Macromolecules

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Multimodal Stimuli-Responsive Poly(2-isopropyl-2-oxazoline) with Dual Molecular Logic Gate Operations

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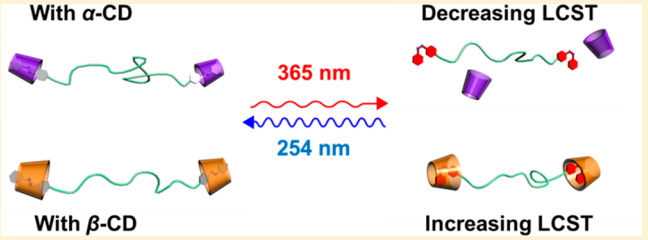
Supporting Information

ABSTRACT: Azobenzene end-functionalized telechelic POx (Az-POx-Az) was designed for as multimodal stimuli-responsive polymer. Az-POx-Az (0.25 g/L) in physiological saline (150 mM NaCl) phosphate buffered solution (10 mM PBS, pH 7.4) exhibited fully reversible *trans*−*cis* photoisomerism upon alternate irradiation with 365 and 254 nm UV light. The photoisomerization of the azobenzene moieties influenced the lower critical solution temperature (LCST), and the *cis* form exhibited a slightly higher LCST than the *trans* form. Circular dichroism measurements of Az-POx-Az with cyclodextrins (CDs) exhibited induced circular dichroism at the absorption band of the azobenzene moiety, indicating the formation of host−guest complexes between the azobenzene moieties in Az-POx-Az and the CDs. After formation of host−guest complexes consisting of the azobenzene moieties and the CDs, Az-POx-Az exhibited increased LCSTs. Interestingly, the LCSTs of Az-POx-Az with α-CD and β-CD moved in opposite directions upon photoisomerization. By the changing from the *trans* to *cis* form, Az-POx-Az with α-CD exhibited a decreased LCST; however, Az-POx-Az with β-CD exhibited an increased LCST. Using the interconversions between the transparent and turbid states of the Az-POx-Az solution, we could realize two different logic circuit modes using three different external stimuli, i.e., temperature, UV light, and cyclodextrins.



INTRODUCTION

Thermoresponsive polymers have great potentials in the field of biomedical, catalyst supports, sensors, and separation processes.[1−4] Poly(2-isopropyl-2-oxazoline) (POx) is a typical thermoresponsive polymer that exhibits the lower critical solution temperature (LCST) around body temperature.[5−10] The biocompatible characteristics of POx provide promising applications in biomedical fields.[8,11,12] Appreciably narrow molecular weight distributions of POx can be achieved by well-controlled living cationic ring-opening polymerization. Owing to the narrow molecular weight distribution, POx generally shows very rapid response to the temperature changes. The fine-tuning of thermoresponsiveness might expand the application of POx. In this regard, we recently reported dual stimuli-responsive dendritic−linear block copolymers formed from poly(benzyl ether) dendrons and POx that exhibited tunable LCST by changing pH.[6] On the other hand, various functional groups can be easily introduced to both initiation and termination ends of POx because the polymerization of 2-isopropyl-2-oxazoline proceeds by living cationic process. The initiation end can be functionalized by using functional initiators.[13] The cationic end of living chain is also easily convertible to other functional groups by treating with functional nucleophiles. In this study, we demonstrate multimodal stimuli-responsiveness of azobenzene end-functionalized telechelic POx (Scheme 1; Az-POx-Az). Az-POx-Az exhibited a rapid and reversible hydrophilic/hydrophobic propensity change by changing temperature. Moreover, the LCST of Az-POx-Az was further controlled by the addition of cyclodextrins (CDs) as well as the UV light irradiations. Such multimodal stimuli-responsiveness is applicable for the design of logic gate operations.[14,15]

