

Doubly Photoresponsive and Water-Soluble Block Copolymers: Synthesis and Thermosensitivity

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ABSTRACT: We report the synthesis and investigation of a new type of photoresponsive block copolymers (BCPs). They were designed to comprise two water-soluble polymers containing two different photoisomerizable moieties (either azobenzene and spiropyran or two different azobenzenes), with the two constituting blocks that, when separated, exhibit a lower critical solution temperature (LCST) in water and can shift their LCST in opposite directions upon photoisomerization (decrease of LCST for one polymer and increase for the other). A variety of such doubly photoresponsive BCPs were synthesized using either azobenzene- or spiropyran-containing poly(*N,N*-dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM) and poly[methoxydi(ethylene glycol) methacrylate] (PDEGMA). Their thermal phase transition behaviors in aqueous solution before and after simultaneous photoreactions on the two blocks were investigated in comparison with

their constituting blocks, by means of solution transmittance (turbidity) and variable-temperature ¹H NMR measurements. The results show that BCPs displayed a single LCST whose shift upon two photoisomerizations appeared to be determined by the competing and opposing photoinduced effects on the two blocks. Moreover, optically controlling the relative photoisomerization degrees of *trans* azobenzene-to-*cis* azobenzene and spiropyran-to-merocyanine could be used to tune the LCST of BCP solution. This study demonstrates the potential of exploring a more complex photoreaction scheme to optically control the solution properties of water-soluble thermosensitive BCPs. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 4055–4066, 2010

KEYWORDS: block copolymers; photoresponsive polymer; stimuli-responsive polymer; stimuli-sensitive polymers; synthesis

INTRODUCTION Photoresponsive block copolymers (BCPs) have received an increased attention in recent years. Generally, this type of BCPs is obtained by having one block that bears a number of photochromic groups that can undergo a photoreaction upon absorption of light (isomerization, dimerization, or cleavage). Through rational BCP design, the photoreaction can be utilized to promote a specific property or to achieve a particular function for the BCP, both in solution^{1,2} and in the solid state.^{3–5} Among the noticeable examples are photocontrollable BCP micellar aggregates in solution^{1,2} and photocontrolled alignment or patterning of microphase-separated cylindrical domains in thin films.^{3(b),4(b,c)} These recent achievements suggest that the full potential interest of photoresponsive BCPs remains to be unveiled, and for this, more fundamental studies are needed. We envision that one possible new direction would be to explore BCPs subjected to a more complicated photoreaction scheme and to investigate the effect on their behaviors. As a first step towards this end, we report herein the synthesis and study of a variety of new BCPs whose two blocks contain

each a different chromophore in their structure (Fig. 1). When exposed to light, two photoreactions can occur simultaneously and exert effect on the two blocks and the BCP as a whole. We refer to this type of BCPs as doubly photoresponsive BCPs.

To investigate the possible effect of the double-photoreaction on the behaviors of BCPs, we chose in this work to synthesize diblock copolymers that consisted of two water-soluble polymers exhibiting a lower critical solution temperature (LCST). An example of our synthesized BCPs is shown in Figure 1, being built up with a poly(*N,N*-dimethylacrylamide) (PDMA) block and a poly(*N*-isopropylacrylamide) (PNIPAM) block that bear a number of azobenzene and spiropyran side groups, respectively. As depicted, upon absorption of UV light, both photochromic molecules undergo a photoisomerization reaction, with azobenzene in the elongated *trans* form (*trans* azo) converting to the bent *cis* isomer (*cis* azo) on the PDMA block, and the neutral spiropyran (SP) switching to the charged merocyanine (MC) form on the PNIPAM block.

Additional Supporting Information may be found in the online version of this article. Correspondence to: Y. Zhao (E-mail: yue.zhao@usherbrooke.ca)
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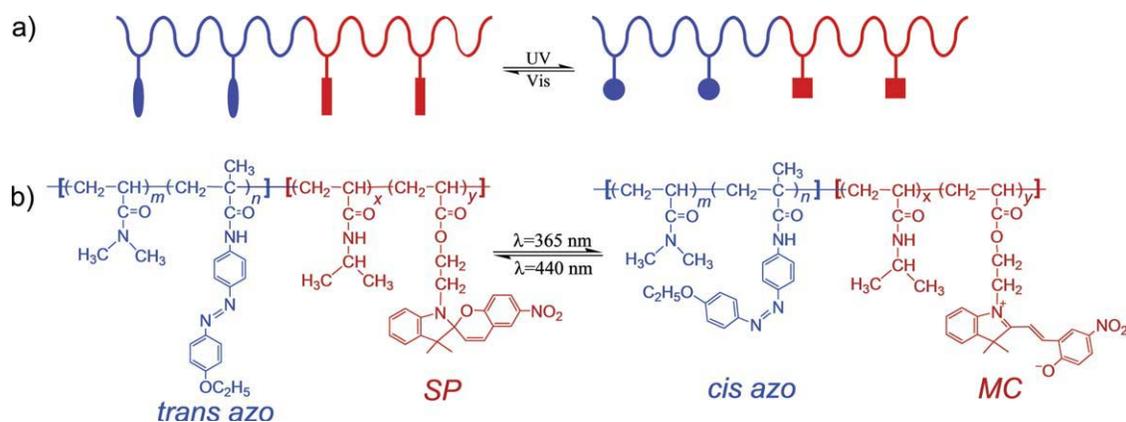


FIGURE 1 (a) Schematic of doubly photoresponsive block copolymers. (b) Chemical structure of a synthesized diblock copolymer whose azobenzene and spiropyran side groups can undergo reversible *trans-cis* and spiropyran-merocyanine photoisomerizations upon exposure to UV and visible light.

Since the two photoisomerizations are reversible, upon absorption of visible light, the reversed photoreactions could bring the two chromophores back to their initial forms. One would imagine that the two photoreactions could have coupled effects on the BCP in aqueous solution and their interplay may generate more complicated behaviors. There are many reports on the incorporation of either azobenzene⁶ or spiropyran⁷ in water-soluble polymers and investigation of the chromophore's reversible photoisomerization on the polymer properties in aqueous solution, but the concept of bringing together two photosensitive water-soluble polymers to form doubly photoresponsive BCPs has not been proposed and studied. This article reports the design and synthesis of a variety of such doubly photoresponsive BCPs, as well as an investigation of the effect of double-photoreaction on the thermosensitivity (thermal phase transition) of these water-soluble BCPs characterized by their LCST.

RESULTS AND DISCUSSION

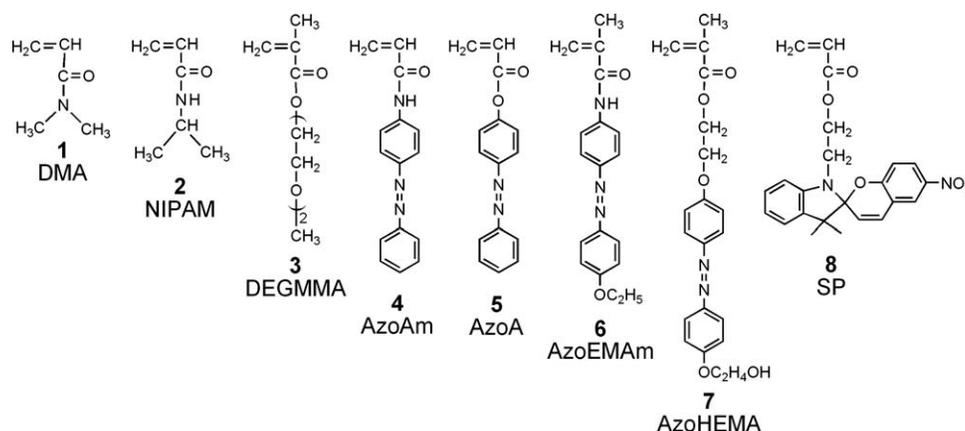
Design and Synthesis of Block Copolymers

A polymer like PNIPAM is soluble (hydrated) in water below its LCST and becomes insoluble (dehydrated) above the LCST. The incorporation of photochromic groups like azobenzene onto such a polymer makes it possible to change the LCST by the photoreaction. Generally, the *trans*-to-*cis* isomerization of azobenzene results in a small increase in LCST, being generally attributed to an increase in polarity with *cis* azo groups.⁶ An interesting exception is DMA copolymerized with an azobenzene-containing (meth)acrylamide monomer (Fig. 1), for which the LCST of the polymer shifts to lower temperatures upon the *trans*-to-*cis* isomerization. This peculiar behavior was thought to be related to the amide groups that could favor intramolecular hydrophobic interactions of pendant groups.⁸ In designing our first doubly photoresponsive water-soluble BCPs, on the basis of the above knowledge, we chose to use two chromophores whose photoreactions might result in LCST shift of the two blocks in the opposite directions, i.e., decrease in LCST for one block

and increase for another. With the BCP in Figure 1, the *trans* azo-to-*cis* azo and the SP-to-MC isomerization induced by UV light might shift the LCST of PDMA to lower temperatures and the LCST of PNIPAM to higher temperatures, respectively. Investigating the possibility of optically controlling the solubility of each block in water is an appealing example of exploring BCPs with a more complicated photoreaction scheme to achieve a more sophisticated photocontrol of the polymer properties. This is the main rationale behind the design of the BCPs reported herein.

