

Research Article

Thermoresponsive and Redox Behaviors of Poly(*N*-isopropylacrylamide)-Based Block Copolymers Having TEMPO Groups as Their Side Chains

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Received 18 April 2013; Revised 24 May 2013; Accepted 10 June 2013

Academic Editor: Haojun Liang

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Thermoresponsive and redox-active block copolymers having 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moieties have been synthesized by using the reversible addition-fragmentation chain transfer (RAFT) polymerization technique. *N*-Isopropylacrylamide (NIPAAm) and 2,2,6,6-tetramethylpiperidyl methacrylate (TEMPMA) monomers were copolymerized stepwise under RAFT polymerization conditions to afford the thermoresponsive block copolymers, PNIPAAm-*block*-PTEMPMA and PNIPAAm-*block*-PTEMPMA-*block*-PNIPAAm. Oxidation of tetramethylpiperidine groups in the copolymers successfully afforded the corresponding TEMPO-containing block copolymers. The resulting triblock copolymer was found to be thermoresponsive showing lower critical solution temperature (LCST) at 34°C in its aqueous solution. Redox behavior of the resulting copolymer was observed by cyclic voltammetry. The potential of anodic current peak changed below and above the LCST of the block copolymer. These results indicate that the phase transition of thermoresponsive polymer influences the redox potential of TEMPO moieties.

1. Introduction

Much attention has been paid to stimuli-responsive polymers in chemistry and materials science, because of their unique reversible change of physical properties in response to a chemical or physical stimulus [1–3]. Responsive behavior typically involves physical changes in polymer's properties. For instance, unique changes in solubility are often exhibited by the polymers that have lower critical solution temperature (LCST). While many synthetic polymers exhibit LCSTs, poly(*N*-isopropylacrylamide) (PNIPAAm) and its copolymers are the most popular materials with LCSTs. Drug delivery systems [4–6], chromatographic separations [7, 8], separation and purification of metal ions [9, 10], and molecular recognition [11] are among the most important fields in which thermoresponsive polymers are used. In previous study, we have found that the phase transition behavior of PNIPAAm-based polymer having pyrrolidine groups as side chains was influenced by pH values [12]. Their LCST's changes were influenced by deionization of pyrrolidine hydrogen

chloride moieties. Moreover, the pyrrolidine side chains of the thermoresponsive copolymer promoted the aldol reaction between cyclohexanone and *p*-nitrobenzaldehyde in water, and the reaction proceeded most smoothly at its LCST. The thermoresponsive polymer in water aggregate to form a rather hydrophobic reaction field and the substrates are probably concentrated and promoted the aldol reaction in the resulting hydrophobic field. Thus, such a hydrophobic field formed by thermoresponsive polymers could be utilized for various organic reactions in aqueous media. Beside the pH dependence on phase transition, several examples of thermoresponsive polymers with redox responsiveness have been reported such as PNIPAAm-based polymers containing ferrocenyl pendant groups or 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) groups [13–16]. The polymers containing TEMPO moieties, which were prepared by the polymer reaction of poly(*N*-acryloxysuccinimide) with a mixture of 4-amino TEMPO and isopropylamine, were reported to show redox-sensitive LCST behavior [14]. These polymers are promising for the application to the TEMPO-mediated

redox reactions in the hydrophobic field generated by the phase transition of the thermoresponsive polymers. For this purpose it is important to control the repeat units sequence so that the redox centers are effectively surrounded by the thermoresponsive polymer chains. However, most hitherto known thermoresponsive polymers having TEMPO moieties have been prepared in a random manner [14–16], and few thermoresponsive behaviors with redox responsiveness of the corresponding polymers having block structures have been reported. In this study, sequence-ordered thermoresponsive polymers having TEMPO pendant groups as mediatory centers were synthesized by using the reversible addition-fragmentation chain transfer (RAFT) polymerization technique, and thermoresponsivity and redox behaviors of the resulting polymers were investigated.

2. Experimental

2.1. General. IR spectra were obtained on an FT-IR-470 Plus spectrometer. ^1H NMR spectra were measured on a Varian OXFORD NMR300 (300 MHz) or JEOL JNM-AL400 (400 MHz) spectrometer, and the chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. The molecular weights of polymers were determined by using a gel permeation chromatography (GPC). The GPC analyses were carried out on a Hitachi L-6000 high-performance liquid chromatograph, L-3350 RI detector, and Shodex GPC KF-804L column. THF was used as the eluent with a flow rate of 1.0 mL/min, and molecular weight values were relative to the polystyrene standards (Shodex STANDARD SM-105 and SL-105). UV-visible spectra were recorded with Jasco V-630 spectrometer (Tokyo, Japan). ESR spectra were recorded by JEOL JES-PX1050. Cyclic voltammetry was measured by BAS CV-50.

