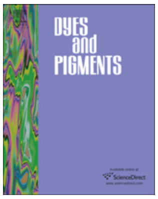
Dyes and Pigments 87 (2010) 84–88

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



The thermoresponsive behaviour of a poly(*N*-isopropylacrylamide) hydrogel with a D-π-A type pyran-based fluorescent dye

Sung-Hoon Kim [a,*], In-Jeong Hwang [b], Seon-Yeong Gwon [a], Young-A. Son [c]

[a] *Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea*
[b] *Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea*
[c] *Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea*

ARTICLE INFO

Article history:
Received 2 January 2010
Received in revised form
24 February 2010
Accepted 26 February 2010
Available online 4 March 2010

Keywords:
D-π-A dye
Pyran-based fluorescent dye
Poly(*N*-isopropylacrylamide)
Hydrogel
Low critical solution temperature (LCST)
Hydrodynamic radius

ABSTRACT

A thermoresponsive poly(NIPAM-co-fluorophore) hydrogel labeled with pyran-based fluorescent dye was prepared using conventional radical copolymerization. The low critical solution temperature behaviour was investigated using UV–vis spectroscopy which allowed the measurement of the phase transition over a wide range of temperature. The poly(NIPAM-co-fluorophore) in aqueous solution underwent a phase transition at 36–58 °C. The fluorescence intensities of the polymer in aqueous solution increased with increasing temperature across the low critical solution temperature transition range. The fluorophore displayed a blue shift in emission with increase in temperature due to destabilization of the excited state. Evidence from fluorescence and dynamic light scattering demonstrated that, >58 °C, the size of the polymer aggregates was 12,500 m. The morphology of the internal microstructure of the poly(NIPAM-co-fluorophore) hydrogel was observed using scanning electron microscopy.

1. Introduction

Temperature-responsive polymers and hydrogels have gained scientific and technological importance and the characteristics of these materials have been studied extensively for applications such as drug delivery, fluorescent thermometer and separation systems [1–4]. One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide) (PNIPAM) which exhibits a low critical solution temperature (LCST) transition from 30 to 45 °C [5,6]. The polymer is hydrophilic and soluble in water $<$ LCST but becomes hydrophobic and forms a macroscopic coacervate phase above that temperature, owing to the fluctuation of hydrophobic interactions and hydrogen bonding [7]. This phase transition is accompanied by a release of water bound to the polymer chain, which is an endothermic process. In previous papers [8,9], we have reported bistable photoswitching in poly(*N*-isopropylacrylamide) using a photochromic spironaphthoxazine hydrogel for optical data storage. Some copolymers with fluorophore have been reported [10–15], in which the fluorescence intensity of the fluorophores was controlled by temperature as external stimuli. To the best of our knowledge, there are no reports of PNIPAM copolymers with electron donor-π-conjugate-electron acceptor (D-π-A) type fluorophores. D-π-A type pyran-based fluorescent dyes such as 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM) have been intensively developed for applications as photo- and electroluminescent materials in the fields of dye lasers [16], sensors [17] and dye-sensitized solar cells [18]. Their fluorescence properties are highly sensitive to changes in external environment such as polarity and pH because of their intrinsic intramolecular charge transfer character [19,20]. Previous work [21] by the present research group reported the synthesis, photophysical properties and unusual aggregation-induced fluorescence changes in some a novel pyran-based fluorophore copolymer. This paper concerns fluorescence-based investigations of the thermoresponsive behaviour of a poly(*N*-isopropylacrylamide) hydrogel with D-π-A type pyran-based fluorescent dye.

