

# Adjustable Temperature Sensor with Double Thermoresponsiveness Based on the Aggregation Property of Binary Diblock Copolymers

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Received 23 August 2005; accepted 13 February 2006

DOI 10.1002/app.24300

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This article presents a new and promising way to design a temperature sensor, which is based on the micellization or aggregation behavior of binary diblock copolymers of poly(ethylene glycol)-*b*-poly(*N*-isopropylacrylamide) (PEG-*b*-PNIPAM) and poly(ethylene glycol)-*b*-poly(4-vinylpyridine) (PEG-*b*-P(4-VP)). The temperature sensor presents both a lower critical response temperature (LCRT) and an upper critical response temperature (UCRT), where the thermoreversible aggregating of PEG-*b*-P(4-VP)

and H<sub>2</sub>SO<sub>4</sub> is used to control the LCRT, and the thermoreversible micellization of PEG-*b*-PNIPAM is used to control the UCRT. Furthermore, the LCRT can be altered by changing the H<sub>2</sub>SO<sub>4</sub> concentration, and the UCRT can be adjusted by altering the PEG-*b*-PNIPAM concentration. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3144–3148, 2006

**Key words:** block copolymers; micelles; aggregates; thermoresponsiveness

## INTRODUCTION

Thermoresponsive polymeric micelles have attracted much attention from researchers in recent years.<sup>1–15</sup> In particular, thermally controlled micellization of copolymers of poly(ethylene glycol) (PEG) and poly(*N*-isopropylacrylamide) (PNIPAM) has been well studied.<sup>1–14</sup> Feijen and coworkers reported the synthesis of PEG-*b*-PNIPAM and its micellization behavior.<sup>1</sup> Many groups studied the effects of the composition of copolymer, the concentration of microgels, and heating rate on the aggregation of aqueous PEG-*g*-PNIPAM or PEG-*b*-PNIPAM solutions.<sup>2–14</sup> Since the thermally controlled micellization of PEG-*b*-PNIPAM leads to the rapid increase of the scattered light intensity, it may be used as the temperature sensor. However, the solution of PEG-*b*-PNIPAM can form colloidal aggregates only at high temperatures, which limits its use as a temperature sensor. Recently, Laschewsky's group and Maeda's group have used a new type of complex, switchable block copolymers of PNIPAM and poly(3-[*N*-(3-methacrylamidopropyl)-*N,N*-dimethyl] ammoniopropane sulfonate) (PNIPAM-*b*-PSPP),<sup>15–17</sup> which

exhibits a double thermoresponsive behavior in water: the PNIPAM block shows a lower critical solution temperature (LCST), whereas the PSPP block exhibits an upper critical solution temperature (UCST). However, the synthesis of such block copolymers containing hydrophilic and zwitterionic blocks is inherently difficult. Besides, the LCST and UCST cannot be easily adjusted.

An applicable temperature sensor should present both a lower critical response temperature (LCRT) and an upper critical response temperature (UCRT). Thus, adjusting the LCRT and UCRT of the sensor can make it useful in monitoring different temperature ranges. Since the critical aggregation temperature of PEG-*b*-PNIPAM microgels can be easily adjusted,<sup>[4a]</sup> it may be used to control the UCRT. It is known that a zwitterionic polymer may exhibit an UCST because of the thermosensitivity of the intermolecular attraction of the zwitterionic groups.<sup>15–19</sup> Therefore, the clusters formed by ionic crosslinks between two opposing charges may exhibit thermoresponsiveness similar to that shown by the UCST. Herein, we use 4-vinylpyridine (4-VP) copolymers such as PEG-*b*-P(4-VP) to control the LCRT because protonated 4-VP blocks can form clusters with anions such as SO<sub>4</sub><sup>2-</sup> through ionic crosslinks. Thus, a temperature sensor with double thermoresponsiveness can be constructed by mixing the aqueous solutions of PEG-*b*-P(4-VP), H<sub>2</sub>SO<sub>4</sub>, and PEG-*b*-PNIPAM, where PEG-*b*-P(4-VP) is used to control the LCRT and PEG-*b*-PNIPAM to control the UCRT. This is a new and sensitive way to monitor

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20328407.

