Synthesis of Polymeric Temperature Sensor Based on Photophysical Property of Fullerene and Thermal Sensitivity of Poly(*N*-isopropylacrylamide)

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ABSTRACT: Two types of temperature sensor which have pyrene (Pyr) and fullerene (C60) attached to poly(*N*-isopropylacrylamide) (PNIPAM) are synthesized, and their thermal sensitivities are examined in terms of the fluorescence quenching efficiency of C60: One is pyrene−poly(*N*-isopropylacrylamide)−fullerene (Pyr-PNIPAM-C60) which has Pyr and C60 attached to each chain end of PNIPAM, and the other is pyrene−poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (Pyr-P(NIPAM-*co*-C60)) which has Pyr attached to one chain end of PNIAPM and two C60s attached onto PNIPAM backbone. Both of them exhibit the same conformational change from coil to globule at a specific temperature, which results in drastic on-and-off quenching efficiency. The quenching efficiency of Pyr-P(NIPAM-*co*-C60) is larger than Pyr-PNIPAM-C60, since Pyr-P(NIPAN-*co*-C60) has more C60s located closer to Pyr than Pyr-PNIPAM-C60. These C60-based thermosensitive polymers exhibit well-defined on-and-off behavior at a small change in temperature.

Introduction

For the past decades, fullerene (C60), which is known as a spherical molecule that resembles a perfect carbon nanoparticle of 1 nm in diameter,[1,2] has attracted great interest from both academia and industry because of its excellent ability to accept and transport electrons.[3−6] Although it is expected that C60 can also play a role as an effective fluorescence quencher like gold nanoparticle,[7−12] only a few efforts have been made to utilize its optical signal as a transducer for sensing many important stimuli in biological environment.[13,14] The change of optical signal arising from C60 under different condition may provide a more facile way for observing the change of many important properties at a molecular level. Furthermore, C60 has several advantages over other materials in preparation of stimuli-responsive sensors because it can be readily functionalized for various applications.[1]

One of the prospective methods that exploit C60 for bio- and/or environmental applications is to conjugate C60 with a stimuli-sensitive polymer, where the stimuli-sensitive polymer is generally defined as a smart polymer which exhibits a drastic change in its properties, responding to small variations in physical or chemical stimuli such as pH, temperature, and ionic species. In this study, poly(*N*-isopropylacrylamide) (PNIPAM) is selected as a temperature-sensitive polymer since PNIPAM has been reported to undergo a unique temperature-induced and reversible phase transition at the lower critical solution temperature (LCST) in water[15−20] and therefore has been widely used for optical/electronic devices,[21−23] biomedical applications,[24−31] and responsive surfaces.[32−35]

In this study, two types of polymeric temperature sensor based on C60 and PNIPAM are synthesized for effective sensing of temperature: One has a fluorophore (pyrene) attached to one end of PNIPAM and C60 attached to the other chain end of PNIPAM; the other has the fluorophore attached to one end of PNIPAM and two C60s attached onto the middle part of PNIPAM backbone. Since it is well-known that PNIPAM exhibits the temperature-induced coil−globule transition which is rapid enough to show a typical two-state transition,[36−38] PNIPAM can provide a general platform to design an alarm-type temperature sensor. To our best knowledge, an effort to develop a stimuli-responsive optical sensor based on the concept combining the photophysical characteristics of C60 and the coil−globule transition of PNIPAM has not been reported yet. Here, we report the synthesis of a new polymeric temperature sensor based on the photophysical characteristics of C60 and the thermal sensitivity of PNIPAM.

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich unless noted. Tetrahydrofuran (THF) (Daejung Chemicals & Metals) was dried over sodium and distilled under atmospheric pressure. *N*-Isopropylacrylamide (NIPAM) (98%, Tokyo Chemical Industry) was recrystallized from hexane−ethyl acetate (v/v = 11/1) and dried under vacuum prior to use. 2-Hydroxyethyl methacrylate (HEMA) (97%) was distilled from calcium hydride under pressure before use. 1-Pyrenemethylamine hydrochloride (95%), 2-chloroisobutyryl chloride (95%, Tokyo Chemical Industry), triethylamine (TEA) (99.5%), sodium bicarbonate (Daejung Chemicals & Metals), magnesium sulfate anhydrous (Daejung Chemicals & Metals), ethanol (Daejung Chemicals & Metals), *N,N*-dimethylformamide anhydrous (DMF) (99.8%), copper(I) chloride (CuCl) (99.995%), neutral Al_2O_3, methanol (Daejung Chemicals & Metals), sodium azide (99.5%), 1,2-dichlorobenzene (99%), fullerene (C60) (Lancaster Synthesis) (99.5%), ether (Daejung Chemicals & Metals), phenyl-C_{61}-butric acid (C60COOH) (Materials Technologies Reaserch) (99%), thionyl chloride ($SOCl_2$) (Fluka) (99%), anhydrous carbon disulfide (CS_2) (99.9%), toluene (99.8%), and Celite were used as received.