2. Experimental

Melting points were determined using Electrothermal IA 900 apparatus and were uncorrected. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using an electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra was recorded in $CDCl_3$ using a Varian Inova 400 MHz FT NMR Spectrometer using TMS as internal standard. The weight-average molecular weight

---

* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

0143-7208/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2010.02.008

(Mn) and polydispersity (Mw/Mn) of the polymer was measured on a PL-GPC model 210 chromatograph at 25 °C using THF as the eluent and standard polystyrene as the reference. Fluorescence spectra were measured on a Shimadzu RF-5301PC Fluorescence spectrophotometer. The UV–vis spectra and transmittance were obtained on an Agilent 8457 UV–vis spectrophotometer. The LCST values were also determined by spectrophotometric detection of the changes in transmittance ($\lambda_{max} = 300$ nm) of aqueous polymer solutions heated at a constant rate (0.2 °C min^{-1}) with a thermostatically controlled cuvette. Dynamic light scattering (DLS) measurements was carried out on a Wyatt Technology Dynapro Titan instrument at fixed with the 828.6 nm line of a laser as excitation source.

2.1. Materials

2,6-Dimethylpyran-4-pyrone, allyl cyanoacetate and 4-(diphenylamino)benzaldehyde were purchased from Aldrich. *N*-Isopropylacrylamide (Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried in vacuum. 2,2′-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol. The other chemicals were of the highest grade available and were used without further purification. All employed solvents were analytically pure and were employed without any further drying or purification.

2.2. Synthesis of monomer **5**

2.2.1. Allyl-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate **3**

A mixture of 2,6-dimethylpyran-4-pyrone (3 g, 24 mmol) **1**, allyl cyanoacetate **2**, (3 g, 24 mmol), and acetic acid (12.5 ml) was refluxed for 24 h. The crude solid obtained was filtered, washed with methanol, and recrystallized from methanol several times. Yield: 32%; mass (m/z) 231 (M^+). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.27 (s, 6H), 4.65 (d, 2H), 5.20(d, 1H), 5.36 (d, 1H), 5.94 (m, 1H), 6.59 (s, 1H), 7.87 (s, 1H). EA: Anal. calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.17; H, 5.72; N, 6.03%.

2.2.2. Allyl-2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate **5**

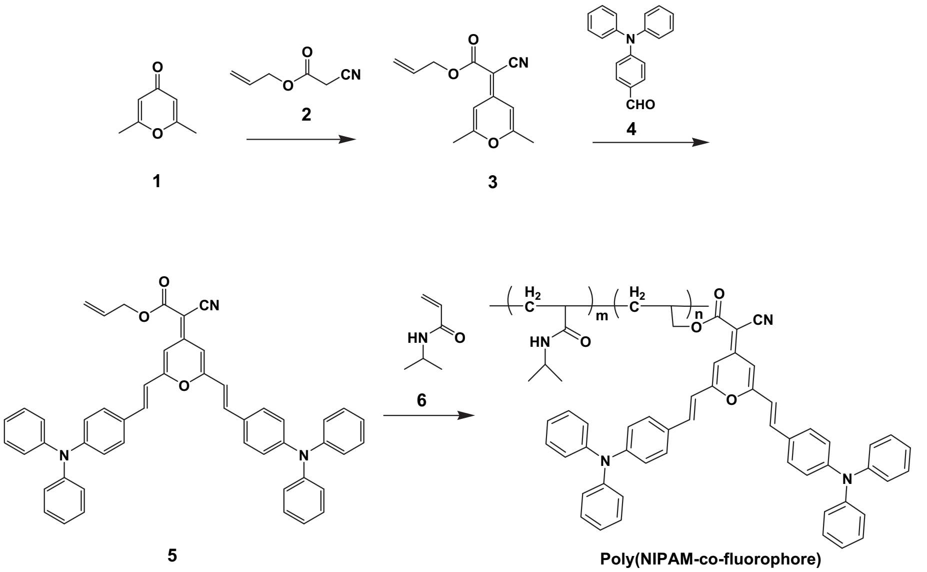
A solution of allyl-2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate **3** (1 g, 4.3 mmol), 4-(diphenylamino)benzaldehyde **4** (1.4 g, 5.2 mmol), and piperidine (0.3 ml) in 1-propane (50 ml) was refluxed for 24 h using Dean–Stark trap. The ensuing solution was cooled to room temperature and the solid product was isolated and washed well with 1-propanol and then dried. The reaction mixture was evaporated to remove solvent and separated by column chromatography using chloroform. Yield: 30%; mp 229–231 °C; mass (m/z) 741 (M^+). ^{1}H NMR (400MHz, $CDCl_3$): δ 4.69 (dt, $J = 1.48$ Hz, 2H), 5.23 (dd, $J = 3.96$ Hz, 1H), 5.37 (dd, $J = 4.64$ Hz, 1H), 5.94 (m, 1H), 6.60 (d, $J = 6.44$ Hz, 1H), 6.64 (d, $J = 6.36$ Hz, 1H), 6.73 (s, 1H), 7.02 (m, 30H), 8.04 (s, 1H). EA: Anal. calcd for $C_{51}H_{39}N_3O_3$: C, 82.57; H, 5.66; N, 5.30. Found: C, 81.84; H, 5.78; N, 5.44%.