2.2. Materials. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid was synthesized from 4,4'-azobis (4-cyanopentanoic acid), carbon disulfide (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and 1-dodecanethiol (SIGMA-ALDRICH) [17]. *N*-Isopropylacrylamide (NIPAAm) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was purified by recrystallization from hexane-benzene (95 : 5). 2,2'-Azobisisobutyronitrile (AIBN) as a radical initiator was recrystallized from methanol below 40°C. Tetrahydrofuran (THF) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was distilled from Na-benzophenoneketyl under Ar atmosphere. 2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TEMPMA) and the other materials were commercially available and used without further purification.

2.3. Synthesis of Poly(TEMPMA-*ran*-NIPAAm) (1). TEMPMA (0.26 g, 1.1 mmol), NIPAAm (3.16 g, 27.9 mmol), AIBN (0.1 mol% relative to monomers) as an initiator, and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (1.0 mol% relative to monomers) were dissolved in THF (4 mL). After oxygen was removed repeatedly by freeze-evacuation-thaw cycles, polymerization was carried out at 60°C for 15 h. After cooling in an ice-water bath,

the polymer solution was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from THF into diethyl ether. ^1H NMR (CDCl_3) δ 0.88–2.87 (m, NIPAAm unit, TEMPMA unit), 3.87–4.12 (bs, $\text{CH}(\text{CH}_3)_2$), 5.03–5.19 (bs, O-CH); IR (KBr) 3299, 3077, 1726, 1653, 1545 cm^{-1} .

2.4. Synthesis of PNIPAAm-*block*-PTEMPMA-*block*-PNIPAAm

2.4.1. RAFT Reagent Terminated PNIPAAm. NIPAAm (6.40 g, 56.6 mmol), AIBN (0.1 mol% relative to monomer) as an initiator, and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (1.0 mol% relative to monomer) as a chain transfer reagent (RAFT reagent) were dissolved in THF (6 mL). After oxygen was removed repeatedly by freeze-evacuation-thaw cycles, polymerization was carried out at 60°C for 15 h. After cooling in an ice-water bath, the polymer solution was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from THF into diethyl ether. ^1H NMR (CDCl_3) δ 1.02–3.17 (m, CH_2 -CH, $\text{CH}(\text{CH}_3)_2$), 3.85–4.18 (bs, $\text{CH}(\text{CH}_3)_2$); IR (KBr) 3293, 3079, 1650, 1550 cm^{-1} .

2.4.2. PNIPAAm-*block*-PTEMPMA (2). TEMPMA (1.03 g, 4.55 mmol), AIBN (0.1 mol% relative to monomer) as an initiator, and RAFT reagent terminated PNIPAAm (1.0 mol% relative to monomer) as a macrochain transfer agent (macro-CTA) were dissolved in THF (4 mL). After oxygen was removed repeatedly by freeze-evacuation-thaw cycles, polymerization was carried out at 60°C for 60 h. After cooling in an ice-water bath, the polymer solution was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from THF into diethyl ether. ^1H NMR (CDCl_3) δ 0.76–2.85 (m, NIPAAm unit, TEMPMA unit), 3.86–4.19 (bs, $\text{CH}(\text{CH}_3)_2$), 4.96–5.18 (bs, O-CH); IR (KBr) 3299, 3074, 1730, 1652, 1559 cm^{-1} .

2.4.3. PNIPAAm-*block*-PTEMPMA-*block*-PNIPAAm (3). NIPAAm (1.66 g, 1.47 mmol), AIBN (1.7 mg, 0.01 mmol) as an initiator and PNIPAAm-*block*-PTEMPMA (2) (0.69 g) as a macro-CTA were dissolved in THF (4 mL). After oxygen was removed repeatedly by freeze-evacuation-thaw cycles, polymerization was carried out at 60°C for 80 h. After cooling in an ice-water bath, the polymer solution was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from THF into diethyl ether. ^1H NMR (CDCl_3) δ 0.80–3.17 (m, NIPAAm unit, TEMPMA unit), 3.90–4.17 (bs, $\text{CH}(\text{CH}_3)_2$), 4.98–5.18 (bs, O-CH); IR (KBr) 3298, 3074, 1726, 1649, 1546 cm^{-1} .