Synthesis of Pyrene−Poly(*N*-isopropylacrylamide)−Fullerene (4). For all reactions, the flasks were degassed and backfilled with Ar gas. Pyrene-based initiator (**1** in Scheme 1) was synthesized according to our previous report,[39] except for the use of 2-chloroisobutyryl chloride instead of 2-bromoisobutyryl bromide, and was used as an initiator for atom transfer radical polymerization (ATRP). DMF was degassed for removal of oxygen by three freeze-and-thaw cycles, and distilled water was degassed by boiling for 48 h and bubbling with N_2 gas for 12 h to completely remove dissolved oxygen. NIPAM (2 g, 1.736×10^{-2} mol) was put in a three-neck round-bottom flask, to which DMF (5 mL) and H_2O (2.5 mL) were sequentially added to dissolve NIPAM. After tris(2-dimethylaminoethyl)amine (Me_6TREN) (0.098 mL, 3.534×10^{-4} mol) and CuCl

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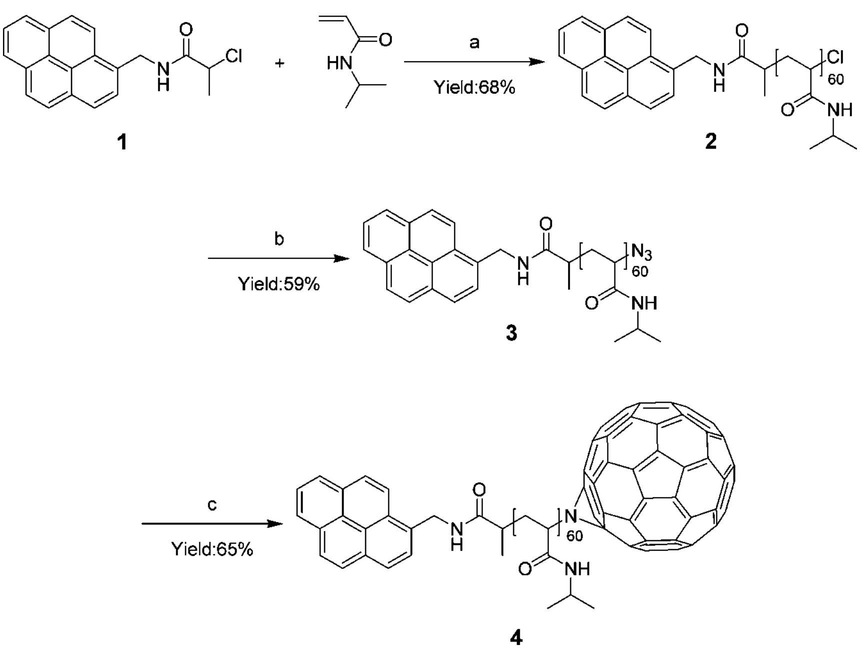
Scheme 1. Overall Scheme for Synthesis of Pyrene−Poly(*N*-isopropylacrylamide)−Fullerene (4)[a]



[a] Conditions: (a) CuCl, Me_6TREN, DMF/H_2O, 20 °C, 2 h; (b) NaN_3, DMF, 70 °C, 48 h; (c) C60, 1,2-dichlorobenzene, 150 °C, 48 h.

(0.035 g, 3.534×10^{-4} mol) were added to the NIPAM solution, a solution of **1** (0.113 g, 3.534×10^{-4} mol) in DMF (2.5 mL) was then added. The resulting solution was stirred at 20 °C for 2 h to allow ATRP. At the end of reaction, a solution of the crude product was passed through neutral Al_2O_3 column to remove metal catalyst and then dialyzed against MeOH for 48 h using a cellulose dialysis membrane (molecular weight cutoff: 3500, Membrane Filtration Products, Inc.). The product, pyrene−poly(*N*-isopropylacrylamide) (**2** in Scheme 1), was obtained by evaporating MeOH and then dried in vacuum at 30 °C. Yield: 68%; $M_{n,NMR}$: 7200, PDI_{GPC}: 1.25. For introduction of an azide group to the chain end of **2**, **2** (1 g) was then placed in a flask and dissolved in DMF (5 mL), to which a mixture of NaN_3 (0.089 g) and DMF (5 mL) was slowly added, and the solution was stirred at 70 °C for 48 h. The product was purified by dialyzing against H_2O for 24 h, and further dialysis against methanol was performed for 24 h. The product, pyrene−poly(*N*-isopropylacrylamide)−N_3 (**3** in Scheme 1), was obtained by evaporating MeOH and then dried in vacuum at 30 °C. Yield: 59%. For introduction of C60 to the chain end of **3**, **3** (0.3 g) was put in a flask and dissolved in 1,2-dichlorobenzene (15 mL), to which a mixture of C60 (0.0864 g) and 1,2-dichlorobenzene (15 mL) was slowly added, and the solution was stirred at 150 °C for 48 h. A solution of the crude product was precipitated in ether. After filtration, the filtered product was purified by Soxhlet extraction using MeOH for 24 h. After evaporating MeOH, the crude product was diluted with THF and centrifuged for further purification. The final product, pyrene−poly(*N*-isopropylacrylamide)−fullerene (**4** in Scheme 1) was obtained by evaporating THF and drying in vacuum at 30 °C. Yield: 65%. See Supporting Information for the NMR spectrum and GPC trace of **2**.