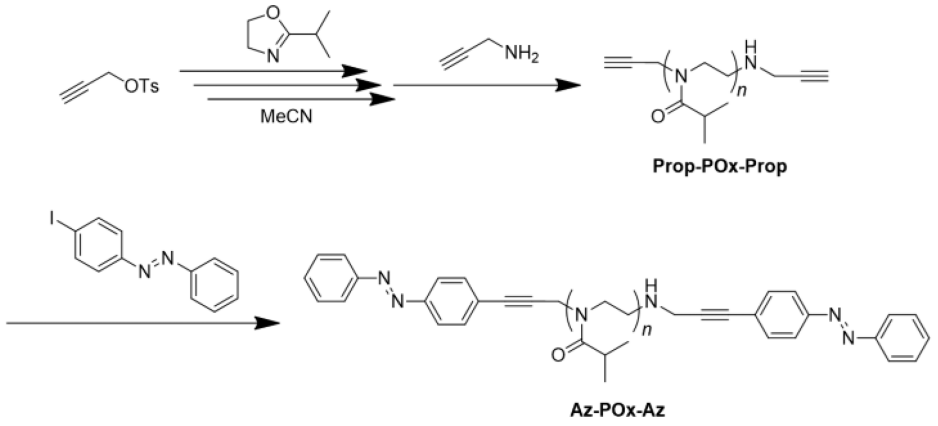
EXPERIMENTAL SECTION

Materials and Equipment. All of the commercially available reagents were reagent grade and used without further purification. Dichloromethane, *n*-hexane, tetrahydrofuran (THF), acetonitrile, and ethyl acetate were freshly distilled before each use. Recycling gel permeation chromatography (GPC) was performed on a LC-9201 (JAI, Tokyo, Japan) instrument equipped with JAIGEL-1H, JAIGEL-2H, and JAIGEL-3H columns using $CHCl_3$ as the eluent. UV−vis absorption spectra were measured using a V-660 spectrophotometer (JASCO, Tokyo, Japan) equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO, Tokyo, Japan) at 20 °C. Circular dichroism spectra were recorded using a JASCO model J-815 spectrometer at 20 °C (scan speed: 400 nm/min; scan number: 8; bandwidth: 5 nm). ^{1}H NMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer in CD_2Cl_2 or $CDCl_3$. Analytical GPC was performed on a JASCO HPLC equipped with HF-403HQ and HF-404HQ columns (Shodex, Tokyo, Japan) using THF as the eluent. MALDI-TOF MS measurements were performed on a Bruker model LRF20 using dithranol as the matrix. UV irradiation experiments were performed using UV hand lamp (Vilber Lourmat, France) equipped with 4 W UV discharge tubes. For the UV

Received: May 15, 2015
Revised: June 19, 2015
Published: July 7, 2015

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956

Scheme 1. Synthesis of Az-POx-Az



irradiation, quartz cells or NMR tubes were placed at a distance of 5 mm from the lamp.

Determination of LCST. The transmittance of the solution at 600 nm was measured using a V-660 spectrophotometer equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO). The heating rate of the sample cells was adjusted to 1.0 °C/min. The LCST points were taken as the temperature at which the transmittance reached 90% in the resulting transmittance versus temperature curves.

Opacity Change Measurement. The scattering of the samples was recorded using a Nanolog 3-211 spectrofluorometer (Horiba Jobin-Yvon, USA) according to previous work.[16] In the front port opening of Figure S1, a 635 nm laser (CPS180, Thorlabs) with a power ca. 0.2 mW was introduced as a scattering-probe beam, whereas 254 and 365 nm light with 14 nm bandwidths whose intensities correspond to 4 and 8 mW, respectively, were controlled by a double monochromator. Simultaneously, a probe beam was focused into a sample solution. The scattered light was collected via a photomultiplier tube.

Synthesis. The synthetic procedures of Prop-POx-Prop and Az-POx-Az are outlined in Scheme 1. 2-Isopropyl-2-oxazoline (Ox) and *p*-iodoazobenzene were synthesized according to literature procedures.[17,18]

Prop-POx-Prop. A Schlenk flask was degassed under high vacuum and backfilled with N_2; this process was repeated three times. A solution of propargyl *p*-tosylate (0.554 g, 2.63 mmol) in acetonitrile (20 mL) was placed in the flask, and Ox (14.25 g, 125.9 mmol) was added. The mixture solution was stirred for 10 days at 40 °C under a N_2 atmosphere. The reaction mixture was cooled to room temperature, and then propargylamine (0.86 g, 15.6 mmol) was added and stirred for 2 days to introduce another propargyl group at the ω-terminal. The solution of Prop-POx-Prop was purified via dialysis for 2 days against distilled water and then recovered by lyophilization (11.18 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.60−4.25 (m; terminal N−CH_2−CCH), 3.44 (broad s; −CH_2−CH_2− on the polymer backbone), 2.94−2.64 (two broad s; −CH− on the polymer side chain), 1.10 (strong broad s; −CH_3 on the polymer side chain).