2.3. Synthesis of poly(NIPAM-co-fluorophore)

N-Isopropylacrylamide **6** (2.26 g, 20 mmol), allyl-2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate **5** (0.15 g, 0.2 mmol), and 2,2′-azobis-(isobutyronitrile) (0.032 g, 0.2 mmol) were dissolved in anhydrous THF (20 ml) under dry N_2. After being heated for 3 days at 65 °C, the resultant mixture was precipitated from ether. The ensuing polymer was dried in vacuum to give satisfactory yield as orange-colored powder. Yield: 85%; Gel permeation chromatography (GPC): Mn: 21,733, Mw: 25,342, MP: 28,225, Mw/Mn: 1.16.

3. Results and discussion

The organic functional dyes with D-π-A charge transfer are the most important class of compounds for elucidating the relationships between push-pull chromophores and their optical properties [22]. Despite the broad application of these and other D-π-A chromophores [23,24] for the elucidation of reaction rates, chemical equilibria, nonlinear optical properties, and so on, accurately explaining the relationship between substituted groups and optical properties remains the subject of active debate [25]. The synthetic route of an monomer **5** and poly(NIPAM-co-fluorophore) is depicted in Scheme 1. We designed a new D-π-A charge transfer dye **5**,



Scheme 1. Synthesis of a D-π-A charge transfer dye, **5**, and poly(NIPAM-co-fluorophore).

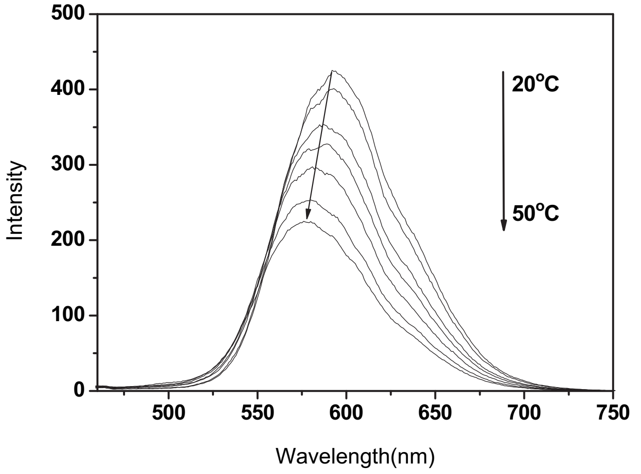


Fig. 1. Fluorescence spectra of monomer **5** at $CHCl_3$ 5×10^{-7}M at various temperatures.