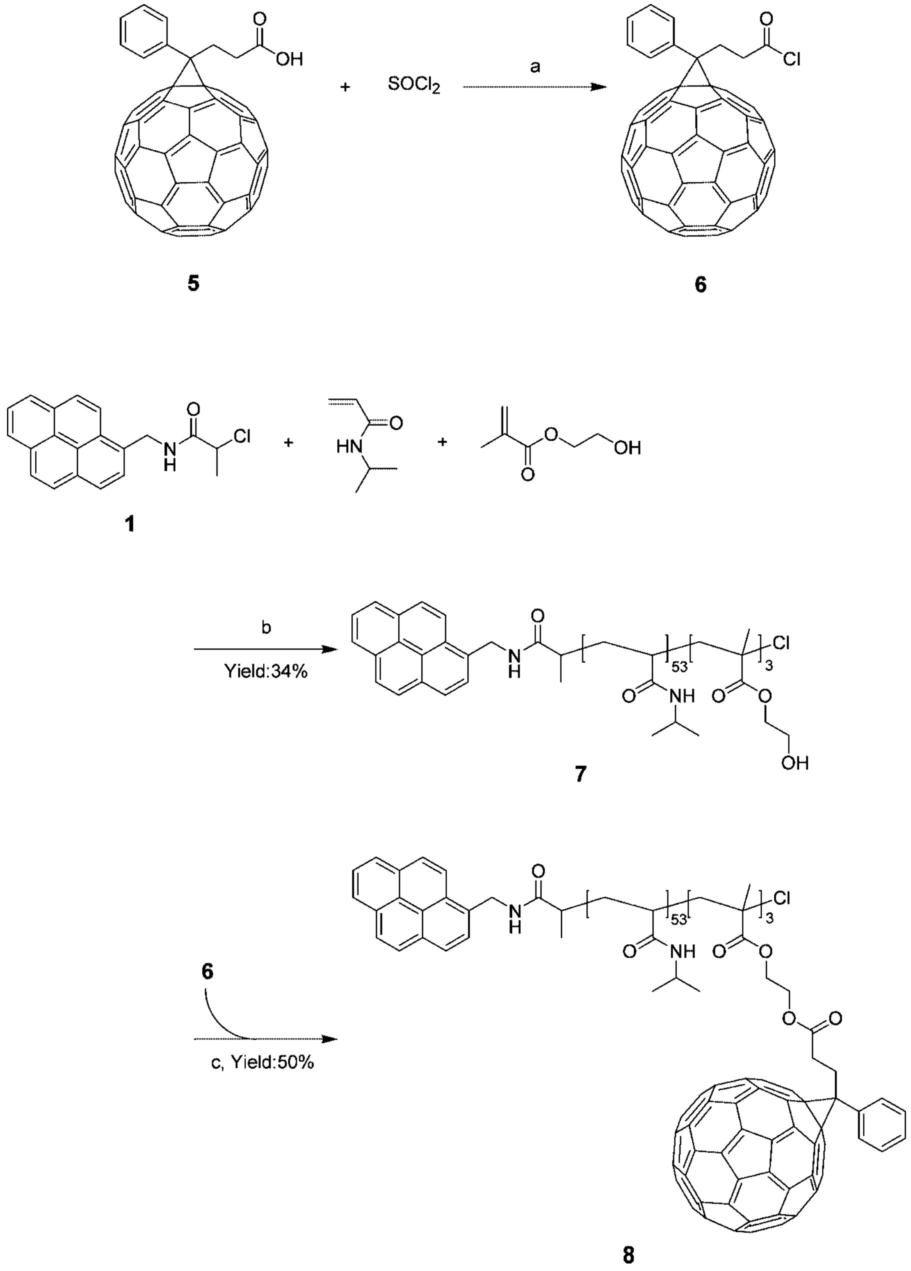
Synthesis of Pyrene−Poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (8). The synthetic route of pyrene−poly(*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate) (**7** in Scheme 2) as a precursor for synthesis of **8** is similar to that of **2**. Briefly describing the experimental procedure, NIPAM (1 g, 8.837×10^{-3} mol), HEMA (0.0214 mL, 3.534×10^{-4} mol), Me_6TREN (0.049 mL, 1.767×10^{-4} mol), and CuCl (0.01749 g, 1.767×10^{-4} mol) were dissolved in a mixed solvent of DMF (5 mL) and H_2O (2.5 mL), to which a solution of **1** (0.0567 g, 1.767×10^{-4} mol) in DMF (2.5 mL) was added, and the solution was stirred at 20 °C for 4 h. For purification of the precursor **7**, the same purification method as the method for **2** was used. Yield: 34%; $M_{n,NMR}$: 6800, PDI_{GPC}: 1.33. For preparation of **8**, C60COOH (**5**) (0.044 g, 4.477×10^{-5} mol) was first activated by reacting with $SOCl_2$ in CS_2 (15 mL) at 60 °C for 12 h to yield C60 with an acyl chloride group (C60COCl) (**6**). A solution of **6** was added to a mixture of **7** (0.1 g), TEA (1 mL), and toluene (10 mL), and the resulting solution was then stirred at room temperature for 96 h. For purification, the crude product was precipitated in ether. After filtration, the filtered product was dissolved in THF, and the solution was passed through Celite column. The filtered solution was dialyzed against H_2O for 48 h and centrifuged for further purification. The final product (**8**) was obtained by evaporating H_2O and drying in vacuum at 30 °C. Yield: 50%. See Supporting Information for the NMR spectrum and GPC trace of **7**.