Az-POx-Az. *p*-Iodoazobenzene (770 mg, 2.50 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 0.0286 mmol), and Prop-POx-Prop (3.00 g) were placed in a flask. The flask was degassed under high vacuum and backfilled with N_2; this process was repeated three times. Dried THF (10 mL) and trimethylamine (20 mL) were added. The mixture was stirred for 3 h, and CuI (10 mg, 0.0535 mmol) was added and refluxed for 36 h. The reaction mixture was filtered through Celite and precipitated against *n*-hexane three times. The mixture was finally purified with recycling GPC as an eluent of $CHCl_3$ and lyophilized to obtain Az-POx-Az as an orange powder (1.87 g, 62%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ (ppm): 8.06−6.70 (m; −CH on terminal azobenzene groups), 4.60−4.25 (m; terminal N−CH_2−), 3.43 (broad m; −CH_2−CH_2− on the polymer backbone), 2.97−2.53 (two broad s; −CH− on the polymer side chain), 1.08 (strong broad s; −CH_3 on the polymer side chain).

RESULTS AND DISCUSSION

Synthesis. The synthesis of Az-POx-Az is summarized in Scheme 1. Briefly, propargyl-functionalized POx was synthesized via the cationic ring-opening polymerization of Ox at 40 °C in acetonitrile for 10 days using propargyl tosylate as the initiator. After 10 days of polymerization, the polymer was quenched with propargylamine to prepare propargyl-functionalized telechelic POx (Prop-POx-Prop). The Az-POx-Az was prepared by end-group modification of Prop-POx-Prop through the Sonogashira coupling reaction with *p*-iodoazobenzene. The reaction product was then characterized with ^{1}H NMR, GPC, and MALDI-TOF-MS analyses (Figure S2). The MALDI-TOF-MS analysis indicated that over 75% of POx was converted to Prop-POx-Prop. The estimated number-average molecular weight of Prop-POx-Prop ($M_{n,GPC}$ = 5538, $M_{n,MALDI\text{-}TOF\text{-}MS}$ = 6000) was close to the value predicted from the initial monomer/initiator ratio [$M_{n,calc}$ = 5500], and its polydispersity index (PDI = M_w/M_n) was determined to be 1.1. After the Sonogashira coupling reaction, the Az-POx-Az was further purified using a reprecipitation processes against *n*-hexane and preparative recycled GPC to remove the byproducts formed by the homocoupling reaction. The ^{1}H NMR study indicated that 95% of propargyl end-functional groups were converted to azobenzene.

Photochromism of Az-POx-Az. Photochromism of the resulting azobenzene-functionalized polymers was investigated. Az-POx-Az (0.25 g/L) in physiological saline (150 mM NaCl) phosphate buffered solution (10 mM PBS, pH 7.4) was alternatively irradiated with 365 and 254 nm UV light for 30 min using a UV hand lamp. Figure 1a shows the absorption spectra of Az-POx-Az in the course of photoisomerization from *trans* to *cis* isomers, and Figure 1b shows the reverse process. The spectra exhibit clear isosbestic points at 241, 292, and 403 nm for both processes. Upon 365 nm UV irradiation, the absorption peak at 338 nm gradually decreased, and the absorption peaks at 256 and 428 nm increased. The photostationary state was reached after 30 min. After that the recovery of the original state commenced due to the 254 nm irradiation. As shown in Figure 1c, the *trans*−*cis* photoisomerism of Az-POx-Az occurred in a fully reversible manner during four cycles of repeated processes.

The photoisomerization processes of Az-POx-Az were compared to *p*-iodoazobenzene using ^{1}H NMR spectroscopy. Deuterated dichloromethane solutions of Az-POx- Az (0.66 mM) and *p*-iodoazobenzene (6.5 mM) were irradiated with 365 or 254 nm UV light for 5 h using a UV hand lamp to reach