Contract grant sponsors: Nankai University and the Canada Research Chair program.

temperature changes and may have useful applications.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) (PEG) monomethyl ether ( $\text{CH}_3\text{O-PEG}_{45}\text{-OH}$ ) ( $M_w = 2000$  and the polydispersity index  $\text{PDI} = 1.10$ ) was obtained from Fluka (St. Louis, MO). 4-Vinylpyridine (4VP, Aldrich) was stirred with a small amount of  $\text{CaH}_2$  at  $40\text{--}50^\circ\text{C}$  for 2 h. Then 4VP was decanted, degassed via three freeze-thaw cycles, and distilled under vacuum into a Schlenk tube. *N*-isopropylacrylamide (99%, Aldrich) was recrystallized from benzene/*n*-hexane (6/4, v/v).  $\text{CuBr}$  (98+%, Aldrich) were used as received. Tris-(2-dimethylaminoethyl) amine ( $\text{Me}_6\text{TREN}$ ) was prepared from TREN by a procedure similar to that in Ref. 20. Other solvents were analytical chemical reagents and used as received without further purification.

### Synthesis of PEG macroinitiator

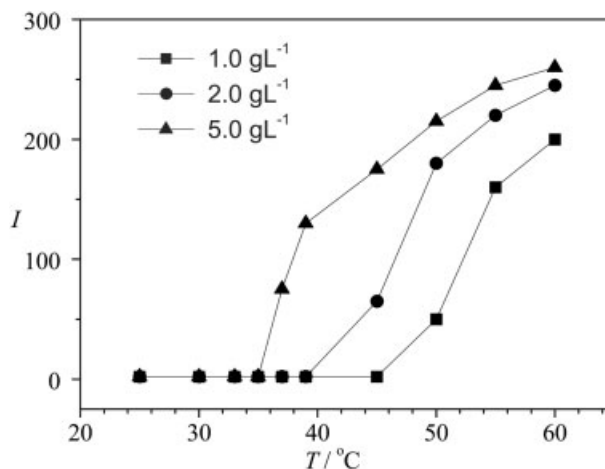
Bromide-tailed macroinitiator  $\text{PEG}_{45}\text{-Br}$  was synthesized according to Ref. 21. The synthetic procedures and the  $^1\text{H}$  NMR spectrums of  $\text{CH}_3\text{O-PEG}_{45}\text{-OH}$  and  $\text{PEG}_{45}\text{-Br}$  can be seen in supplementary material.

### Synthesis of $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$ and $\text{PEG}_{45}\text{-}b\text{-P}(4\text{-VP})_{21}$

$\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$  and  $\text{PEG}_{45}\text{-}b\text{-P}(4\text{-VP})_{21}$  were synthesized by atom transfer radical polymerization (ATRP) of NIPAM and 4-VP, respectively, with  $\text{PEG-Br}$  as the macroinitiator.<sup>22–24</sup> The synthetic procedures were similar to those in Refs. 22–24, where  $\text{CuBr}$  complexed by  $\text{Me}_6\text{TREN}$  is used as the ATRP catalyst. The degree of polymerization ( $\text{DP}_n$ ) of the polymers was determined by the use of  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  (see supplementary material). The polydispersity ( $M_w/M_n$ ) of  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$  and  $\text{PEG}_{45}\text{-}b\text{-P}(4\text{-VP})_{21}$  was determined to be 1.14 and 1.19, respectively, by gel permeation chromatography (GPC) in *N,N*-dimethylformamide (DMF) with poly(methyl methacrylate) standards (see supplementary material).

### Solutions preparation

The copolymer  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$  was directly dissolved in deionized water ( $>18\text{ M}\Omega$ , Milli-Q, Millipore) and kept at room temperature for 3 days to make a stock polymer solution with the concentration of  $10\text{ gL}^{-1}$ . Then a series of polymer solutions of different concentration were prepared by diluting the stock solution. Direct dissolution of  $\text{PEG}_{45}\text{-}b\text{-P}(4\text{-VP})_{21}$  in deionized water at  $50^\circ\text{C}$  for 5 days resulted in a