Characterization. The chemical structures of materials used in this study were identified by ^1H NMR (Avance DPX-300 and Avance 500, Bruker). Molecular weights and its distributions were measured by gel permeation chromatography (CTO-10A, Shimadzu) equipped with a refractive index detector (RDI-10A, Shimadzu) using THF as an eluent, where the columns were calibrated against three standard polystyrene samples (Shodex: $M_n = 1.31 \times 10^{-3}$, 1.39×10^{-4}, and 2.05×10^{-5}). Infrared (IR) spectra were recorded with an IR spectrometer (FT/IR-660, Jasco). Thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere at the heating of 20 °C min^{-1} using a thermogravimetric analyzer (TA 2050). UV−vis absorption and fluorescence spectra were obtained by using a UV/vis spectrometer (HP 8452A, Hewlett-Packard) and a fluorescence spectrometer (Quanta Master QM-4/2006SE, Photon Technology International), respectively. For fluorescence measurement at different temperatures, the sample was allowed to equilibrate for 5 min at a given temperature, and the sample was heated at 0.2 °C min^{-1}. All the polymer solutions were filtered using a syringe filter (pore size: 0.20 μm, Minisart, Satorius) before the absorption/fluorescence spectra were obtained.

Results and Discussion

The synthetic route for preparation of **4** is shown in Scheme 1. Me_6TREN was used as a ligand for atom transfer radical polymerization (ATRP) in this study, since it has been known to effectively control ATRP of NIPAM.[40] Pyrene was chosen as a fluorophore and modified to be used as an ATRP initiator according to the similar method as reported previously.[39] Since

Scheme 2. Overall Scheme for Synthesis of Pyrene−Poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (8)[a]



[a] Conditions: (a) CS_2, 60 °C, 12 h; (b) CuCl, Me_6TREN, DMF/H_2O, 20 °C, 4 h; (c) TEA, toluene, room temperature, 96 h.

the pyrene-based initiator (**1**) acts as not only an initiator for ATRP but also a fluorophore, the resulting polymeric linker (**2**) synthesized from ATRP of NIPAM intrinsically has a fluorescent dye (pyrene) linked to one end of PNIPAM chain. Since all the peaks in the NMR spectrum of **2** are appropriately assigned (see Supporting Information), it is assumed that **2** is successfully synthesized. It should be also noted that, since the growing chain end of **2** obtained from ATRP is *sec*-halide group, the chain end can be transformed into various functional groups through a simple S_N reaction.[41] In this study, an azide group was introduced to the chain end of **2** to yield **3**. One of the most important reasons for introducing the azide group is because the azide group can easily conjugate with fullerene (C60).[1] When the IR spectrum of **2** is compared with that of **3**, as shown in Figure 1, it is found that the characteristic band of azide group appears at 2100 cm^{-1} after the introduction of azide group, indicating that the azide group was successfully conjugated with a *sec*-halide group of **2**. Finally, **3** was then conjugated with C60 to yield **4**, as represented in Scheme 1. Comparison of the UV−vis spectra (see Supporting Information) of **2** and **4** clearly shows that the absorbance of the UV−vis spectrum of **4** is significantly increased in the range from 300 to 400 nm as compared with that of **2**, indicating that C60 was successfully conjugated with the azide group of **3**. Furthermore, the complete disappearance of the peak at 2100 cm^{-1} in the IR spectrum of Figure 1 corresponding to the azide group after conjugation with C60 provides another evidence for successful conjugation of the azide group with C60. When the TGA thermogram of **2** is compared with those of **4** and C60, as shown in Figure 2A, it is realized that the significant weight loss from 300 to 600 °C in the TGA thermogram of **4** is primarily due to the decomposition of **2**. Since C60 exhibits negligible weight loss up to 600 °C, the weight fraction of C60 in **4** is estimated to be 6.3%.

