (4.33 g/L) (before, ▲; after, △); (b) LCST (cloud points) of aqueous solutions of PDMAA-*co*-PAPA (5 g/L) as a function of azobenzene content using UV irradiation (before, ■; after, □) and at presence of α-CD (α-CD:AZO = 1 : 1) (before, ▲; after, △).

whether α-CD is present or not, and increases considerably after the addition of equivalent α-CD. Especially in the copolymer with high content of azobenzene, the addition of α-CD makes the insoluble copolymer soluble. Upon UV irradiation, the change of LCST is larger with higher content of azobenzene moiety in the presence of α-CD. It is 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.[18] 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 increase the solubility of the polymer due to the less hydrophobic property, which results in an increase of LCST. But photoisomerization of azobenzene moiety affects slightly on the LCST of the copolymers without α-CD. At presence of α-CD, the polymer becomes soluble due to the outer hydrophilic essence of α-CD binding equivalent *trans* azobenzene moiety of the polymer, which results in a large increase of the LCST, especially in the polymer of high azobenzene content. After UV irradiation, *cis* azobenzene moiety formed decomplexes from the inner of α-CD due to large steric hindrance, and the polymer precipitates because of the larger hydrophobicity of *cis* azobenzene moiety compared with the inclusion state, which results in a corresponding large decrease of the LCST.

Light-triggered reversible solubility behavior of the inclusion complexes

Figure 5 shows the reversible change of transmittance of 0.5% aqueous solution at presence of α-CD at a certain temperature upon UV and Vis light irradiation for 40 min, respectively, and the corresponding photographs for macroscopic transparent-opaque reversible transition and microscopic mechanism are shown in Figure 6. After 365-nm UV irradiation at a fixed
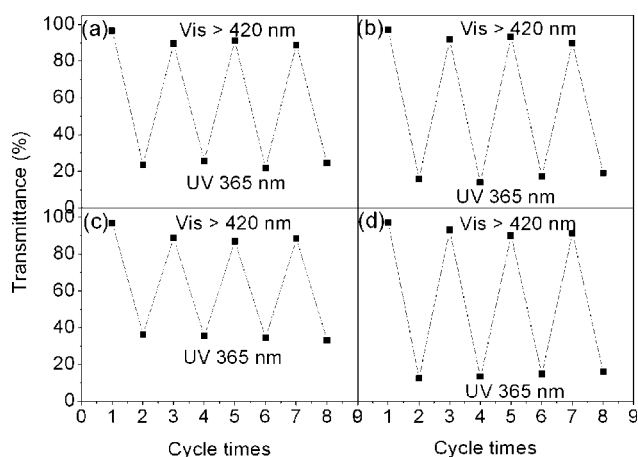

Figure 5 Transparent–opaque reversible recycle of PDMAA-*co*-PAPA/α-CD using UV and visual light irradiation, respectively. (a): PDMAA-*co*-PAPA-11.3/α-CD, *T* = 43°C; (b): PDMAA-*co*-PAPA-12.5/α-CD, *T* = 37.5°C; (c): PDMAA-*co*-PAPA-14.3/α-CD, *T* = 36°C; (d): PDMAA-*co*-PAPA-15.7/α-CD, *T* = 32°C.
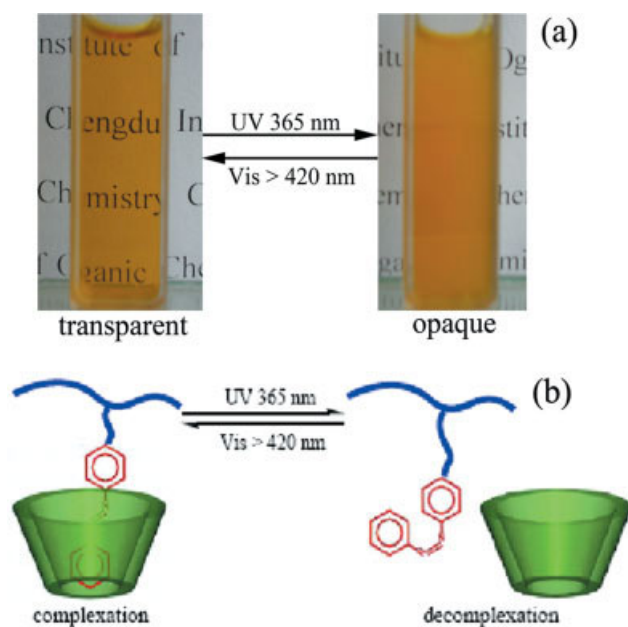
Figure 6 (a) Photographs for transparent–opaque reversible transition of PDMAA-*co*-PAPA-11.3 (5 g/L)/α-CD (4.33 g/L) upon UV and Vis light irradiation; (b) Mechanism illustration of the phase separation upon photoirradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature between two LCST such as 43°C on the PDMAA-*co*-PAPA-11.3/α-CD solution, the polymer solution becomes opaque. Meanwhile it recovers the transparent state by visual light (>420 nm) nm irradiation at the same temperature again. However, only in the solution of the polymers with azobenzene content above 11% can transparent–opaque reversible transi-

tion be observed obviously. Two conditions were required to obtain transparent–opaque reversible transition: one is significant change around LCST, another is wide temperature gap between two photostationary states.[19] 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, here which is resolved by the introduction of α-CD into the polymer solution. After UV irradiation at a fixed temperature such as 43°C on PDMAA-*co*-PAPA-11.3/α-CD, the polymer solution becomes opaque due to the azobenzene moiety decomplexing from the inner cavity of α-CD (Fig. 6). Also by visual light irradiation, α-CD forms inclusion complexes with azobenzene pendant group again, resulting in a recovery of transparent properties of polymer solution at the same 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.