2.5. Oxidation of Tetramethylpiperidine Moieties in the Polymers. Polymer having TEMPMA moieties (**1**, **2**, or **3**) (0.80 g), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.37 g, 1.1 mmolL), and 30% H_2O_2 (6 mL) was dissolved in H_2O (24 mL). This reaction mixture was stirred at 4°C for 24 h. Into the mixture was added K_2CO_3 until the solution was saturated. The aqueous solution was extracted with ethyl acetate until the organic layer was colorless. The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to give an orange to pale red powder.

Poly(TEMPOMA-ran-NIPAAm); IR (KBr) 3308, 3081, 1719, 1653, 1539 cm^{-1} .

PNIPAAm-block-PTEMPOMA; IR (KBr) 3298, 3080, 1726, 1649, 1546 cm^{-1} .

PNIPAAm-block-PTEMPOMA-block-PNIPAAm; IR (KBr) 3297, 3080, 1730, 1650, 1548 cm^{-1} .

2.6. Measurement of Cloud Points. The cloud points of aqueous polymer solutions (1.0 w/v%) were determined by transmittance measurements using a UV-visible spectrometer equipped with a temperature controller. The transmittance of the polymer solutions was recorded as a function of temperature (15–45°C). The wavelength was fixed at 500 nm, and the temperature was raised at 1.0°C/min. The cloud points of the polymer solutions were defined as the temperatures when the transmittance was decreased to half of final transmittance from initial.

2.7. Electrochemical Testing of the Copolymers. Cyclic voltammograms were measured in 0.1M KCl aqueous solution after bubbling with nitrogen gas (20 min) at various temperatures (5–55°C). As a working electrode and a counter electrode were used a GCE Glassy carbon (BAS 6.0 × 1.6 mm) and a platinum wire (BAS VC-3 cell 5 cm Pt), respectively, and a reference electrode consisted of Ag/AgCl (BAS RE-1B). Scan rate was 100 mV/s. The concentration of aqueous solution of poly(TEMPOMA-ran-NIPAAm) or PNIPAAm-block-PTEMPOMA was adjusted at 2.0 mM (based on TEMPO moieties). The concentration of aqueous solution of PNIPAAm-block-PTEMPOMA-block-PNIPAAm was 0.47 g/mL.

3. Results and Discussion

3.1. Synthesis and Characterization of Poly(TEMPOMA-ran-NIPAAm). Thermoresponsive polymers having 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) pendant groups as mediatory centers were synthesized by using the reversible addition-fragmentation chain transfer (RAFT) polymerization technique and oxidation of 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TEMPMA) units. *N*-Isopropylacrylamide (NIPAAm) and TEMPMA were copolymerized in a random manner in the presence of 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid to afford poly(TEMPMA-ran-NIPAAm) (Scheme 1). The resulting random copolymer was analyzed by ^1H NMR spectroscopy; the ratio of TEMPMA/NIPAAm units was determined to

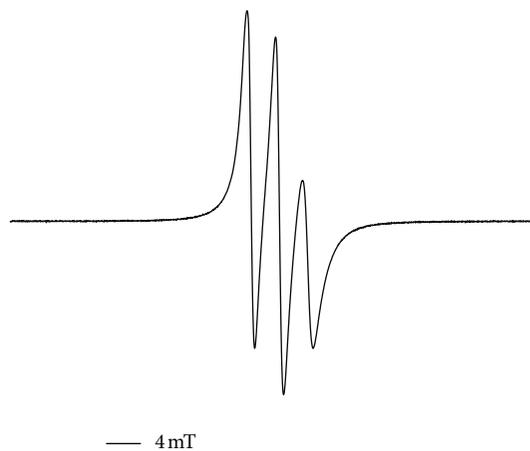


FIGURE 1: ESR spectrum of poly(TEMPOMA-ran-NIPAAm).

be 6:94. The number average molecular weight (M_n) of the random copolymer was estimated by GPC based on polystyrene standard to be 4840 ($M_w/M_n = 1.26$). Oxidation of the TEMPMA units afforded poly(TEMPOMA-ran-NIPAAm). The resulting TEMPO-containing random copolymer was characterized by ESR spectroscopy, and its spectrum showed characteristic three-line signals of a nitroxyl group (Figure 1) [14, 15]. The random copolymer, poly(TEMPMA-ran-NIPAAm), showed thermoresponsivity, and its lower critical solution temperature (LCST) was observed at 31°C, which was slightly increased to 33°C after oxidation of tetramethylpiperidine moieties (Figure 2(a)). The transmittance of the oxidized random copolymer solution was observed to be decreased from 25°C, and at 0.1°C/min of heating rate the thermoresponsivity was still slow, but the LCST was observed at 32°C, which was almost unchanged in comparison with that before oxidation of the TEMPMA moieties.