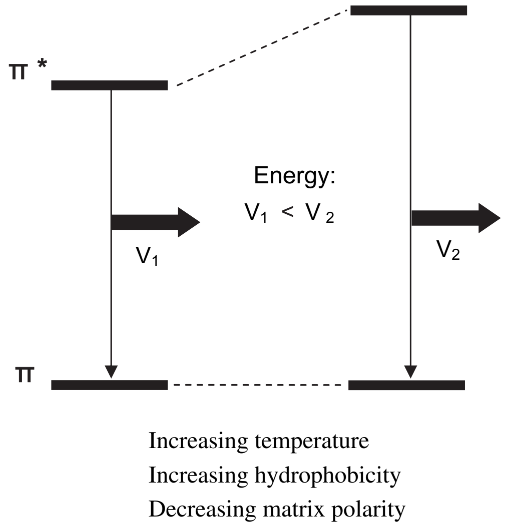


Fig. 3. A proposed transition energy diagram of poly(NIPAM-co-fluorophore) along with the aggregation.

containing a polymerizable functional allyl group. As shown in Scheme 1, the synthetic method was very simple. The ^{1}H spectrum of **5** verified its well-defined chemical structure. Characteristic NMR peaks due to the allyl group appeared at 5.23(dd), 5.37(dd) and 5.94(m). Reaction of a monomer **5** and *N*-isopropylacrylamide **6** in THF affords a orange-colored powder of poly(NIPAM-co-fluorophore).

Fig. 1 shows the fluorescence spectra of the monomer **5** in $CHCl_3$ at different temperature from 20 to 50 °C. It can be seen that the fluorescent intensities of this compound decreased with increasing temperature. It can be assigned to increase in non-radiative decay process with increase of temperature.

The temperature-dependent emission spectra of the poly (NIPAM-co-fluorophore) in temperature range from 20 to 65 °C is shown in Fig. 2.

The emission intensity of the poly(NIPAM-co-fluorophore) increased with rising temperature when excitation wavelength was 445 nm. The emission enhancement at higher temperature is due to the formation of hydrophobic domain near the isopropylacrylamide units. As shown in Fig. 2, the emission spectra of the fluorophore unit linked to NIPAM hydrogel in water show blue shift with the increase in temperature (the maximum emission wavelength is 599 nm at the lower temperature, while 569 nm is found at the higher temperature). Poly(NIPAM-co-fluorophore) is hydrophilic at low temperature, but a rise in temperature leads to a formation of hydrophobic domain inside the polymer, along with an increase in the size of polymer particles [26,27]. As proposed by the transition energy diagram shown in Fig. 3, the aggregation of polymer reduces the polarity of environment surrounding fluorophore, and thus, the energy of the CT excited state will increase, leading to a shorter wavelength light emission.

UV–vis spectrometry is an easy and widely used method for the determination of the LCST. In Fig. 4, we show the absorption spectra of aqueous poly(NIPAM-co-fluorophore) solution at different temperature. As solution is heated, it becomes turbid; these temperature-responsive changes are entirely reversible. This kind of gelation behaviour induced by temperature is well-known as an LCST, resulting from a balance between hydrogen-bond formation with water and intramolecular hydrophobic forces [28].

The values of transmittance (A300) of aqueous solution containing poly(NIPAM-co-fluorophore) are plotted against the temperature of the solution in Fig. 5; an obvious transmittance decrease at >36 °C:LCST = 36–58 °C. The results of thermoresponse of poly(NIPAM-co-fluorophore) solution characterized by

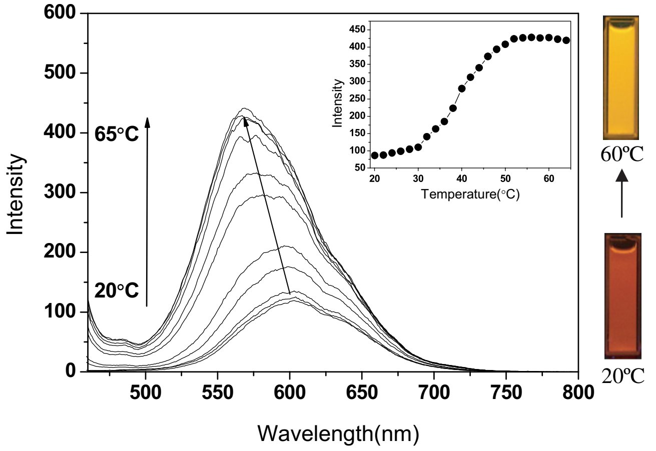


Fig. 2. Fluorescence spectra and images of poly(NIPAM-co-fluorophore) in aqueous solution (0.025 g/ml) at various temperatures.