The synthetic route for preparation of **8** is similar to that of **4**, and the detailed procedure is represented in Scheme 2. As

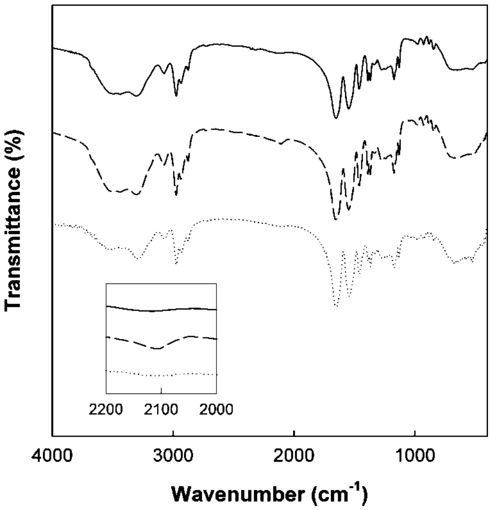


Figure 1. FT-IR spectra of pyrene−poly(*N*-isopropylacrylamide) (**2**) (solid line), pyrene−poly(*N*-isopropylacrylamide)−N_3 (**3**) (dashed line), and pyrene−poly(*N*-isopropylacrylamide)−fullerene (**4**) (dotted line).

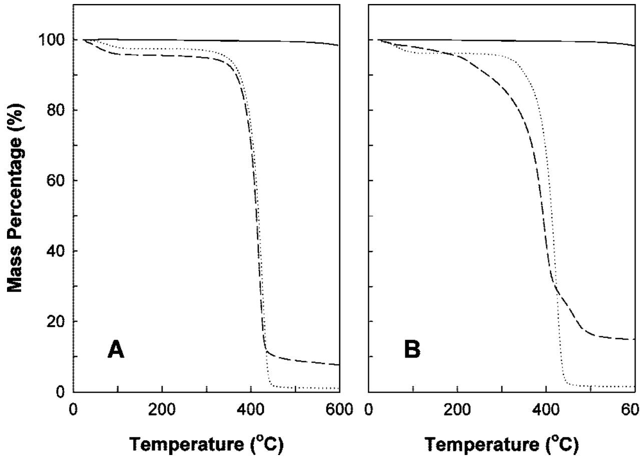
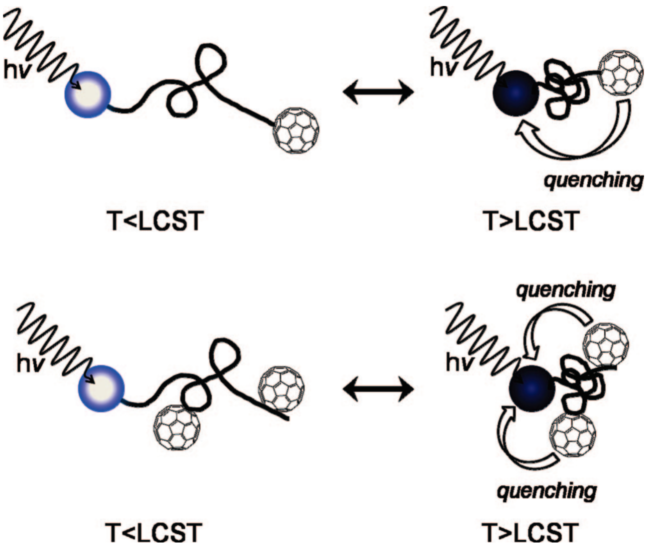


Figure 2. TGA curves of (A) C60 (solid line), pyrene−poly(*N*-isopropylacrylamide) (**2**) (dotted line), and pyrene−poly(*N*-isopropylacrylamide)−fullerene (**4**) (dashed line); (B) C60 (solid line), pyrene−poly(*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate) (**7**) (dotted line), and pyrene−poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (**8**) (dashed line).

the first step, NIPAM and 2-hydroxylethyl methacrylate (HEMA) are copolymerized via ATRP using the pyrene-based initiator (**1**) to yield **7**. Since all peaks in the NMR spectrum of **7** can be appropriately assigned (see Supporting Information), it is concluded that **7** is successfully synthesized. Here it should be noted that the hydroxyl group of the HEMA moiety in **7** can conjugate with a carboxyl acid group of C60COOH (**5**). However, since the carbodiimide-based esterification between hydroxyl group of **7** and carboxyl acid group of **5** yielded a low degree of esterification, the carboxyl acid group of **5** was converted to an acyl halide group for better esterification by reacting **5** with thionyl chloride in this study. Finally, C60 with the acyl chloride group (**6**) was then reacted with **7** to yield **8**, as illustrated in Scheme 2. When the UV−vis spectrum of **7** is compared with that of **8**, it is also found that the UV−vis absorption of **8** is significantly increased in the range of 300−400 nm, indicating that **6** was successfully conjugated with the hydroxyl group of **7** (see Supporting Information). From analysis of TGA thermograms in Figure 2B, the weight fraction of C60 in **8** is calculated to be 13.4%. Since the molecular weight of **7** is nearly equal to that of **2**, it is estimated that one molecule of **8** has two C60s on the average by comparing the weight fraction of C60 in **8** (13.4%) with that of **4** (6.3%).