Details on the monomer and polymer syntheses are given in Supporting Information. Scheme 1 shows the chemical structures of the monomers used. DMA **1**, NIPAM **2**, and methoxydi(ethylene glycol) methacrylate (DEGMMA) **3** were used to copolymerize with a chromophore-containing monomer **4–8** to obtain photoresponsive polymers with a LCST. Of the comonomers **4–8**, to our knowledge, **6** and **7** are new while others are known in the literature.^{6,7} PDMA, PNIPAM, and PDEGMMA are frequently used to build thermosensitive BCPs.⁹ 4-(Acrylamide)azobenzene **4**, 4-(acrylate)azobenzene **5**, 4-ethoxy-4'-(methacrylamide)azobenzene **6**, and 4-(2-hydroxyethoxy)-4'-(2-methacryloxyethoxy)azobenzene **7** are azobenzene-containing monomers, while 5-{1,3-dihydro-3,3-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]}ethyl acrylate (**8**) is the monomer bearing SP moiety. In constructing a BCP, the random copolymer made from **1** and **4**, or **1** and **6**, was used as the block whose LCST would be reduced upon the *trans*-to-*cis* isomerization of azobenzene groups, while the other block was prepared by using either **2** or **3** copolymerized with **5** or **7** or **8**, for which the photoisomerization would lead to an increase in LCST. In all cases, the content of the photochromic groups in either a random copolymer or in one block of a BCP was readily controlled by changing the feed ratio of the two monomers.

Scheme 2 shows the syntheses of a number of photoresponsive random copolymers by means of reversible addition-fragmentation chain transfer polymerization (RAFT). On the one hand, some of them were utilized as the macromolecular

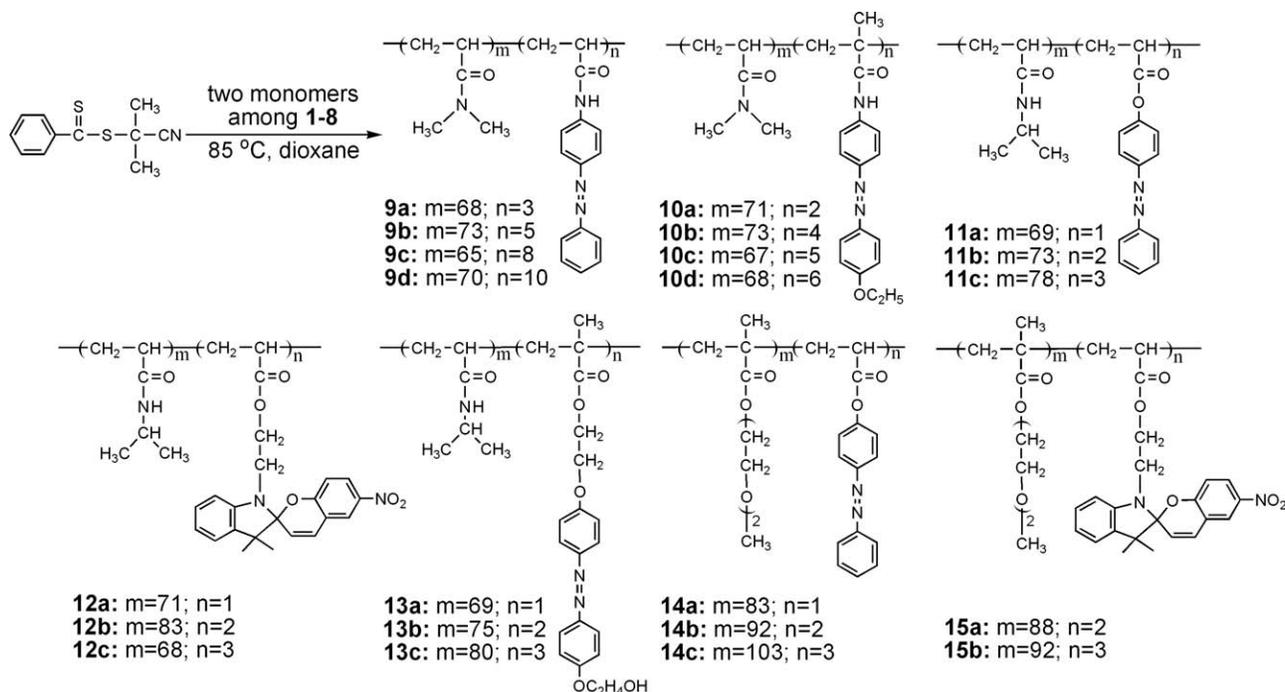


SCHEME 1 Chemical structures and acronyms of the monomers. DMA, *N,N*-dimethylacrylamide; NIPAM, *N*-isopropylacrylamide; DEGMMA, methoxydi(ethylene glycol) methacrylate; AzoAm, 4-(acrylamide)azobenzene; AzoA, 4-(acrylate)azobenzene; AzoEMAm, 4-ethoxy-4'-(methacrylamide)azobenzene; AzoHEMA, 4-(2-hydroxyethoxy)-4'-(2-methacryloxyethoxy)azobenzene; SP, 5-(1,3-dihydro-3,3-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole])ethyl acrylate.