3.2. Synthesis and Characterization of the Diblock and Triblock Copolymers. The diblock and triblock polymers were also synthesized by using the RAFT polymerization technique and oxidation of TEMPMA units. Firstly, the RAFT reagent terminated PNIPAAm was prepared, and, in the second step, PNIPAAm-block-PTEMPMA was synthesized by using the RAFT reagent terminated PNIPAAm as a macro-chain transfer agent (macro-CTA) (yield 58%). Finally, PNIPAAm-block-PTEMPMA-block-PNIPAAm was synthesized by using the resulting diblock polymer as a macro-CTA (yield 94%) (Scheme 2). The M_n of the resulting block polymers having TEMPO precursor as side chains were estimated by determining the molar ratio of the repeating units and the end group from the ratio of signal intensities of $-\text{NHCH}(\text{CH}_3)_2$ of NIPAAm units, the proton at 4-position of piperidine moieties, and $-\text{S}-\text{CH}_2-$ of the end group in the ^1H NMR spectra. The molecular weight increased stepwise with the progress of polymerization and the M_n values estimated from ^1H NMR were almost same as those estimated from GPC (Table 1). Oxidation of tetramethylpiperidine moieties in the resulting diblock and triblock copolymers

TABLE 1: Molecular weight data of the resulting copolymers.

	Content of TEMPMA units ^a (%)	M_n^a	M_n^b	M_w/M_n^b
Poly(TEMPOMA- <i>ran</i> -NIPAAm) 1	6	—	4840	1.26
RAFT reagent terminated PNIPAAm	—	6310	6600	1.20
PNIPAAm- <i>block</i> -PTEMPMA 2	4	7750	6970	1.17
PNIPAAm- <i>block</i> -PTEMPMA- <i>block</i> -PNIPAAm 3	1	15200	13940	1.35

^aDetermined by integrated intensity of ¹H NMR spectra. ^bEstimated by GPC based on polystyrene standard in THF.