**Figure 1** Scattered light intensity ( $I$ ) as function of temperature ( $T$ ) for aqueous solutions of  $\text{PEO}_{45}\text{-}b\text{-PNIPAM}_{35}$  at different concentrations ( $\text{gL}^{-1}$ ): 1.0 (squares), 2.0 (circles), 5.0 (triangles).

light blue solution with the concentration of  $1.0\text{ gL}^{-1}$ . Aqueous  $\text{H}_2\text{SO}_4$  solutions with different concentrations were made by diluting concentrated sulfuric acid (98%) and the concentrations were determined by measuring the pH values of solution. All the solutions were filtered through Millipore  $0.45\text{ }\mu\text{m}$  membranes before mixing. Before the light scattering (LS) measurement, all the samples were equilibrated for a week at a given temperature (from  $25$  to  $60^\circ\text{C}$ ) and at least three “heat-cool” cycles were performed.

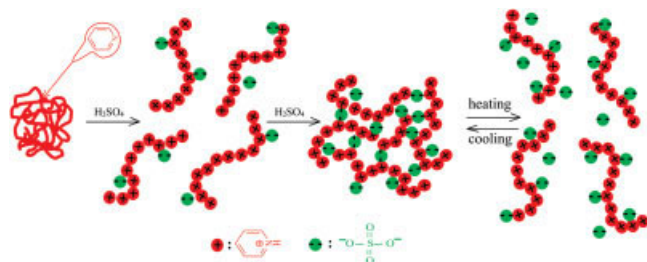
### Light scattering

LS was performed on a laser LS spectrometer (BI-200SM) at  $514\text{ nm}$  and at a given intensity of incident beam. Experiments were carried out in a temperature range from  $25$  to  $60^\circ\text{C}$  at the scattering angle  $90^\circ$  and all samples were equilibrated for  $60\text{ min}$  at each temperature.

## RESULTS AND DISCUSSION

### The concentration dependence of the critical aggregation temperature for the microgels of $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$

LS was used to measure the scattered light intensity, which can indicate the aggregation or dissolution of polymers. Figure 1 shows the concentration dependence of the critical aggregation temperature for the microgels of  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$ . Clearly, the critical aggregation temperature increases with decreasing microgel concentration. The critical aggregation temperatures are at  $35$ ,  $39$ , and  $45^\circ\text{C}$ , for the microgels at concentrations of  $5.0$ ,  $2.0$ , and  $1.0\text{ gL}^{-1}$ , respectively. Thus, by adjusting the microgel concentration, differ-

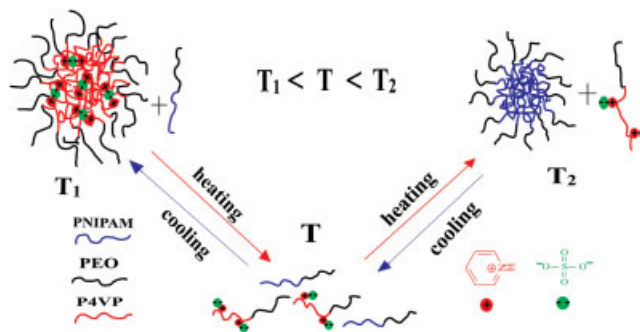


**Scheme 1** Schematic representation of formation and dissociation of cluster formed by P(4-VP) polycations and  $\text{SO}_4^{2-}$  anions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ent UCRTs can be obtained to meet the desired requirements.

### The thermoreversible aggregating of $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$ in $\text{H}_2\text{SO}_4$ aqueous solution and the $\text{H}_2\text{SO}_4$ concentration dependence of the critical dissociation temperature