Mechanism of phase separation upon photoirradiation

NOESY and ROESY are very powerful tools for investigating the host–guest interaction. Here, 2D NOESY spectra were used to investigate that α-CD interacts with the azobenzene moiety of the PDMAA-*co*-PAPA-11.3 after 365 nm UV photoirradiation. As shown in Figure 7(a), The NOESY spectrum for PDMAA-*co*-PAPA-11.3/α-CD before UV irradiation demonstrates correlation peaks between
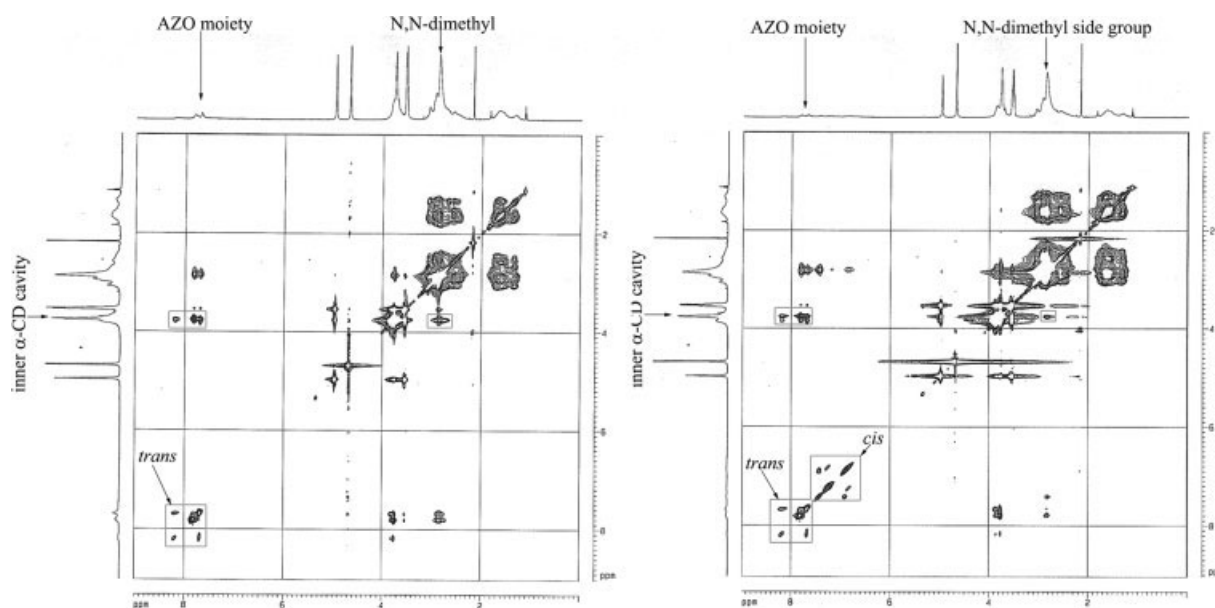

Figure 7 2D NOESY spectra of PDMAA-*co*-PAPA-11.3 (10 g/L) at presence of α-CD (8.7 g/L) in D₂O at 25°C with mixing time of 500 ms, measured before (a) and after (b) UV irradiation for 3 h.

inner 3,5-protons in α-CD cavity and protons in *trans* azobenzene and *N,N*-dimethyl moiety, indicating that α-CD includes polymer side chains both *trans* azobenzene moiety and dimethyl side group. After UV irradiation, PDMAA-*co*-PAPA-11.3/α-CD exhibits no correlation peaks between α-CD and *cis* azobenzene moiety [Fig. 7(b)], indicating that *cis* azobenzene moiety goes out of the inner cavity of α-CD. For the NOESY signals are collected for 7 h, the thermal isomerization reaction of azobenzene moiety leads to the partly recovery of *cis* to *trans* azobenzene moiety inevitably. These results are constant with the above mentioned in Figure 6. Here the interaction of α-CD with dimethyl side group is weak and hardly affects on the change of the LCST, which is concluded from the fact that α-CD has no effect on the LCST of poly(*N*-isopropylacrylamide) and poly(*N,N*-diethylacrylamide) homopolymers (date not shown). Therefore, the NOESY data well confirm in the mechanism that the transparent–opaque reversible transition is resulted from azobenzene moiety going out of the inner cavity of α-CD after UV irradiation and going into again after visual light irradiation.