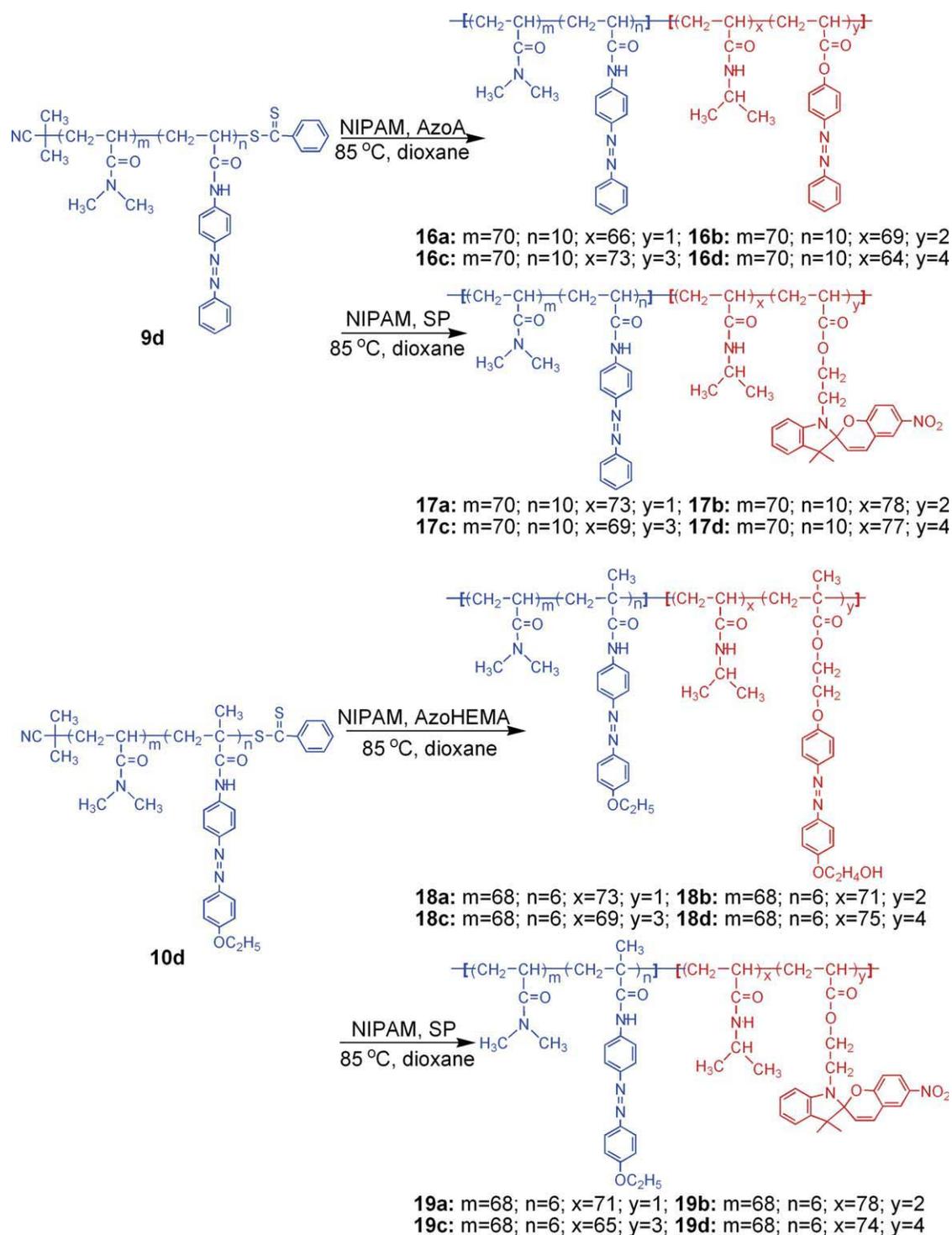
chain transfer agent (macro-CTA) to grow the second photo-responsive block to obtain BCPs, in particular **9d**, **10d**, **14c**, and **15b**. On the other hand, the thermosensitivity (LCST) and the effect of a photoreaction were investigated for some of these random copolymers to compare the behaviors of a BCP with its constituting two blocks.

Two groups of doubly photoresponsive water-soluble BCPs were synthesized by using RAFT, namely PDMA-*b*-PNIPAM and PDMA-*b*-PDEGMMA. Their syntheses are summarized in Schemes 3 and 4, respectively. For both series, while PDMA always contains azobenzene (meth)acrylamide side groups, the other block, PNIPAM or PDEGMMA, contains either a dif-

ferent azobenzene chromophore (acrylate or methacrylate comonomer units) or SP groups. The numbers of monomer units for the random and BCPs synthesized in Schemes 2–4 were determined from 600 MHz ^1H NMR spectra by comparing the relative integrals of the resonance peaks attributed to each monomer. Figure 2 shows an example of how NMR spectra were used to determine BCP compositions. In this case, **10d** (P(DMA-*co*-AzoEMAm)) was used as macro-CTA to obtain BCP **19b** (P(DMA-*co*-AzoEMAm)-*b*-P(NIPAM-*co*-SP)). In **10d**, the resonance signal from chain transfer agent at chain end (peak *a*: 7.30–7.40 ppm, 2H) was used as a label to calculate the numbers of units of DMA (peak *b*: 2.40–



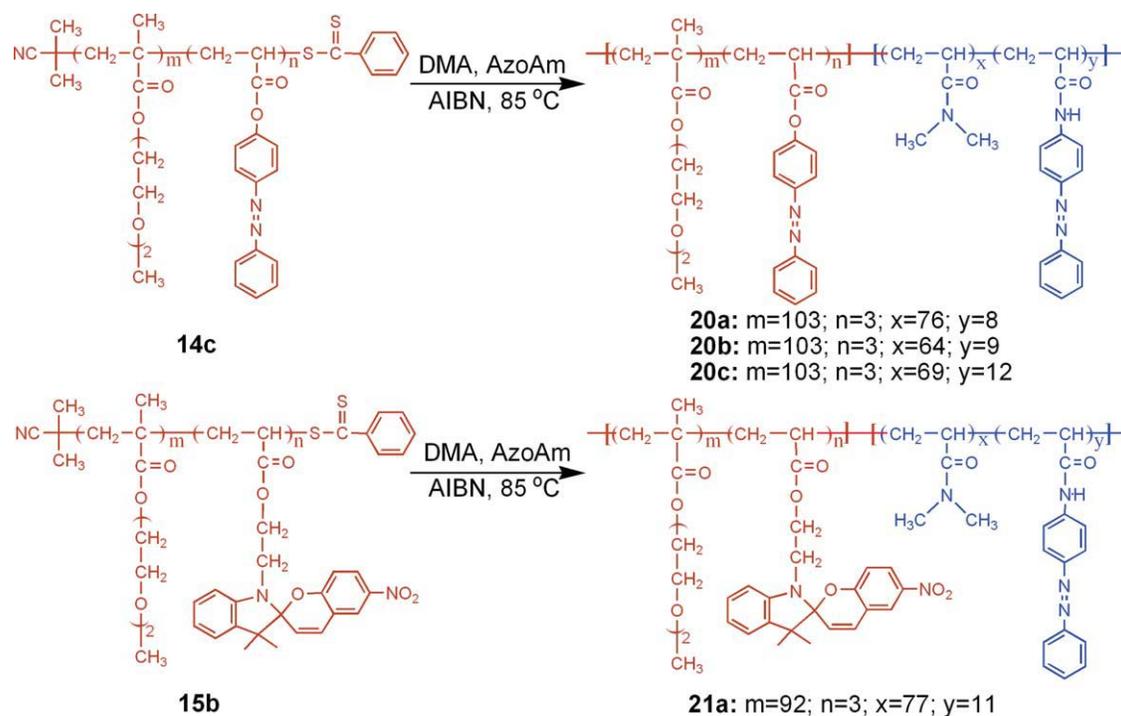
SCHEME 2 Synthesis of photoresponsive random copolymers through RAFT polymerization (chain end groups are omitted).



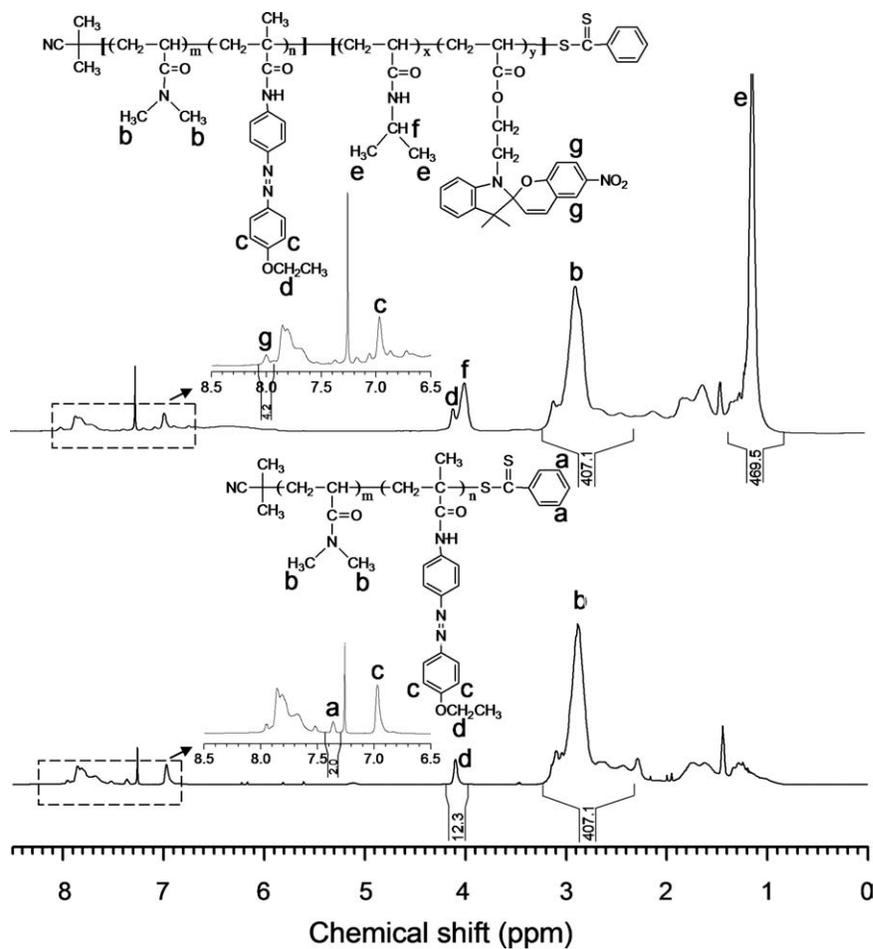
SCHEME 3 Synthesis of doubly photoresponsive block copolymers based on PDMA and PNIPAM (chain end groups are omitted). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3.40 ppm, 6H) and AzoEMAM (peak c: 4.0–4.15 ppm, 2H) by comparing the peak integrals. For BCP **19b**, the resonance signal of NIPAM (peak e: 0.8–1.2 ppm, 6 H) was compared to that of DMA (peak b) to yield the number of NIPAM units, while similarly, the ratio of peak integrals of SP (peak g: 7.95–8.10 ppm, 2 H) and DMA (peak b) allowed the number