Direct dissolution of  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$  in water at  $50^\circ\text{C}$  for 5 days resulted in a light blue solution, which was a sign of the formation of micelles. However, when aqueous  $\text{H}_2\text{SO}_4$  solution was added slowly, it turned white–blue, a sign of the formation of micelle-like aggregates. The solution cleared up gradually with increasing temperature, which suggested that the micelle-like aggregates dissociated gradually and finally disappeared. The solution turned white–blue again when the temperature was decreased to room temperature. This behavior can be rationalized as follows: when  $\text{H}_2\text{SO}_4$  is added, the 4-VP units are protonated, which means that the P(4-VP) blocks become polycation chains. Because of the formation of the ion pairs between  $\text{SO}_4^{2-}$  anions and protonated pyridine cations, these polycation chains will aggregate and form clusters driven by the electrostatic short-range attractions (as shown in Scheme 1).<sup>25–31</sup> The existence of water-soluble PEG blocks prevents the clusters from aggregating further and precipitating, which leads to the formation of the micelle-like aggregates (as shown in Scheme 2) with the P(4-VP) ionic clusters as the core and PEG blocks as the shell. When the temperature is increased, the ion pairs between  $\text{SO}_4^{2-}$  and protonated pyridine cations are interrupted and the ionic clusters dissociate. Besides, the increase in the concentration of  $\text{SO}_4^{2-}$  can promote the formation of ion pairs, which means that more ion pairs form with increasing  $\text{H}_2\text{SO}_4$  concentration and the critical dissociation temperature of clusters increases. Figure 2 shows the effects of the temperature and ionic strength on the formation of the clusters. Clearly, the clusters dissociate gradually with the rising temperature and the critical dissociation temperature increases with increasing  $\text{H}_2\text{SO}_4$  concentration. The critical dis-

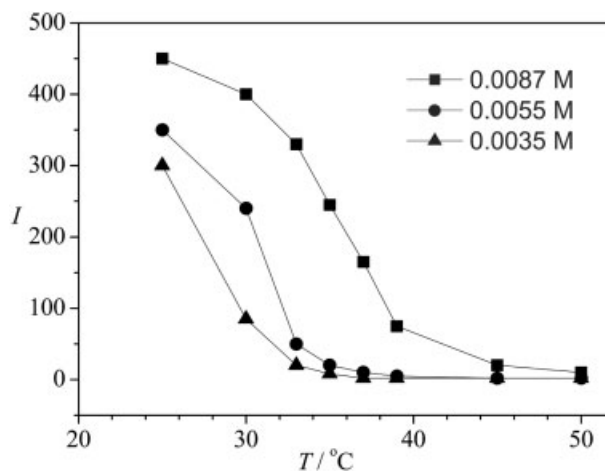


**Scheme 2** Illustration of the mechanism of the temperature sensor with double thermoresponsiveness formed by binary diblock copolymers of  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$  (protonated with  $\text{H}_2\text{SO}_4$ ) and  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

sociation temperatures are at  $35$ ,  $37$ , and  $45^\circ\text{C}$ , corresponding to the  $\text{H}_2\text{SO}_4$  concentrations of  $0.0035$ ,  $0.0055$ , and  $0.0087\text{M}$ , respectively. Thus, the LCRT can be adjusted by changing the  $\text{H}_2\text{SO}_4$  concentrations in the  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$  solutions.

### The construction of adjustable temperature sensor

The aqueous solution of  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$  is mixed with the aqueous solution of  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$  and  $\text{H}_2\text{SO}_4$  to construct a temperature sensor with double thermoresponsiveness. The mechanism of the temperature sensor is shown in Scheme 2. The  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}/\text{H}_2\text{SO}_4$  is used as the control of the LCRT and the  $\text{PEG}_{45}\text{-}b\text{-PNIPAM}_{35}$  as the control of the UCRT. When the temperature is below the LCRT ( $T_1$ ), the protonated  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{21}$  and  $\text{SO}_4^{2-}$  form clusters, which causes a rapid increase in



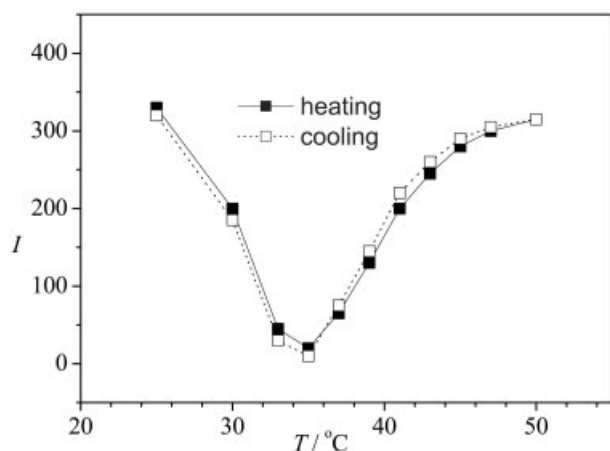
**Figure 2** Scattered light intensity ( $I$ ) vs. temperature ( $T$ ) for aqueous  $\text{PEG}_{45}\text{-}b\text{-P(4-VP)}_{22}$  solutions ( $0.50\text{ g L}^{-1}$ ) at different  $\text{H}_2\text{SO}_4$  concentrations:  $0.0087\text{M}$  (squares),  $0.0055\text{M}$  (circles),  $0.0035\text{M}$  (triangles).