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956

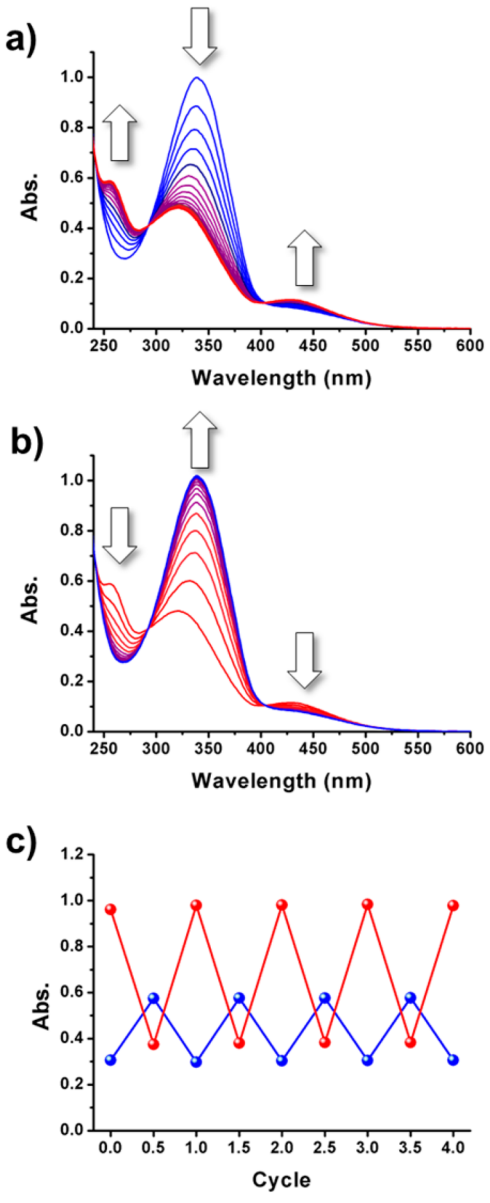


Figure 1. UV−vis absorption spectral change of Az-POx-Az in PBS (0.25 g/L) upon (a) 365 and (b) 254 nm irradiation. (c) Absorbance changes at 260 (blue) and 347 nm (red) after the 365 and 254 nm irradiation cycles.

the steady states, and then the ^{1}H NMR spectra of each solution were recorded (Figure 2). From the ^{1}H NMR study, Az-POx-Az showed successful interconversion, where the maximum conversions to *cis* and *trans* isomers were estimated to be 73 and 84%, respectively, which were slightly lower than those (81 and 87%) of *p*-iodoazobenzene photoisomerization.

Host−Guest Complex Formation of Az-POx-Az with Cyclodextrins. CDs are a family of macrocyclic oligosaccharides that can accommodate hydrophobic guest molecules.[19−22] Although *β*-CD can accommodate both *trans* and *cis* azobenzene moieties,[23−25] the *α*-CD can only accommodate the *trans*-azobenzene moiety due to its small cavity size (i.e., 0.57 nm).[26−29] To verify the formation of Az-POx-Az and CD complexes, the induced circular dichroism of the azobenzene moiety was measured. Figure 3 shows the circular dichroism spectra of Az-POx-Az in PBS (0.5 g/L) with or without 2 mM CDs. Each sample was irradiated with 365 or 254 nm light

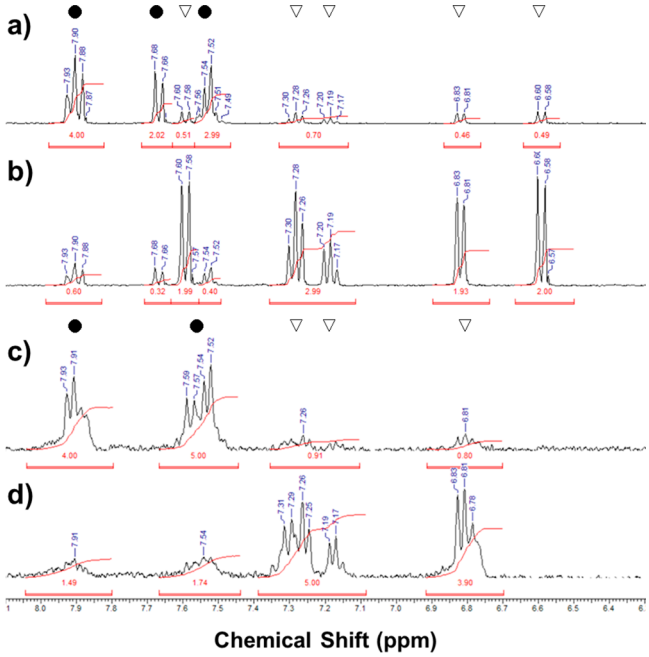


Figure 2. ^{1}H NMR spectra of *p*-iodoazobenzene (6.5 mM) and Az-POx-Az (0.66 mM) after photoirradiation at 254 and 365 nm in CD_2Cl_2. After (a) 254 and (b) 365 nm irradiation of *p*-iodoazobenzene and (c) 254 and (d) 365 nm irradiation of Az-POx-Az. Peaks under circle and triangle indicates the *trans* and *cis* forms of azobenzene groups, respectively.