CONCLUSIONS

By the introduction of α-CD into the PDMAA-*co*-PAPA aqueous systems, we have successfully obtained photoresponsive polymer systems in which photoreversible solubility change takes place after photoirradiation. After 365-nm UV irradiation, the LCST of the PDMAA-*co*-PAPA/α-CD decreases sharply, forming an opaque solution at constant temperature. Meanwhile, the opaque polymer solution becomes transparent again after visual light (>420 nm) irradiation for 40 min, due to the complex formation of α-CD with azobenzene moiety. The effect of α-CD on the properties of phase separation upon UV irradiation is more obvious in the higher azobenzene content sample. The 2D NOESY spectra confirm that α-CD forms inclusion complexes not with *cis* azobenzene moiety but *trans* azobenzene moiety. After UV irradiation, the azobenzene moiety goes out of the inner cavity of α-CD while it goes into the cavity again using visual light irradiation. 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.

References

1. Suzuki, A.; Tanaka, T. Nature 1990, 346, 345.
2. Mamada, A.; Tanaka, T.; Kungwatchakun, D.; Irie, M. Macromolecules 1990, 23, 1517.
3. Juodkazis, S.; Mukai, N.; Wakaki, R.; Yamaguchi, A.; Matsuo, S.; Misawa, H. Nature 2000, 408, 178.
4. Lee, H.; Pietrasik, J.; Matyjaszewski, K. Macromolecules 2006, 39, 3914.
5. Sumaru, K.; Ohi, K.; Takagi, T.; Kanamori, T.; Shinbo, T. Langmuir 2006, 22, 4353.
6. Xia, Y.; Yin, X.; Brurke, N. A. D.; Stoever, H. D. H. Macromolecules 2005, 38, 5937.
7. Zhang, H.; Ruehe, J. Macromolecules 2005, 38, 4855.
8. Lokuge, I. S.; Bohn, P. W. Langmuir 2005, 21, 1979.
9. Gallyamov, M. O.; Tartsch, B.; Khokholov, A. R.; Sheiko, S. S.; Boerner, H. G.; Matyjaszewski, K. Macromol Rapid Commun 2004, 25, 1703.
10. Dürr, H.; Bouas-Laurent, H. Photochromism: Molecules and Systems; Elsevier: Amsterdam, 1990.
11. Pieroni, O.; Fissi, A.; Angelini, N.; Lenci, F. Acc Chem Res 2001, 34, 9.
12. Shimoboji, T.; Ding, Z. L.; Stayton, P. S.; Hoffman, A. S. Bioconjugate Chem 2002, 13, 915.
13. Yuan, W.; Jiang, G.; Wang, J.; Wang, G.; Song, Y.; Jiang, L. Macromolecules 2006, 39, 1300.
14. Irie, M. Adv Polym Sci 1993, 110, 49.
15. Yu, Y.; Nakano, M.; Ikeda, T. Nature 2003, 425, 145.
16. Otsuki, N.; Fujioka, N.; Kawatsuki, N.; Ono, H. Mol Cryst Liq Cryst 2006, 458, 139.
17. Khoukh, S.; Oda, R.; Labrot, T.; Perrin, P.; Tribet, C. Langmuir 2007, 23, 94.
18. Kungwatchakun, D.; Irie, M. Makromol Chem Rapid Commun 1988, 9, 243.
19. Kroger, R.; Menzel, H.; Hallensleben, M. L. Makromol Chem Phys 1994, 195, 2291.
20. Szejtli, J. Chem Rev 1998, 98, 1743.
21. Easton, C. J.; Lincoln, S. F. Modified Cyclodextrins: Scaffolds and Templates for Supramolecular Chemistry; Imperial College Press: London, 1999.
22. Zheng, P. J.; Hu, X.; Zhao, X. Y.; Li, L.; Tam, K. C.; Gan, L. H. Macromol Rapid Commun 2004, 25, 678.
23. Hu, X.; Zheng, P. J.; Zhao, X. Y.; Li, L.; Tam, K. C.; Gan, L. H. Polymer 2004, 45, 6219.
24. Takashima, Y.; Nakayama, T.; Miyauchi, M.; Kawaguchi, Y.; Yamaguchi, H.; Harada, A. Chem Lett 2004, 33, 890.
25. Tomatsu, I.; Hashidzume, A.; Harada, A. Macromol Rapid Commun 2005, 26, 825.
26. Tomatsu, I.; Hashidzume, A.; Harada, A. Macromolecules 2005, 38, 5223.
27. Tomatsu, I.; Hashidzume, A.; Harada, A. J Am Chem Soc 2006, 128, 2226.
28. Moniruzzaman, M.; Fernando, G. F.; Talbot, J. D. R. J Polym Sci Part A: Polym Chem 2004, 42, 2886.
29. Dyer, J. R. In Applications for Absorption Spectroscopy or Organic Compounds; Prentice Hall: Englewood Cliffs, NJ, 1965. p 139.