Scheme 3. Diagrammatic Representation of the Induction of Fluorescence Quenching under Temperature Change



Scheme 3 illustrates the sensing mechanism of **4** and **8**. When the temperature is lower than the LCST of PNIPAM, PNIPAM has an extended conformation so that pyrene and C60 are thus located apart from each other. As a result, C60 hardly affects the fluorescence emitting from pyrene. On the other hand, when the temperature is higher than the LCST of PNIPAM, the PNIPAM chain becomes collapsed, and therefore the distance between pyrene and C60 becomes short enough for C60 to effectively quench the fluorescent emission of pyrene due to the photoinduced electron transfer.[42] It has been reported that the fluorescence quenching due to the photoinduced electron transfer is inversely proportional to the sixth power of the distance between donor and acceptor.[43]

Figure 3 shows the variation of emission spectra of **2**, **4**, and **8** as a function of temperature, where all emission spectra are obtained after irradiating the solution at 340 nm corresponding to the absorption wavelength of pyrene. Figure 3A shows that the intensity of **2** does not change significantly as the temperature increases from 25 to 35 °C. On the other hand, when the emission spectra of **4** and **8** are compared with those of **2**, it reveals that the fluorescence emitting from pyrene in **4** and **8** is considerably quenched at the temperatures above 31 °C, as shown in Figure 3B,C. This phenomenon is easily explained by considering the change of the end-to-end distance of PNIPAM with variation of temperature, where the end-to-end distance corresponds to the distance between pyrene and C60 in the polymer molecule. Since PNIPAM is hydrophilic at the temperature below its LCST, PNIPAM has an expanded chain conformation in aqueous solution, which causes an increase in the distance between pyrene and C60, as shown in Scheme 3. However, when the temperature is above its LCST, the PNIPAM chain becomes collapsed and forms the globular structure due to the temperature-dependent hydrophilic/hydrophobic interactions. Consequently, the conformational change of PNIPAM from coiled structure to globular structure at its LCST results in a decrease in the distance between pyrene and C60, which effectively induces the quenching of fluorescence emitting from pyrene by C60, as demonstrated in Scheme 3. Here it should be noted that all the fluorescence emission spectra were measured at very low concentration of 10^{-7} M in order to avoid the scattering effect induced by the interchain aggregation on the fluorescence.[36,44] When all the emission spectra of **2**, **4**, and

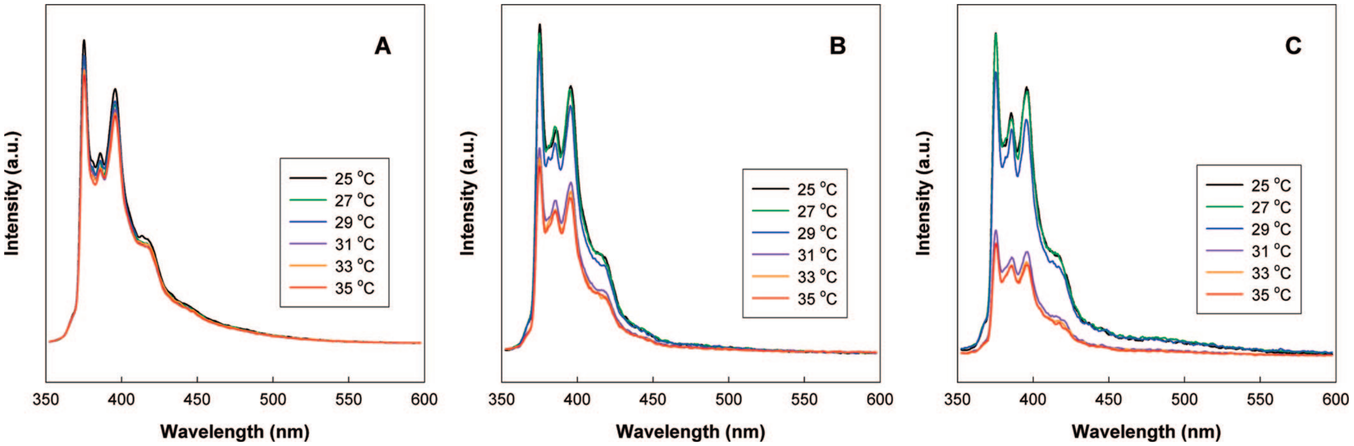


Figure 3. Fluorescence emission spectra of (A) pyrene−poly(*N*-isopropylacrylamide) (**2**), (B) pyrene−poly(*N*-isopropylacrylamide)−fullerene (**4**), and (C) pyrene−poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (**8**) at various temperatures when the excitation wavelength of 340 nm is irradiated. All the fluorescence emission spectra are measured at the concentration of 10^{-7} M.