of SP units to be estimated. To confer good water solubility to BCPs, the contents of hydrophobic photochromic monomers were purposely kept low; because of this, the numbers of azobenzene- and SP-containing comonomer units as determined from NMR spectra contained an amount of uncertainty. In the case discussed with Figure 2, the number of SP



SCHEME 4 Synthesis of doubly photoresponsive block copolymers based on PDMA and PDEGMMA (chain end groups are omitted). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]



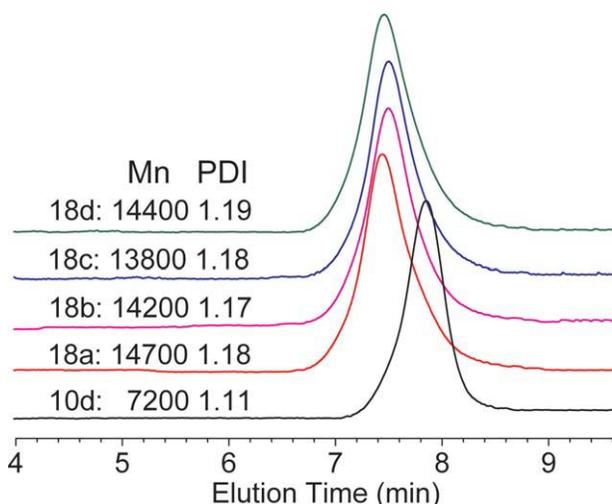


FIGURE 3 SEC curves of a macro-CTA and a series of BCPs obtained by using this macro-CTA, their number-average molecular weights and polydispersity indices with respect to polystyrene standards being indicated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

units calculated from the peak integrals was 2.1, which was rounded to 2 as shown in Scheme 3. Similar approximation about the decimal numbers was applied to other samples. It can be seen from Schemes 3 and 4, for most BCPs, the content of photochromic groups on the respective block, with respect to the major monomer, is between 1 and 15% by mole. Figure 3 shows representative examples of SEC curves comparing a macro-CTA **10d** with some resulting BCPs **18a–d**. By adjusting the feed ratio of the two monomers for the second block and keeping the same reaction conditions, this series of BCPs were designed to have a second block with a similar length while differing in the content of azobenzene groups. Their similar molecular weights were confirmed by the SEC measurements as all samples exhibited a similar elution time, with a narrow polydispersity index (PDI) that increased slightly as compared to the macro-CTA.

Photoisomerization and Thermosensitivity: BCPs Based on PDMA and PNIPAM

Using our doubly photoresponsive BCPs, the effect of the photoreactions on the BCP water solubility was investigated. In what follows, we report representative results obtained with a number of BCPs that show the main features in this regard. Unless otherwise stated, the transmittance measurements used to determine the cloud point (LCST behavior) were carried out by using a polymer concentration of 2 mg mL⁻¹, and the transmittance data were taken at 700 nm that is sufficiently apart from the absorptions of the chromophores. The solution heating rate was about 0.5 °C/min. UV-vis spectra of a diluted polymer concentration of 0.1–0.2 mg mL⁻¹ were recorded to monitor the progress of photoreactions. Summarized in Figure 4 are the results obtained with BCP **19b** and, for comparison, the two constituting blocks,

samples **10d** and **12b**. First, for PDMA bearing azobenzene groups, P(DMA₆₈-co-AzoEMA₆), from the cloud point, the solubility change of the polymer is visible showing a LCST at about 29 °C [Fig. 4(a)]. After resolubilization at low temperature (0 °C), the solution was exposed to UV light for the *trans*-to-*cis* photoisomerization of azobenzene. From the UV-vis spectra [Fig. 4(b)] and the decrease in absorption of *trans* azo at 365 nm, about 80% of *trans* azo were converted to *cis* azo under the used irradiation conditions. After turning off the UV light, the solution was subjected to heating; the polymer displayed a LCST almost 10 °C lower than that prior to the photoisomerization [Fig. 4(a)]. This peculiar photoinduced decrease of LCST, with azobenzene acrylamide, is consistent with a previous report in the literature.⁷ The *cis* isomer of this azobenzene chromophore is stable against thermal relaxation, most *cis* azo remained after the measurements (~70% *cis* azo even after 30 min at 50 °C). Secondly, for PNIPAM containing 2% of SP groups, P(NIPAM₈₃-co-SP₂), the LCST appeared at 30 °C [Fig. 4(c)]. After UV irradiation at 0 °C for the SP-to-MC photoisomerization, the formation of MC can be seen from the appearance of its absorption band at 535 nm [Fig. 4(d)]. Again, after the photoisomerization reached the photostationary state [the inset of Fig. 4(d) shows the increase in absorbance of MC moieties], UV light was turned off and the solution of PNIPAM with MC was heated; the apparent LCST shifted to a higher temperature, while the related decrease in transmittance was much smaller than the solution of azobenzene-containing PDMA. This result shows that with charged MC groups, the dehydration of PNIPAM occurs at a higher temperature; however, the increased water solubility seems to prevent PNIPAM chains from forming large aggregates. As compared to azobenzene, MC groups are thermally less stable. At the end of the heating process (50 °C), almost all MEs were relaxed back to SP. But the thermal relaxation mainly took place above 40 °C, as indicated by UV-vis spectra and from visual observation (disappearance of the color of MC). These results confirm that the two homopolymers display an opposite LCST shift after the photoreactions of the chromophores incorporated in their structures. Now, what happens with the diblock copolymer **19b**, P(DMA₆₈-co-AzoEMA₆)-*b*-P(NIPAM₇₈-co-SP₂), whose constituting blocks are basically the two random copolymers investigated (the PNIPAM block is slightly shorter than the homopolymer)?

Prior to the photoreactions, the transmittance measurements showed a LCST at about 30 °C [Fig. 4(e)]. This is no surprise since the two blocks, when separated, have a similar LCST. The solution was then irradiated with UV light at 0 °C, and the occurrence of the two photoisomerization reactions, i.e., *trans* azo-to-*cis* azo on the PDMA block and SP-to-MC on the PNIPAM block, could be seen from the UV-vis spectra [Fig. 4(f)]. Even though the isomerization degrees could not be determined with certainty due to the overlap of the absorptions of *trans* azo and SP in the 360 nm region, it is reasonable to assume similar extents of the photoreactions to the two separated blocks under the used irradiation conditions [reaching the photostationary states as shown by the