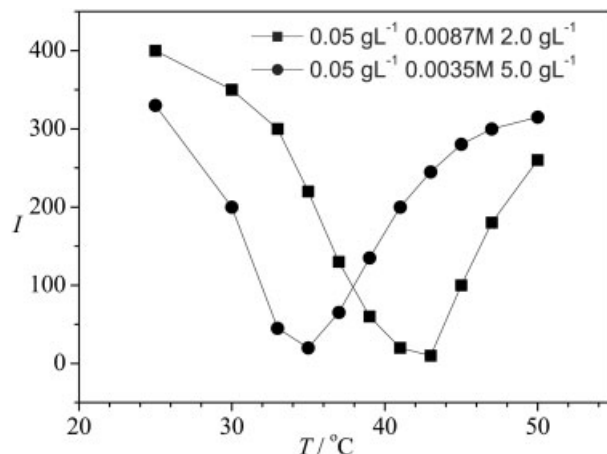
the scattered light intensity. When the temperature is above the UCRT ( $T_2$ ), the micellization of PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub> leads to a rapid increase in the scattered light intensity. Then, at temperatures ( $T$ ) between the LCRT ( $T_1$ ) and the UCRT ( $T_2$ ), scattered light intensity is close to zero. Thus, the temperature sensor can respond very quickly to the change of temperature with the scattered light intensity as the indication. Figure 3 shows a typical temperature sensor with double thermoresponsiveness and its response temperature is about 35°C. Obviously, temperature sensors with different response temperatures can be constructed since the LCRT can be altered by changing the H<sub>2</sub>SO<sub>4</sub> concentration and the UCRT can be adjusted by altering the PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub> concentration. For example, the two temperature sensors shown in Figure 4 present different response temperatures: 35°C, 43°C, respectively.

## CONCLUSIONS

We propose a facile and promising strategy to design a temperature sensor, which is based on the aggregation or micellization behavior of binary diblock copolymers of PEG<sub>45</sub>-*b*-P(4-VP)<sub>21</sub> and PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub>. The thermoreversible aggregating of PEG<sub>45</sub>-*b*-P(4-VP)<sub>21</sub>/H<sub>2</sub>SO<sub>4</sub> is used as the control of the LCRT and the thermally controlled micellization of PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub> as the control of the UCRT. Moreover, the temperature sensor can be easily adjusted to monitor different temperatures by changing the concentrations of H<sub>2</sub>SO<sub>4</sub> and PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub>. By the medium of the temperature sensor, the change of temperature can be easily trans-



**Figure 3** Scattered light intensity ( $I$ ) vs. temperature ( $T$ ) for ternary aqueous solutions of PEG<sub>45</sub>-*b*-P(4-VP)<sub>21</sub>, H<sub>2</sub>SO<sub>4</sub>, and PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub> with concentrations of 0.50 gL<sup>-1</sup>, 0.0035M, 5.0 gL<sup>-1</sup>, respectively. Heating (solid line) and cooling (dash line).



**Figure 4** Scattered light intensity ( $I$ ) vs. temperature ( $T$ ) for ternary aqueous solution of PEG<sub>45</sub>-*b*-P(4-VP)<sub>21</sub>, H<sub>2</sub>SO<sub>4</sub>, and PEG<sub>45</sub>-*b*-PNIPAM<sub>35</sub> at concentrations of 0.50 gL<sup>-1</sup>, 0.0035M, 5.0 gL<sup>-1</sup> (circles); 0.50 gL<sup>-1</sup>, 0.0087M, 2.0 gL<sup>-1</sup> (squares), respectively.

formed to optical signals and electric signals, and this gives us an applicable method to monitor temperature.

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