using a UV hand lamp to reach the stationary state of the *trans* or the *cis* form, respectively. Without the addition of CDs, neither the *trans* nor *cis* forms of Az-POx-Az exhibited an induced circular dichroism signal in the absorption band of the azobenzene moiety near 350 nm. However, remarkable induced circular dichroism bands were observed after the addition of the CDs. Notably, the circular dichroism intensity at 343 nm of the Az-POx-Az that contained *α*-CD decreased significantly when the configuration changed from *trans* to *cis*, indicating the dissociation of the host−guest complex between *α*-CD and the azobenzene moiety. As mentioned previously, when the solution reached the saturation state, 27% of the *trans* isomer still remained in the solution. Therefore, the circular dichroism band could not entirely disappear due to the 365 nm irradiation. In contrast, Az-POx-Az containing *β*-CD exhibited a different shape of the circular dichroism band between the *trans* and *cis* forms. The circular dichroism bands for both the *trans* and *cis* forms were well matched with the absorption bands of the corresponding isomer forms of the azobenzene moiety, indicating that *β*-CD had a sufficiently large cavity to accommodate both the *trans* and *cis* isomers of the azobenzene moiety.

Thermal Responsiveness of Az-POx-Az. The thermal transition temperature of POx could be tuned by the introduction of hydrophobic end-functional groups. By increasing the hydrophobicity of POx, the thermal transition temperature decreases.[30] For example, the introduction of azobenzene groups to Prop-POx-Prop decreased the LCST from 35.4 to 21.9 °C (Figure 4a,b and Figure S3). The LCST of Az-POx-Az slightly increased to 22.8 °C due to the photoisomerization of the terminal azobenzene groups induced by irradiation with 365 nm UV light from a UV hand lamp. This change could also be explained by the polarity change of the

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956

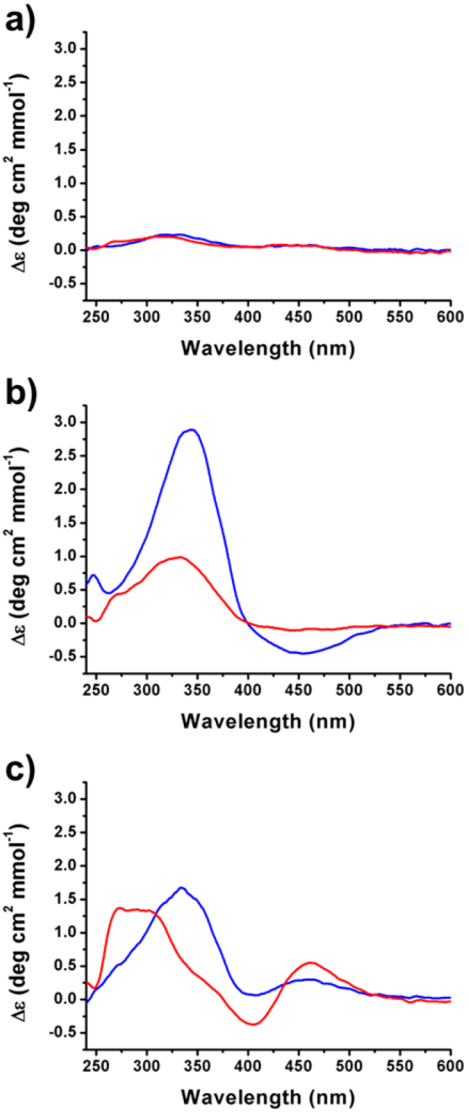


Figure 3. Circular dichroism spectra of the *trans* (blue) and *cis* (red) forms of Az-POx-Az in PBS (0.5 g/L) (a) without CD, (b) with α-CD, and (c) with β-CD.