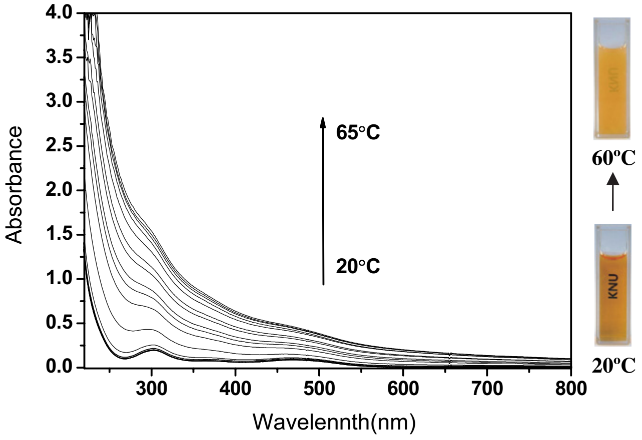


Fig. 4. Absorption spectra of poly(NIPAM-co-fluorophore) in aqueous solution (0.025 g/ml) at various temperatures.

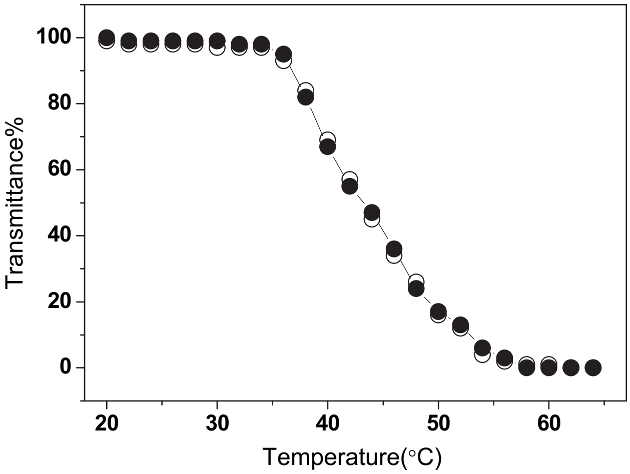


Fig. 5. Transmittance of a solution of poly(NIPAM-co-fluorophore) in aqueous solution (0.025 g/ml). ●, heating; ○, cooling.

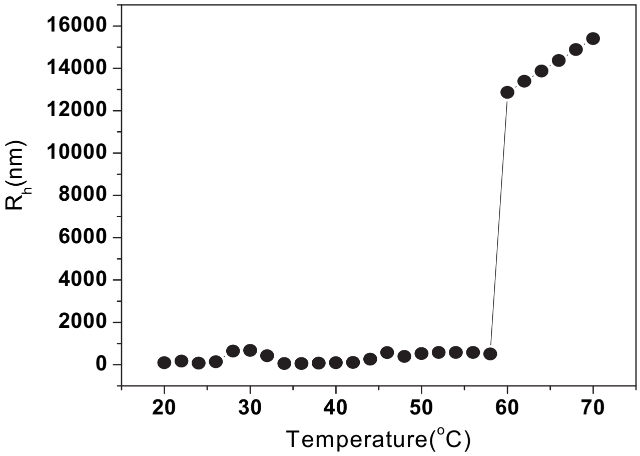


Fig. 6. Hydrodynamic radius(R_h) of poly(NIPAM-co-fluorophore) in aqueous solution (0.025 g/ml) at various temperatures.