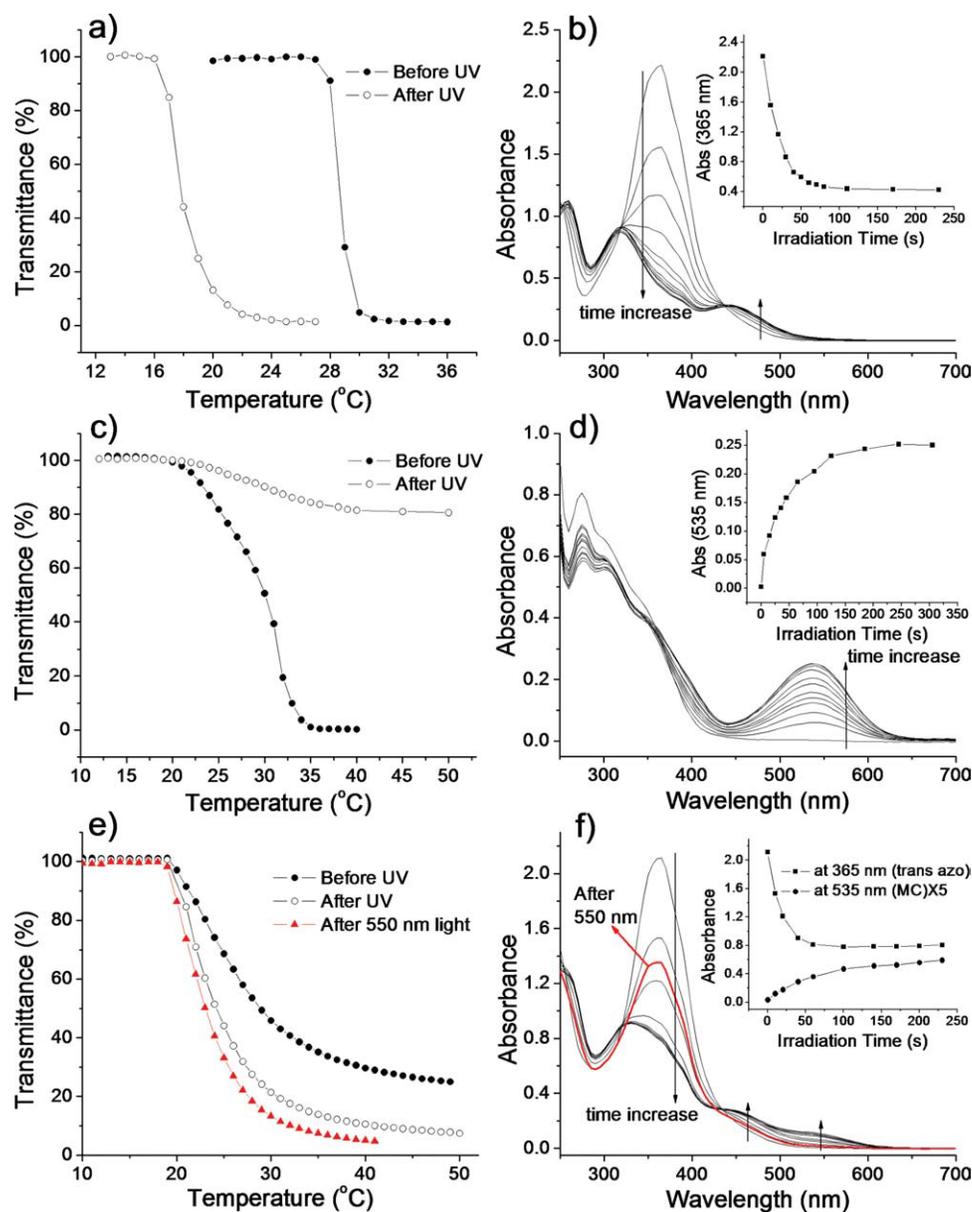


FIGURE 4 Transmittance versus temperature for aqueous solutions (polymer concentration: 2 mg mL⁻¹) before and after UV light-induced photoisomerization of pendant photochromic groups, as well as absorption spectra upon UV irradiation inducing the photoisomerization (solutions diluted to 0.1–0.2 mg mL⁻¹), with the inset showing the change in absorbance of either *trans* azobenzene or merocyanine groups. (a) and (b): P(DMA₆₈-co-Azo-EMAm₆); (c,d) P(NIPAM₈₃-co-SP₂); (e,f) P(DMA₆₈-co-AzoEMAm₆)-b-P(NIPAM₇₈-co-SP₂). In the inset of (f), the absorbance at 535 nm is multiplied by 5 for the sake of clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

inset of Fig. 4(f)]. We note that the SP-to-MC photoisomerization was also indicated by an increased fluorescence emission of MC groups upon UV irradiation of the BCP solution (Supporting Information). When this BCP solution after photoreactions was subjected to heating, the transmittance change indicated one LCST shifting to a lower temperature by 5 °C. It appears that the photoinduced change in LCST of the BCP was dominated by the azobenzene-containing PDMA block. However, as compared to P(DMA₆₈-co-AzoEMA₆), the decrease of LCST for BCP is significantly smaller. This indicates the effect of the PNIPAM block whose MC groups could exert an opposite LCST shift. The immediate conclusion that can be drawn from these results is that the two blocks are coupled each other and interact between them. In other words, the two photoreactions could not drive the two blocks to behave independently from each other. If they

could, one would expect two separate LCST, with one belonging to the PDMA block at a much lower temperature and one arising from the PNIPAM block at a higher temperature than the LCST before the photoreactions. The results suggest that upon heating the phase separation of azobenzene-containing PDMA was hindered by the more water soluble MC-containing PNIPAM block; when the phase transition occurs, both blocks become insoluble and contribute to the observed single LCST. Using this BCP solution, another experiment was also conducted to demonstrate the increasing complexity and possibility of exploring two different photoreactions on the two blocks. As mentioned, exposure to UV light at 365 nm generates both *cis* azo and MC since *trans* azo and SP groups absorb in a similar wavelength region. However, the absorption of *cis* azo (peaked at 450 nm) is significantly separated from the maximum absorption of MC (535 nm),