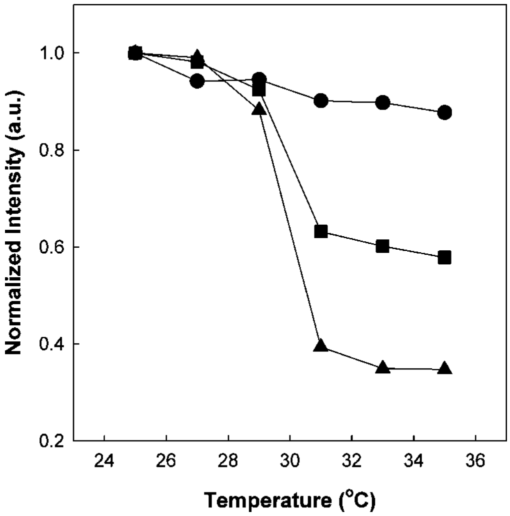


Figure 4. Plots of the normalized fluorescence emission intensity at 375 nm against temperature: pyrene−poly(*N*-isopropylacrylamide) (**2**) (circle); pyrene−poly(*N*-isopropylacrylamide)−fullerene (**4**) (square); pyrene−poly(*N*-isopropylacrylamide-*co*-fullerenylethyl methacrylate) (**8**) (triangle).

8 are normalized with respect to the intensity at 375 nm at 25 °C for quantitative comparison and the normalized intensity is plotted as a function of temperature, as shown in Figure 4, it reveals that the normalized intensity of **2** does not change significantly with variation of temperature while the normalized intensity of **4** and **8** is abruptly decreased at 31 °C as the temperature is increased. Figure 3 shows another interesting feature that **8** exhibits a larger decrease in intensity than **4** at 31 °C, when the normalized fluorescence intensity of **4** is compared with that of **8**. This can be explained by two reasons: One is that **8** has more C60s than **4** in a chain. Since C60 is critically responsible for quenching the fluorescence of pyrene, it is easily expected that the quenching efficiency becomes higher if the polymeric linker contains more C60s. The other is that the distance between C60 and pyrene in **8** is shorter than the distance in **4** so that the quenching efficiency of **8** becomes higher than **4**. It is also noted from Figure 4 that both **4** and **8** show a sharp transition in a narrow region of temperature, which strongly suggests that this type of C60-based sensor can be used as an alarm-type probe for detecting a specific temperature. It should be also noted that, since this type of ratiometric measurement generally shows concentration independence, it can accurately detect a delicate change in the biological and environmental phenomena being concerned even at very low concentration: this is one of the important advantages of the present sensor over the other conventional sensors using turbidity measurement. Moreover, since the thermal sensitivity depends upon the type of monomer used for preparation of the polymeric linker, the selection of a specific monomer may easily enable us to prepare the thermal sensor for detecting a specific temperature as one wish.

Conclusions

Two types of thermosensitive polymers composed of pyrene and C60 are synthesized, and their photophysical behaviors are examined as a function of temperature. Since the polymeric linker composed of PNIPAM undergoes the coil−globule transition as the temperature is changed, the distance between pyrene and C60 attached to each chain end of PNIPAM is changed with temperature, which controls the fluorescence quenching efficiency of C60. Compared with the case when only one C60 is attached to the end of the linker, the quenching efficiency is significantly enhanced when two C60s are attached onto the chain backbone. Since this C60-based polymeric sensor responds to a small change in temperature with well-defined on-and-off behavior, this type of temperature sensor provides a platform for designing a new effective temperature sensor.

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Supporting Information Available: ^{1}H NMR spectrum of **2**, UV−vis spectra of **2** and **4**, ^{1}H NMR spectrum of **7**, and UV−vis spectra of **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kadish, K. M.; Ruoff, R. S. *Fullerenes: Chemistry, Physics, and Technology*; Wiley-Interscience: New York, 2000.
(2) Martin, R. B.; Fu, K.; Sun, Y.-P. *Chem. Phys. Lett.* **2003**, *375*, 619.
(3) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.
(4) Kim, Y. K.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; Mcculloch, I.; Ha, C. S.; Ree, M. H. *Nat. Mater.* **2006**, *5*, 197.
(5) Kim, J. Y.; Lee, K. H.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222.
(6) Quiles, M. C.; Ferenczi, T.; Agostinelli, T.; Etchegoin, P. G.; Kim, Y. K.; Anthopoulos, T. D.; Stravrinou, P. N.; Bradley, D. D. C.; Nelson, J. *Nat. Mater.* **2008**, *7*, 158.