Fig. 7. SEM micrographs of poly(NIPAM-co-fluorophore).

UV-vis spectrometry are comparable with those from fluorescence measurement.

Fig. 6 shows the temperature dependence of a hydrodynamic radius of the polymer particle. It is clear that the R_h increased with increasing temperature. At 58 °C, the size of the polymer hydrogels is estimated to be 12,500 nm, due to a formation of the hydrophobic polymer aggregates near LCST. This is the reason why the fluorescent intensities were increased at temperatures over the LCST.

Fig. 7 shows a few representative SEM image of the internal matrix structure of poly(NIPAM-co-fluorophore) hydrogel which has irregular fibrous aggregation and homogeneous coral-like microstructure with a three dimensional network structure. This morphology indicated that poly(NIPAM-co-fluorophore) hydrogel could form stable hydrogel when the temperature was above the LCST of poly(NIPAM-co-fluorophore).

4. Conclusion

In conclusion, we synthesized a thermoresponsive poly(NIPAM-co-fluorophore) hydrogel composed of poly(*N*-isopropylacrylamide) partly modified with pyran-based fluorescent dye **5** and observed that this polymer hydrogel exhibited a low critical solution temperature (LCST) transition from 36 to 58 °C. The phase transition temperature for poly(NIPAM-co-fluorophore) was determined by UV–vis spectroscopic method. The fluorescence intensity increased and the fluorescence maximum emission wavelength was blue-shifted with increasing the temperature due to increasing hydrophobicity around the fluorophore. The aggregation behaviour of the polymer particle was studied by dynamic light scattering. The particle size of the aggregates was estimated to be 12500 nm at 58 °C.

Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation (NRF) grant funded by the Korea government (MEST) (No. 2009-0063408).

References

[1] Umeno D, Kawasaki M, Maeda M. Water-soluble conjugate of double-stranded DNA and poly(*N*-isopropylacrylamide) for one-pot affinity precipitation separation of DNA-binding proteins. Bioconjugate Chemistry 1998;9:719–24.
[2] Hayashi H, Kono K, Takagishi T. Temperature sensitization of liposomes using copolymers of *N*-isopropylacrylamide. Bioconjugate Chemistry 1999;10: 412–8.
[3] Uchiyama S, Matsumura Y, de Silva AP, Iwai K. Modulation of the sensitive temperature range of fluorescent molecular thermometers based on thermoresponsive polymers. Analytical Chemistry 2004;76:1793–8.
[4] Iwai K, Matsumura Y, Uchiyama S, de Silva AP. Development of fluorescent microgel thermometers based on thermoresponsive polymers and their modulation of sensitivity range. Journal of Materials Chemistry 2005;15. 2896–2800.
[5] Wu C, Zhou S. Thermodynamically stable globule state of a single poly(*N*-isopropylacrylamide) chain in water. Macromolecules 1995;28:5388–90.
[6] Akiyoshi K, Kang EC, Kurumada S, Sunamoto J, Principi T, Winnik FM. Controlled association of amphiphilic polymers in water: thermosensitive nanoparticles formed by self-assembly of hydrophobically modified pullulans and poly(*N*-isopropylacrylamides). Macromolecules 2000;33:3244–9.
[7] Otake K, Inomata H, Konno M, Saito S. Thermal analysis of the volume phase transition with *N*-isopropylacrylamide gels. Macromolecules 1990;23:283–9.
[8] Wang S, Choi MS, Kim SH. Bistable photoswitching in poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel for optical data storage. Journal of Photochemistry and Photobiology A: Chemistry 2008;198:150–5.
[9] Wang S, Choi MS, Kim SH. Multiple switching photochromic poly(*N*-isopropylacrylamide) with spironaphthoxazine hydrogel. Dyes and Pigments 2008;78:8–14.
[10] Xiao X, Fu YQ, Zhou JJ, Bo ZS, Li L, Chan CM. Reversible thermally responsive and luminescent coil-rod-coil triblock copolymers. Macromolecuar Rapid Communications 2007;28:1003–9.
[11] Uchiyama S, Matsumura Y, de Silva AP, Iwai K. Fluorescent molecular thermometers based on polymers showing temperature-induced phase transition

and labeled with polarity-responsive benzofurazans. Analytical Chemistry 2003;75:5926–35.