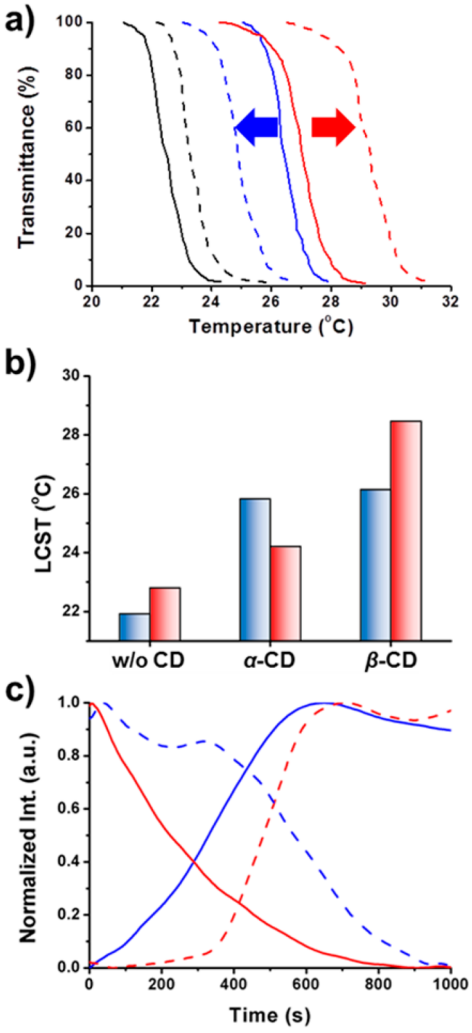
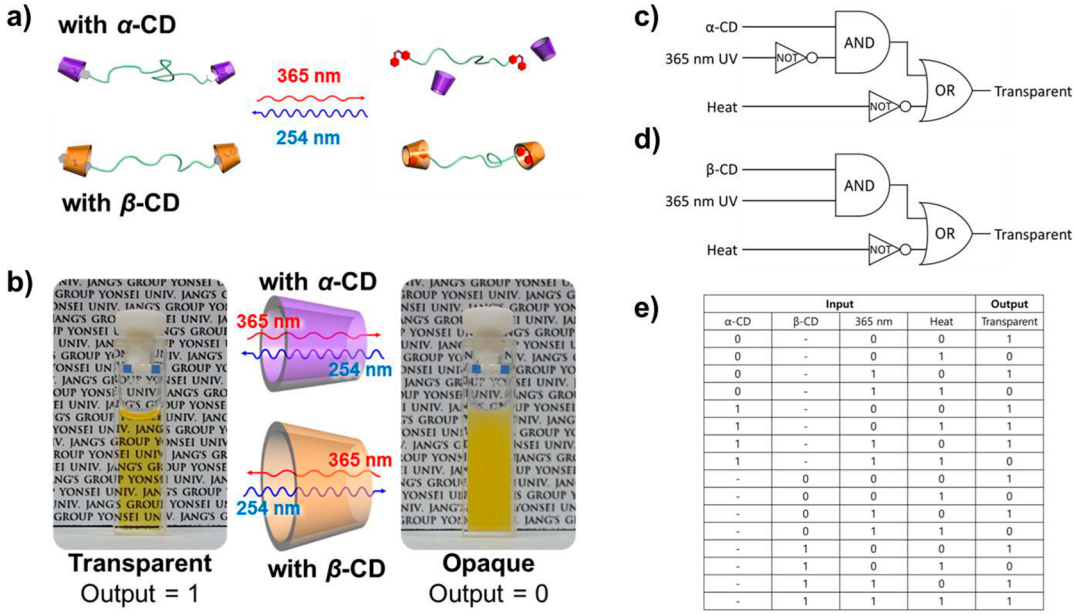


Figure 4. Thermo- and photoresponsiveness of Az-POx-Az. (a) Temperature-dependent transmittance changes of Az-POx-Az. The solid and dotted lines express the *trans* and *cis* forms of Az-POx-Az, respectively. Black: without CDs; blue: with α-CD; red: with β-CD. (b) LCST of each state of Az-POx-Az. (c) Scattered intensity changes of Az-POx-Az with α-CD at 25 °C (solid line) and with β-CD at 28 °C (dashed line) by UV irradiation. The blue and red lines show the changes after continuous irradiation with 365 and 254 nm UV light, respectively. Each solution contains 2.5 g/L of Az-POx-Az and 10 mM CDs.

terminal groups. Compared with *trans*-azobenzene, *cis*-azobenzene would have a higher polarity because of the lone pair electrons biased to one side. As mentioned above, the azobenzene moiety could form a host−guest complex with CDs. If the hydrophobic azobenzene end-functional groups are encapsulated by the CDs, the terminal of Az-POx-Az would have a hydrophilic surface. Therefore, the LCST would be increased by the molecular inclusion in CDs. The LCSTs of Az-POx-Az remarkably increased to 25.8 and 26.1 °C due to the additions of α-CD and β-CD, respectively. Then, the solutions were exposed to 365 nm UV light to induce photoisomerization of the end-functional azobenzene groups. Interestingly, the LCSTs of Az-POx-Az with α-CD and β-CD moved in opposite directions upon photoisomerization; the *cis* forms of Az-POx-Az with α-CD and β-CD exhibited LCSTs of 24.1 and 28.5 °C, respectively. This large difference could be explained by the cavity sizes of the CDs. As mentioned previously, the α-CD could not accommodate the *trans*-azobenzene moiety; however, it is impossible to accommodate the *cis*-azobenzene moiety due to the small cavity size.[26−29] Therefore, the hydrophobic end-functional azobenzene groups in Az-POx-Az would be exposed to the aqueous solvent after the *trans*-to-*cis* photoisomerization. In contrast, β-CD could accommodate both the *trans*- and *cis*-azobenzene moieties.[23−25] Because of the large cavity size of β-CD, the *cis*-azobenzene moiety would bind more tightly to β-CD. Therefore, the surrounding end-functional azobenzene groups in the *cis* form of Az-POx-Az would be more hydrophilic.