(7) Dulkeith, E.; Morteani, A. C.; Niedereichholz, T.; Klar, T. A.; Feldmann, J. *Phys. Rev. Lett.* **2002**, *89*, 203002.
(8) Fan, C.; Wang, S.; Hong, J. W.; Bazan, G. C.; Plaxco, K. W.; Heeger, A. J. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 6297.
(9) Gueroui, Z.; Libchaber, A. *Phys. Rev. Lett.* **2004**, *93*, 166108.
(10) Jennings, T. L.; Singh, M. P.; Strouse, G. F. *J. Am. Chem. Soc.* **2006**, *128*, 5482.
(11) Schneider, G.; Decher, G. *Nano Lett.* **2006**, *6*, 530.
(12) Anger, P.; Bharadwaj, P.; Novotny, L. *Phys. Rev. Lett.* **2006**, *96*, 113002.
(13) Liu, Y.; Liang, P.; Chen, Y.; Zhao, Y.-L.; Ding, F.; Yu, A. *J. Phys. Chem. B* **2005**, *109*, 23739.
(14) Baleizão, C.; Nagl, S.; Schäferling, M.; Berberan-Santos, M. N.; Wolfbeis, O. S. *Anal. Chem.* **2008**, *80*, 6449.
(15) Schild, H. G.; Tirrel, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.
(16) Ilmain, F.; Tanaka, T.; Kokufuta, E. *Nature (London)* **1991**, *349*, 400.
(17) Yagi, Y.; Inomata, H.; Saito, S. *Macromolecules* **1992**, *25*, 2997.
(18) Li, C.; Gunari, N.; Fisher, K.; Janshoff, A.; Schmidt, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1101.
(19) Ono, Y.; Shikata, T. *J. Am. Chem. Soc.* **2006**, *128*, 10030.
(20) An, Z.; Shi, Q.; Tang, W.; Tsung, C.-K.; Hawker, C. J.; Stucky, G. D. *J. Am. Chem. Soc.* **2007**, *129*, 14493.
(21) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959.
(22) Dong, L.; Agarwal, A. K.; Beebe, D. J.; Jiang, H. *Nature (London)* **2006**, *442*, 551.
(23) Sidorenko, A.; Krupenkin, T.; Taylor, A.; Fratzl, P.; Aizenberg, J. *Science* **2007**, *315*, 487.
(24) Cheng, Z.; Liu, S.; Beines, P. W.; Ding, N.; Jakubowicz, P.; Knoll, W. *Chem. Mater.* **2008**, *20*, 7215.
(25) Bromber, L. E.; Ron, E. S. *Adv. Drug Delivery Rev.* **1998**, *31*, 197.
(26) Kiser, P. F.; Wilson, G.; Needham, D. *Nature (London)* **1998**, *394*, 459.
(27) Murthy, N.; Xu, M. C.; Schuck, S.; Kunisawa, J.; Shastri, N.; Fréchet, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 4995.
(28) Kim, J.; Nayak, S.; Lyon, L. A. *J. Am. Chem. Soc.* **2005**, *127*, 9588.
(29) Zhang, Y.; Furyk, S.; Bergbreiter, D. E.; Cremer, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 14505.
(30) Li, Y.; Tang, Y.; Narain, R.; Lewis, A. L.; Armes, S. P. *Langmuir* **2005**, *21*, 9946.
(31) Das, M.; Mardyani, S.; Chan, W. C. W.; Kumacheva, E. *Adv. Mater.* **2006**, *18*, 80.
(32) Koopmans, C.; Ritter, H. *J. Am. Chem. Soc.* **2007**, *129*, 3502.
(33) Yang, M.; Chu, L.-Y.; Wang, H.-D.; Xie, R.; Song, H.; Niu, C. H. *Adv. Funct. Mater.* **2008**, *18*, 652.
(34) Luzinov, I.; Minko, S.; Tsukruk, V. V. *Prog. Polym. Sci.* **2004**, *29*, 635.
(35) Ionov, L.; Stamm, M.; Diez, S. *Nano Lett.* **2006**, *6*, 1982.
(36) Winnik, F. M. *Macromolecules* **1990**, *23*, 233.
(37) Wu, Chi; Wang, X. *Phys. Rev. Lett.* **1998**, *80*, 4092.
(38) Farinha, J. P. S.; Picüarra, S.; Miesel, K.; Martinho, J. M. G. *J. Phys. Chem. B* **2001**, *105*, 10536.
(39) Hong, S. W.; Kim, K. H.; Huh, J.; Ahn, C.-H.; Jo, W. H. *Chem. Mater.* **2005**, *17*, 6213.
(40) Masci, G.; Giacomelli, L.; Crescenzi, V. *Macromol. Rapid Commun.* **2004**, *25*, 559.
(41) Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93.
(42) Sun, Y.-P.; Ramamurthy, V.; Schanze, K. S. *Molecular and Supramolecular Photochemistry*; Marcel Dekker: New York, 1997.
(43) Koeppe, R.; Sariciftci, N. S. *Photochem. Photobiol. Sci.* **2006**, *5*, 1122.
(44) Winnik, F. M. *Polymer* **1990**, *31*, 2125.

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