[12] Uchiyama S, Kawai N, de Silva AP, Iwai K. Fluorescent polymeric AND logic gate with temperature and pH as inputs. Journal of the American Chemical Society 2004;126:3032–3.

[13] Guo Z, Zhu W, Tian H. Hydrophilic copolymer bearing dicyanomethylene-4 *H*-pyran moiety as fluorescent film sensor for Cu^{2+} and pyrophosphate anion. Macromolecules 2010;43:739–44.

[14] Guo Z, Zhu W, Xiong Y, Tian H. Multiple logic fluorescent thermometer system based on *N*-isopropylmethacrylamide copolymer bearing dicyanomethylene-4H-pyran moiety. Macromolecules 2009;42:1448–53.

[15] Zhu LL, Li X, Ji FY, Ma X, Wang QC, Tian H. Photolockable ratiometric viscosity sensitivity of cyclodextrin polypseudorotaxane with light-active rotor graft. Langmuir 2009;25:3482–6.

[16] Antonov VS, Hohla KL. Dye stability under excimer-laser pumping. Applied Physics B 1983;B32:9–14.

[17] de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Signaling recognition events with fluorescent sensors and switches. Chemical Reviews 1997;97:1515–66.

[18] Sansregret J, Drake JM, Thomas WRL, Lesiecki ML. Light transport in planar luminescent solar concentrators: the role of DCM self-absorption. Applied Optics 1983;22:573–7.

[19] Burland DM, Miller RD, Walsh CA. Second-order nonlinearity in poled-polymer system. Chemical Reviews 1994;94:31–75.

[20] Zucchero AJ, Wilson NJ, Bunz UHF. Cruciforms as functional fluorophores: response to protons and selected metal ions. Journal of the American Chemical Society 2006;128:11872–81.

[21] Kwak G, Kim H, Kang IK, Kim SH. Charge transfer dye in various polymers with different polarity: synthesis, photophysical properties, and unusual aggregation-induced fluorescence changes. Macromolecules 2009;42:1733–8.

[22] Reichardt C. Solvents and solvent effects in organic chemistry. 3rd ed. Weinheim: Wiley-VCH; 2003.

[23] Reichardt C. Solvatochromic dyes as solvent polarity indicators. Chemical Reviews 1994;94:2319–58.

[24] Hartman H, Eckert K, Schroder A. New solvatochromic dyes of the 5-dimethylamino-5′-nitro-2,2′-bithiophene type. Angewandte Chemie International Edition 2000;39:556–8.

[25] Ishchenko AA, Kulinich AV, Bondarev SL, Knyukshto VN. Phodynamics of polyene-polymethine transformations and spectral fluorescent properties of merocyanine dyes. Journal of Physical Chemistry A 2007;111:13629–37.

[26] Koizumi H, Kimata Y, Shiraishi Y, Hirai T. Temperature-controlled changeable oxygenation selectivity by singlet oxygen with a polymeric photosensitizer. Chemical Communications; 2007:1846–8.

[27] Koizumi H, Shiraishi Y, Tojo S, Fujitsuka M, Majima T, Hirai T. Temperature-driven oxygenation rate control by polymeric photosensitizer. Journal of the American Chemical Society 2006;128:8752–3.

[28] Garcia A, Marquez M, Cai T, Rosario R, Hu Zhibing, Gust D, et al. Photo-, thermally, and pH-responsive microgels. Langmuir 2007;23:224–9.