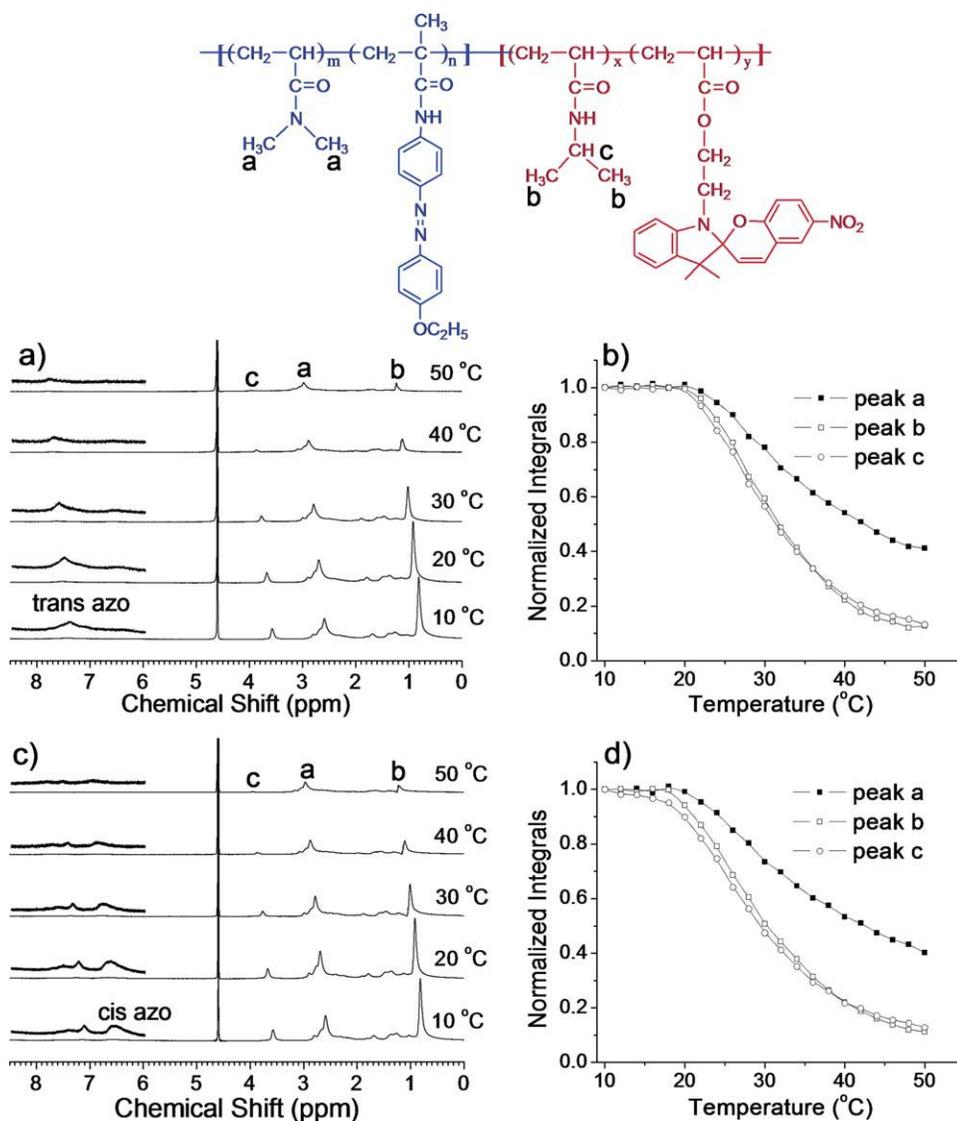


FIGURE 5 Variable-temperature ^1H NMR spectra of $\text{P}(\text{DMA}_{68}\text{-}co\text{-AzoEMA}_6)\text{-}b\text{-P}(\text{NIPAM}_{78}\text{-}co\text{-SP}_2)$ in D_2O (2 mg mL^{-1}) and changes in normalized integrals of labeled resonance peaks as a function of temperature. (a,b) before UV irradiation; (c,d) after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which makes it possible to optically convert MC back to SP on the PNIPAM block while retaining a significant fraction of *cis* azo on the PDMA block. Therefore, after UV irradiation of the BCP solution at 0°C , it was exposed to a monochromatic visible light at 550 nm . The MC-to-SP backisomerization on the PNIPAM block can be seen from the total disappearance of the absorption band of MC, while the remaining population of *cis* azo on the PDMA block is indicated by the non-completely recovered absorption of *trans* azo [spectrum marked in red in Fig. 4(f)]. With this optical treatment, understandably, the PNIPAM block with SP groups had a less important solubilizing effect on the PDMA block; consequently, even with a reduced *cis* azo population, upon heating this solution showed a lower LCST than the solution with both *cis* azo and MC groups on the two blocks [curve marked in red in Fig. 4(e)]. This result shows the possibility of optically controlling the relative photoisomerization degrees of the two chromophores on their respective blocks, which could be used to tune the LCST of the BCP solution.

Variable-temperature ^1H NMR spectra were recorded for the BCP in D_2O , with a temperature interval of 2°C . As shown in Figure 5, the results confirmed the single phase transition temperature for the two blocks, both before and after the photochemical reactions. In Figure 5(a), NMR spectra of the BCP solution prior to UV irradiation at some chosen temperatures are shown with characteristic resonance signals of PDMA and PNIPAM indicated. The decreased solubility in water upon heating can be seen from the reduced intensity of the resonance signals due to aggregation of polymer chains. In Figure 5(b), the normalized integrals of the peak of PDMA at $\sim 2.6 \text{ ppm}$ and those of PNIPAM at ~ 0.8 and 3.6 ppm are plotted versus temperature; the curves are similar, indicating that the solubility of the two blocks changes in a concerted way. The results obtained with the BCP solution after UV irradiation, are shown in Figure 5(c,d), leading to the same observation and conclusion. Overall, the ^1H NMR measurements corroborate well the results of the transmittance changes [Fig. 4(e)]. The BCP bearing *cis* azo and MC groups displayed a LCST lower than that

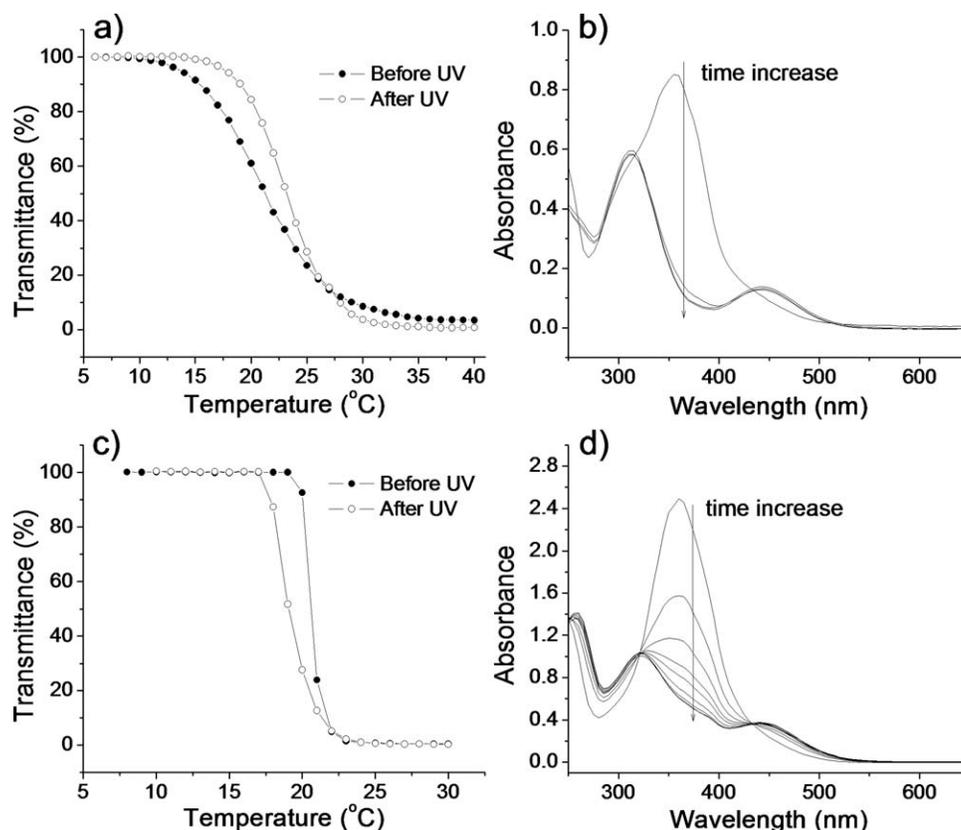


FIGURE 6 Transmittance versus temperature for aqueous solutions (polymer concentration: 2 mg mL⁻¹) before and after UV light-induced photoisomerization of pendant photochromic groups, as well as absorption spectra upon UV irradiation inducing the photoisomerization (solutions diluted to 0.1–0.2 mg mL⁻¹). (a,b) P(NIPAM₇₅-*co*-AzoHEMA₂); (c,d) P(DMA₆₈-*co*-AzoEMAm₆)-*b*-P(NIPAM₇₁-*co*-AzoHEMA₂). Data of P(DMA₆₈-*co*-AzoEMAm₆) are given in Figure 4(a).

of the BCP with *trans* azo and SP groups. The photoisomerization of azobenzene groups can also be noticed from the NMR spectral changes, with the relative thermal stability of *cis* azo corroborating with the observations from UV-vis spectra. Resonance signals of SP and MC groups cannot be detected, likely due to their small concentrations in the BCP.

Figure 6 shows the results obtained with BCP **18b**, P(DMA₆₈-*co*-AzoEMAm₆)-*b*-P(NIPAM₇₁-*co*-AzoHEMA₂). This BCP has the same PDMA block as BCP **19b** but the PNIPAM block contains azobenzene side groups instead of SP. As in the previous case, the two constituting block, when separated, showed opposite LCST shifts upon the *trans*-to-*cis* photoisomerization of azobenzene. Although the LCST of P(DMA₆₈-*co*-AzoEMAm₆) decreased with *cis* azo [Fig. 4(a)], the conversion of *trans* azo to *cis* azo resulted in a small increase in LCST for P(NIPAM₇₅-*co*-AzoHEMA₂) [Fig. 6(a,b)]. For the corresponding BCP, again, the solution displayed a single LCST before irradiation with UV light. After UV irradiation, the simultaneous photoisomerizations of azobenzene groups on the two blocks did not give rise to separate manifestation of LCST for the two blocks. The apparently single LCST was decreased by about 3 °C with *cis* azo groups on the two blocks [Fig. 6(c,d)]. Variable ¹H NMR spectra confirmed the single LCST (spectra not shown).