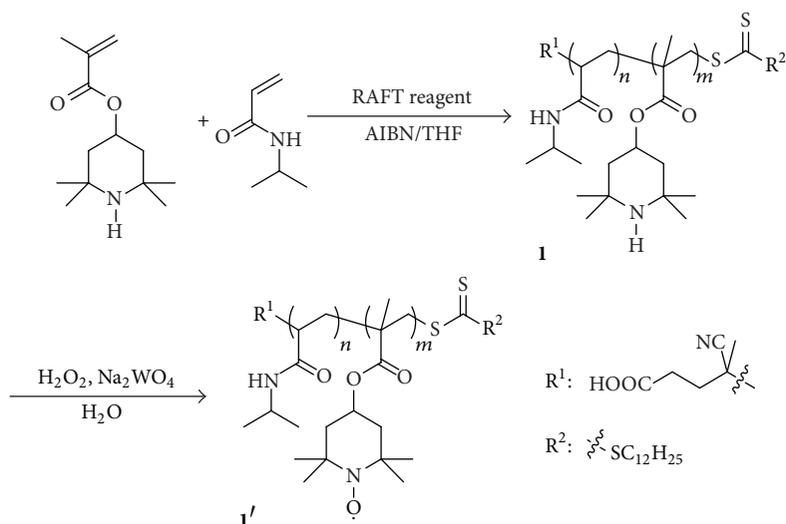
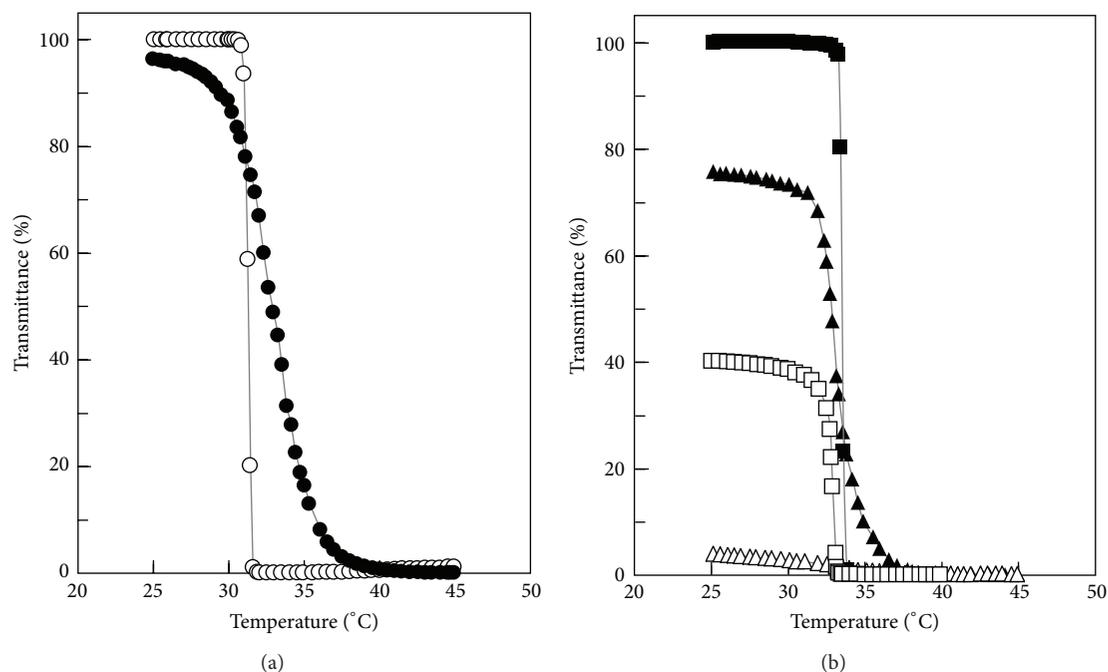
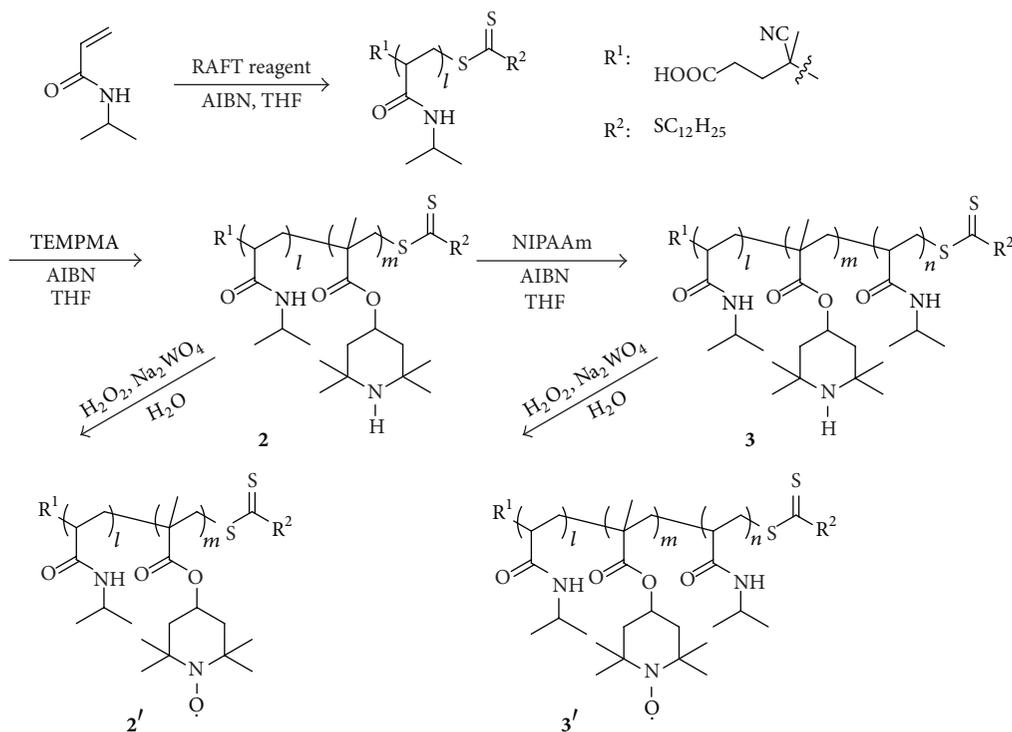
SCHEME 1: Synthesis of poly(TEMPOMA-*ran*-NIPAAm).