Because the LCST of Az-POx-Az was altered by UV exposure and host−guest complex formations, we could control the opacity of the Az-POx-Az solutions using UV irradiation at a constant temperature. The solution of Az-POx-Az containing α-CD was exposed to 254 or 365 nm UV light using a double-monochromated Xe lamp at 25 °C, and the turbidity changes of the sample were monitored by the scattering intensity of 635 nm laser light. As shown in Figure 4c, the transparent solution, the *trans* form of Az-POx-Az with α-CD, became turbid due to

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956



Input				Output
α-CD	β-CD	365 nm	Heat	Transparent
0	-	0	0	1
0	-	0	1	0
0	-	1	0	1
0	-	1	1	0
1	-	0	0	1
1	-	0	1	1
1	-	1	0	1
1	-	1	1	0
-	0	0	0	1
-	0	0	1	0
-	0	1	0	1
-	0	1	1	0
-	1	0	0	1
-	1	0	1	0
-	1	1	0	1
-	1	1	1	1

Figure 5. (a) Schematic expression of photochemical changes. (b) Photographs of Az-POx-Az solutions in transparent and opaque states. Supposed logic circuits of Az-POx-Az with (c) α-CD and (d) β-CD as well as the (e) resulting truth table.

continuous 365 nm irradiation. Alternatively, the turbid solution, the *trans* form of Az-POx-Az with α-CD, became transparent due to continuous 254 nm irradiation. The same experiment was performed for the solution of Az-POx-Az containing β-CD at a constant temperature of 28 °C. In this case, the *cis* form of Az-POx-Az was initially transparent and became turbid due to continuous 254 nm irradiation. Alternatively, the turbid *trans* form of Az-POx-Az with β-CD became transparent due to continuous 365 nm irradiation.

Az-POx-Az-Based Logic Gate Operations. The above interconversions between the transparent and turbid states of the Az-POx-Az solution may be analyzed as combinational logic gates via multimodal stimuli, including chemicals (CD), photoirradiation (light), and thermal energy (Figure 5). The opacity of the resultant Az-POx-Az solution would be the output signal (Figure 5b). Upon heating the solution to 25 °C, the Az-POx-Az solution without CDs would always be turbid. After addition of α-CD without 365 nm UV exposure, the solution would become transparent. However, if we irradiate the sample with 365 nm UV light or thermally heat it, the solution would become turbid. Therefore, we devised the combined logic gate diagram shown in Figure 5c. In contrast, to make the solution of Az-POx-Az transparent at 28 °C, both β-CD addition and 365 nm UV exposure would be needed. Therefore, we could draw a new logic gate diagram, as shown in Figure 5d. We could realize two different modes of logic circuits using Az-POx-Az solutions with α-CD or β-CD. The truth table of Az-POx-Az is depicted in Figure 5e.

CONCLUSIONS

In conclusion, we designed a hybrid polymeric system consisting of thermoresponsive poly(2-isopropyl-2-oxazoline) and photoresponsive azobenzene via living cationic polymerization and successive end-group modification processes. The azobenzene groups in the polymer system exhibited fully reversible conformation changes between the *trans* and *cis* forms via UV irradiation. The hydrophobic end-functional azobenzene groups could be changed to the hydrophilic state through the host−guest complexes with α-CD or β-CD. Moreover, the photoswitching of *trans* and *cis* isomerism enabled control of the temperature responsiveness. Using the unique thermo- and photoresponsive properties and the molecular inclusion phenomena of the polymer, two different modes of logic circuits were designated. This unique multi-stimuli responsive system has significant potential for the creation of molecular-level switching devices.