Photoisomerization and Thermosensitivity: BCPs Based on PDMA and PDEGMMA

For the second group of BCPs, being composed of PDMA and PDEGMMA (Scheme 4), their apparent thermal phase transi-

tion behaviors before and after photoreactions, are different from BCPs composed of PDMA and PNIPAM. The results of the transmittance measurements with BCP **20b**, P(DMA₆₄-*co*-AzoAm₉)-*b*-P(DEGMMA₁₀₃-*co*-AzoA₃) and the two constituting blocks are shown in Figure 7. For the two blocks, a LCST could clearly be observed before and after the UV irradiation. Similar to the other systems discussed above, the photoisomerization resulted in a decrease in LCST for P(DMA₇₀-*co*-AzoAm₁₀) [Fig. 7(a,b)] and an increase in LCST for P(DEGMMA₁₀₃-*co*-AzoA₃) [Fig. 7(c,d)]. Note that the *trans* isomers of the two azobenzene moieties absorb at different wavelengths, around 350 nm for AzoAm (azobenzene acrylamide) and 325 nm for AzoA (azobenzene acrylate). With the BCP, surprisingly, only a very small transmittance change could be observed upon solution heating, both without and with UV irradiation [Fig. 7(e)]. The *trans*-to-*cis* isomerization of the two types of azo groups on the two blocks under UV light was observable from the decrease in absorption of the broad absorption band due to the overlap of the two azobenzenes [Fig. 7(f)], but the photoreactions resulted in no noticeable effect on the behavior of the solution. Despite the apparent solubility of the BCP over the entire temperature range investigated, variable-temperature ¹H-NMR measurements revealed the thermally induced solubility change of the BCP (Fig. 8). As temperature increased to above 20 °C, the various resonance peaks assigned to PDEGMMA (3–4 ppm) and that of PDMA (2.6 ppm) showed reduced areas, indicating dehydration of the two blocks upon LCST. The fact that the solution transmittance remained high hints for the

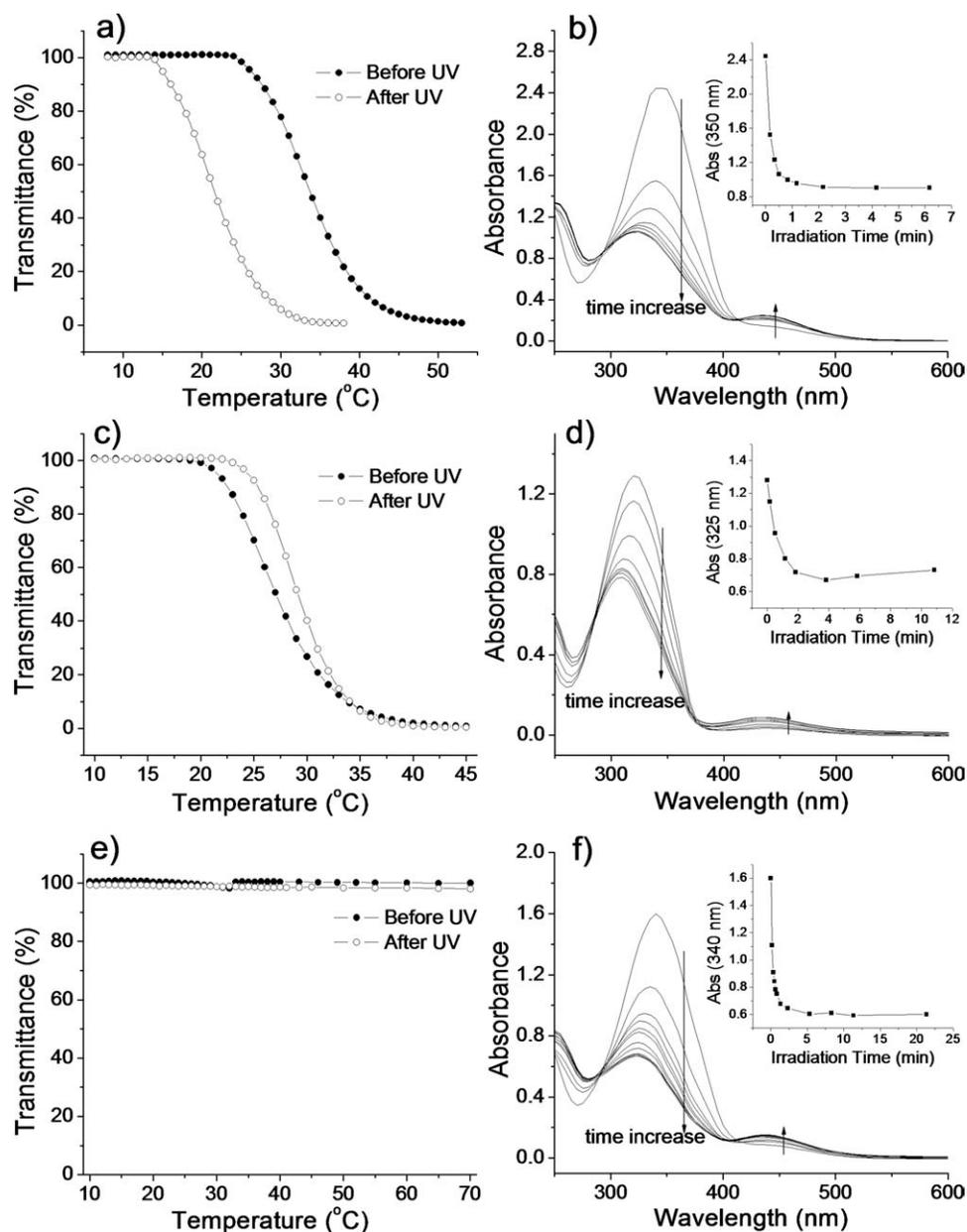


FIGURE 7 Transmittance versus temperature for aqueous solutions (polymer concentration: 2 mg mL⁻¹) before and after UV light-induced photoisomerization of pendant photochromic groups, as well as absorption spectra upon UV irradiation inducing the photoisomerization (solutions diluted to 0.1–0.2 mg mL⁻¹). (a,b) P(DMA₇₀-co-AzoAm₁₀); (c,d) P(DEGMMA₁₀₃-co-AzoA₃); (e,f) P(DMA₆₄-co-AzoA₃)-*b*-P(DEGMMA₁₀₃-co-AzoA₃).

formation of small BCP micelles that may have stable dispersion in water, preventing formation of large BCP aggregates. Indeed, DLS and TEM measurements confirmed the presence of BCP micellar aggregates with diameters in the range of 20–40 nm (Supporting Information). An interesting feature revealed by the ¹H NMR results can be noticed from both the NMR spectra and the plots of normalized peak integrals versus temperature [Fig. 8(a,b)]. Above LCST, as temperature further increased, the resonance signals from protons close to chain backbone of PDEGMMA (methyl group at ~0.6 ppm and the methylene unit next to ester at ~3.9 ppm) became increasingly weak and broadened; by contrast, the signals from other parts on the methyl ethylene glycol side chain of PDEGMMA and from PDMA turned to be more prominent and, at 50 °C, almost recovered to their initial values below LCST. This result indicates that the BCP micelles formed

above LCST could undergo a continuous structural reorganization, which likely results in a more compact and hydrophobic core mainly composed of PDEGMMA chain backbone and hydrophilic corona (hydrated parts) comprising ethylene glycol side chains of PDEGMMA and PDMA. Interestingly, with *cis* azo groups on the two blocks after the photoisomerization, the BCP self-assembly behaviors were not affected [Fig. 8(c,d)], even though the LCST seemed to decrease slightly based on the diminution of the resonance signals. Similar results were obtained with BCP **21a** with azobenzene and SP groups on the two blocks.

The result in Figure 9 is worth being mentioned. When a salt (5 mM NaCl) was added in the same BCP solution as in Figure 7(e), a LCST could clearly be observed from an increased transmittance change. The reduced water solubility

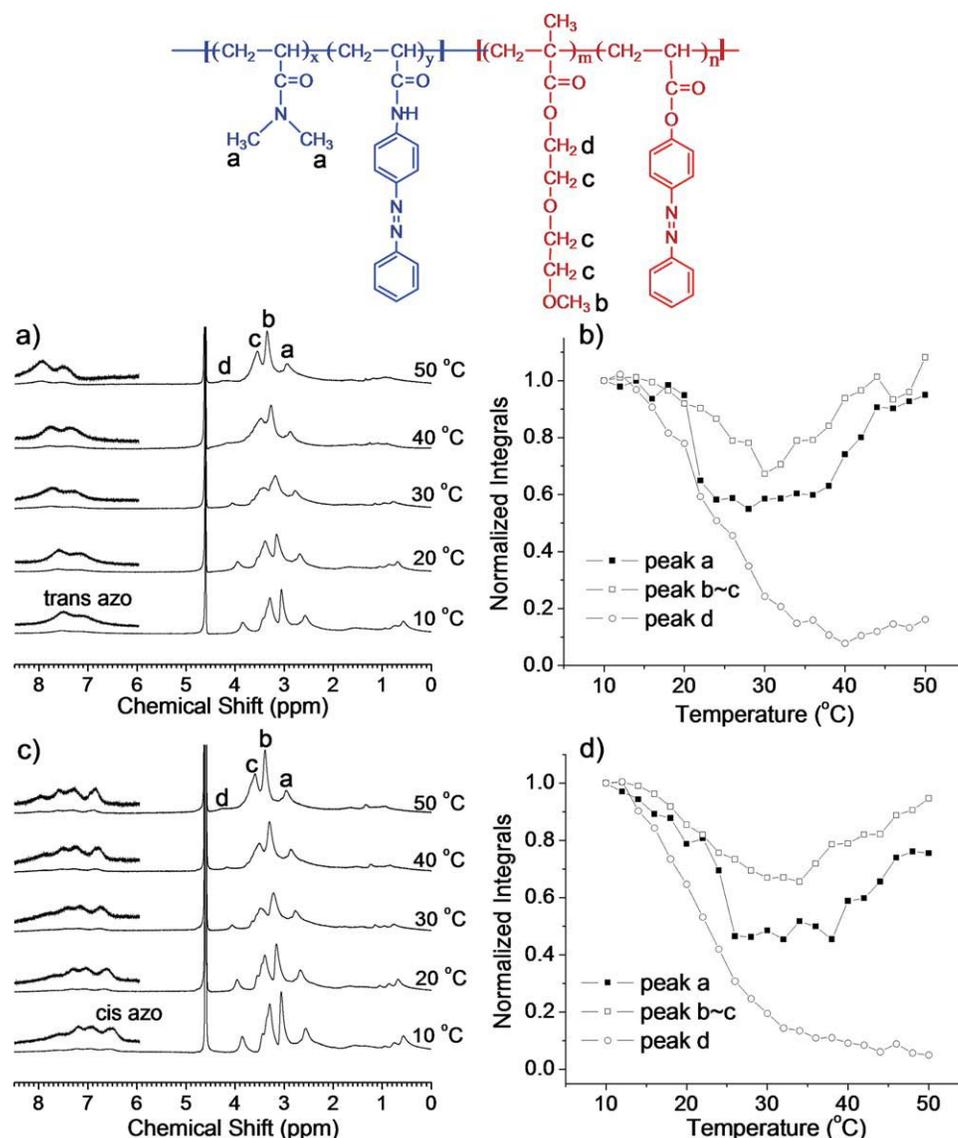


FIGURE 8 Variable-temperature ^1H NMR spectra of $\text{P}(\text{DMA}_{64}\text{-co-AzoAm}_9)\text{-}b\text{-P}(\text{DEGMA}_{103}\text{-co-AzoA}_3)$ in D_2O (2 mg mL^{-1}) and changes in normalized integrals of labeled resonance peaks as a function of temperature. (a,b): before UV irradiation; (c,d) after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

should arise from the salting-out effect. For this BCP solution, after *trans*-to-*cis* photoisomerization of azobenzene groups on the two blocks, a slight decrease of LCST ($\sim 2^\circ\text{C}$) could be noticed. This lowering of LCST of BCP is much smaller than that of the constituting block $\text{P}(\text{DMA}_{70}\text{-co-AzoAm}_{10})$ [Fig. 7(a)], which reveals again the influence of the other block, $\text{P}(\text{DEGMA}_{103}\text{-co-AzoA}_3)$, which has an opposite LCST shift upon photoisomerization [Fig. 7(b)].

A main feature has emerged from our investigations on the two groups of doubly photoresponsive BCPs, PDMA-*b*-PNIPAM and PDMA-*b*-PDEGMA, bearing either azobenzene and SP or two azobenzenes for photoreactions. That is, the opposite photoinduced shift of LCST of the two constituting blocks could not lead to two separate LCST for BCPs. The thermal phase transition behaviors of BCPs appeared to be determined by the interaction and competing photoinduced LCST shift of the two blocks. In all cases, the dehydration of the two blocks appeared to occur at a similar temperature, while the formation of large aggregates or smaller micelles

depended on the nature of BCPs. Moreover, the possibility of controlling the extent of photoreaction on each block could allow an optical tuning of the LCST of BCPs. To this end, the use of SP with azobenzene is particularly interesting because the absorption wavelengths of MC are different from those of *cis* azo, which make it possible to optically convert MC to SP while retaining the *cis* isomer of azobenzene. The thermal relaxation of both *cis* azo and MC might be problematic in case where a long-time stability of the photoswitched states is desired. For optical tuning of LCST, this thermal instability of one isomeric form means that these chromophores should be used with polymers whose LCST is relatively low, i.e., around room temperature, so that the thermally activated MC-to-SP or *cis* azo-to-*trans* azo isomerization would be slow and limited.

CONCLUSIONS

We synthesized a variety of doubly photoresponsive and water-soluble diblock copolymers, each block of which

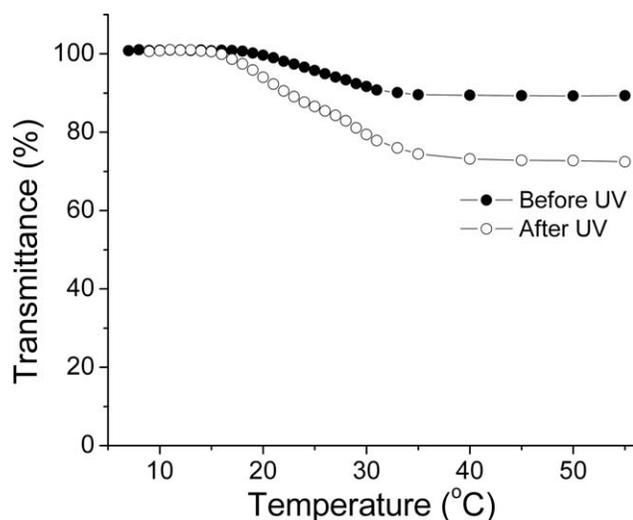


FIGURE 9 Transmittance versus temperature for 5 mM NaCl aqueous solution of P(DMA₆₄-co-AzoAm₉)-*b*-P(DEGMMA₁₀₃-co-AzoA₃) before and after UV light-induced photoisomerization of pendant photochromic groups.

contains a different photoisomerizable chromophore. The rationale of this design is to make a BCP that can undergo two photoreactions on the two blocks simultaneously, and to explore possible effect of such a more sophisticated photoreaction scheme on the polymer properties. Synthesized BCPs were composed of PDMA with either PNIPAM or PDEGMMA, while the comonomers used to incorporate different photochromic groups were a number of azobenzene-containing (meth)acrylamides and (meth)acrylates, and a spiropyran-containing acrylate. BCPs were designed to have two blocks that, when separated, could shift their LCST in opposite directions under their respective photoreaction (decrease of LCST for one and increase for the other). Solution transmittance and variable-temperature ¹H NMR measurements found that those BCPs exhibited a single LCST whose shift upon photoisomerizations appeared to be determined by competition of the opposing photoinduced effects for the two blocks, suggesting their strong interaction in aqueous solution. The use of two photoreactions could provide more possibilities of controlling the relative populations of the isomers involved (e.g., *trans* azo, *cis* azo, SP, and MC), which allowed the LCST of BCP to be tuned optically. The results also showed that it would be challenging to optically control the LCST of each block separately; more doubly photoresponsive BCP designs and studies are needed. Finally, we note that the approach of exploring a more complex photoreaction scheme may also open new perspective on

using light to control microphase-separated morphology and nanostructures of BCPs in the solid state.

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