ASSOCIATED CONTENT

Supporting Information

Characterization of Az-POx-Az, LCST of Prop-POx-Prop, and the experimental setup of the opacity change measurement. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01046.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Mid-Career Researcher Program (2014R1A2A1A10051083) funded by the National Research Foundation (NRF) of Korea.

REFERENCES

(1) Roy, D.; Brooks, W. L. A.; Sumerlin, B. S. *Chem. Soc. Rev.* **2013**, *42*, 7214.
(2) Zayas, H. A.; Lu, A.; Valade, D.; Amir, F.; Jia, Z.; O'Reilly, R. K.; Monteiro, M. J. *ACS Macro Lett.* **2013**, *2*, 327.
(3) Pentela, N.; Murugan, P.; Jaisankar, S. N.; Samanta, D.; Mandal, A. B. *J. Organomet. Chem.* **2015**, *778*, 42.
(4) Lin, M.; Chen, J.-F.; Lu, Y.-T.; Zhang, Y.; Song, J.; Hou, S.; Ke, Z.; Tseng, H.-R. *Acc. Chem. Res.* **2014**, *47*, 2941.

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956

(5) Obeid, R.; Tanaka, F.; Winnik, F. M. *Macromolecules* **2009**, *42*, 5818.
(6) Kim, J.-H.; Lee, E.; Park, J.-S.; Kataoka, K.; Jang, W.-D. *Chem. Commun.* **2012**, *48*, 3662.
(7) Park, J.-S.; Akiyama, Y.; Winnik, F. M.; Kataoka, K. *Macromolecules* **2004**, *37*, 6786.
(8) Park, J.-S.; Akiyama, Y.; Yamasaki, Y.; Kataoka, K. *Langmuir* **2007**, *23*, 138.
(9) Park, J.-S.; Kataoka, K. *Macromolecules* **2006**, *39*, 6622.
(10) Park, J.-S.; Kataoka, K. *Macromolecules* **2007**, *40*, 3599.
(11) Platen, M.; Mathieu, E.; Lück, S.; Schubel, R.; Jordan, R.; Pautot, S. *Biomacromolecules* **2015**, *16*, 1516.
(12) Adams, N.; Schubert, U. S. *Adv. Drug Delivery Rev.* **2007**, *59*, 1504.
(13) Lava, K.; Verbraeken, B.; Hoogenboom, R. *Eur. Polym. J.* **2015**, *65*, 98.
(14) Credi, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5472.
(15) de Silva, A. P.; McClenaghan, N. D. *Chem.—Eur. J.* **2004**, *10*, 574.
(16) Oh, H.; Sim, J.; Ju, S.-Y. *Langmuir* **2013**, *29*, 11154.
(17) Meyer, M.; Schlaad, H. *Macromolecules* **2006**, *39*, 3967.
(18) Segarra-Maset, M. D.; van Leeuwen, P. W. N. M.; Freixa, Z. *Eur. J. Inorg. Chem.* **2010**, *2010*, 2075.
(19) Ogoshi, T.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 4878.
(20) Bruns, C. J.; Stoddart, J. F. *Acc. Chem. Res.* **2014**, *47*, 2186.
(21) Harada, A.; Takashima, Y.; Nakahata, M. *Acc. Chem. Res.* **2014**, *47*, 2128.
(22) Nachtigall, O.; Kördel, C.; Urner, L. H.; Haag, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 9669.
(23) Sanchez, A. M.; de Rossi, R. H. *J. Org. Chem.* **1996**, *61*, 3446.
(24) Barbiric, D.; Castro, E.; De Rossi, R. *J. Mol. Struct.: THEOCHEM* **2000**, *532*, 171.
(25) Lee, W.-S.; Ueno, A. *Macromol. Rapid Commun.* **2001**, *22*, 448.
(26) Engeldinger, E.; Armspach, D.; Matt, D. *Chem. Rev.* **2003**, *103*, 4147.
(27) Tomatsu, I.; Hashidzume, A.; Harada, A. *J. Am. Chem. Soc.* **2006**, *128*, 2226.
(28) Wang, Y.; Ma, N.; Wang, Z.; Zhang, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 2823.
(29) Zheng, X.; Wang, D.; Shuai, Z.; Zhang, X. *J. Phys. Chem. B* **2012**, *116*, 823.
(30) Huber, S.; Hutter, N.; Jordan, R. *Colloid Polym. Sci.* **2008**, *286*, 1653.

DOI: 10.1021/acs.macromol.5b01046
Macromolecules 2015, 48, 4951−4956