FIGURE 2: Temperature dependence of transmittance of 10 mg/mL aqueous solutions of (a) poly(TEMPOMA-*ran*-NIPAAm) (**1**) (solid circle), poly(TEMPOMA-*ran*-NIPAAm) (**1'**) (open circle); (b) PNIPAAm-*block*-PTEMPMA (**2**) (solid triangle) PNIPAAm-*block*-PTEMPOMA (**2'**) (open triangle); PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm (**3**) (solid square) and PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm (**3'**) (open square).



SCHEME 2: Synthesis of the block polymers consisting of NIPAAm and TEMPOMA units.

afforded PNIPAAm-*block*-PTEMPOMA and PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm. The block polymers having TEMPO moieties as side chains were characterized by ESR spectroscopy, and their spectra showed characteristic three-line signals of nitroxyl groups. The diblock and triblock copolymers containing TEMPMA and NIPAAm groups showed thermoresponsivity, and their LCSTs were observed at 33°C and 34°C, respectively. After oxidation of tetramethylpiperidine moieties, the diblock copolymer became insoluble in water; on the other hand, the triblock copolymer was found to have LCST at 33°C (Figure 2(b)). The molecular weight of water-insoluble diblock copolymer was 6970 and contained 4% of TEMPO moiety, while that of the corresponding random copolymers containing 6% of TEMPO moiety was 4840 and soluble in water. Thus a continuous structure of TEMPO moieties probably leads to the insolubility in water, and the NIPAAm unit sequence seems to be too short to form a polymer micelle. On the other hand, TEM images of the triblock copolymer aggregates obtained from their aqueous solutions showed *ca.* 50 nm of spheres under LCST, and these spherical particles aggregated to form more than 100 nm of clusters over LCST. Moreover, the initial transmittance of the oxidized triblock copolymer solution was observed to be 40% (Figure 2(b)). These results indicate the triblock copolymers form a polymer micelle.

3.3. Thermoresponsive Behavior of the Resulting Copolymers. TEMPO derivatives are reduced with L-ascorbic acid to form the corresponding hydroxylamine [18]. The thermoresponsive behavior of the resulting random and block copolymers

having TEMPO moieties was observed in 0.1 M aqueous solution of Na_2SO_4 in presence of L-ascorbic acid. The solution of the random copolymer was found to show LCST at 22°C in 0.1 M Na_2SO_4 , and the LCST value increased to 33°C with increasing concentration of L-ascorbic acid because of the reduction of the TEMPO moieties (Figure 3(a)). The similar PNIPAAm-based polymer having TEMPO moieties has been reported to show almost the same LCST changes from 19°C to 33°C under reduction conditions with L-ascorbic acid [14]. On the other hand, the diblock polymer was slightly soluble in 0.1 M Na_2SO_4 , and after 6.4 mM ascorbic acid was added in 0.1 M Na_2SO_4 the diblock polymer became water-soluble and showed LCST at 30°C (Figure 4(a)). The LCST of the diblock polymer slightly decreased to 28°C with increasing concentration of L-ascorbic acid. The solution of the triblock copolymer was found to show LCST at 27.2°C in 0.1 M Na_2SO_4 , and the LCST was almost unchanged (28°C) with increasing concentration of L-ascorbic acid (Figure 5(a)). Reoxidation of the hydroxylamine-containing copolymer by $\text{K}_3[\text{Fe}(\text{CN})_6]$ reverses the change of the LCST seen on reduction. The LCST of the reduced random copolymer was decreased with increasing concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Figure 3(b)). The reduced diblock copolymer became insoluble again when 4.8 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ was added (Figure 4(b)), and the LCST of the reduced triblock copolymer was slightly decreased by adding $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Figure 5(b)). In Figures 4(b) and 5(b), initial transmittances of solutions of the random and triblock copolymers were decreased with increasing $\text{K}_3[\text{Fe}(\text{CN})_6]$. It is due to the byproduct in the reaction of $\text{K}_3[\text{Fe}(\text{CN})_6]$ with hydroxylamine. In both the reduction with L-ascorbic acid and the reoxidation with $\text{K}_3[\text{Fe}(\text{CN})_6]$, the LCST's shifts

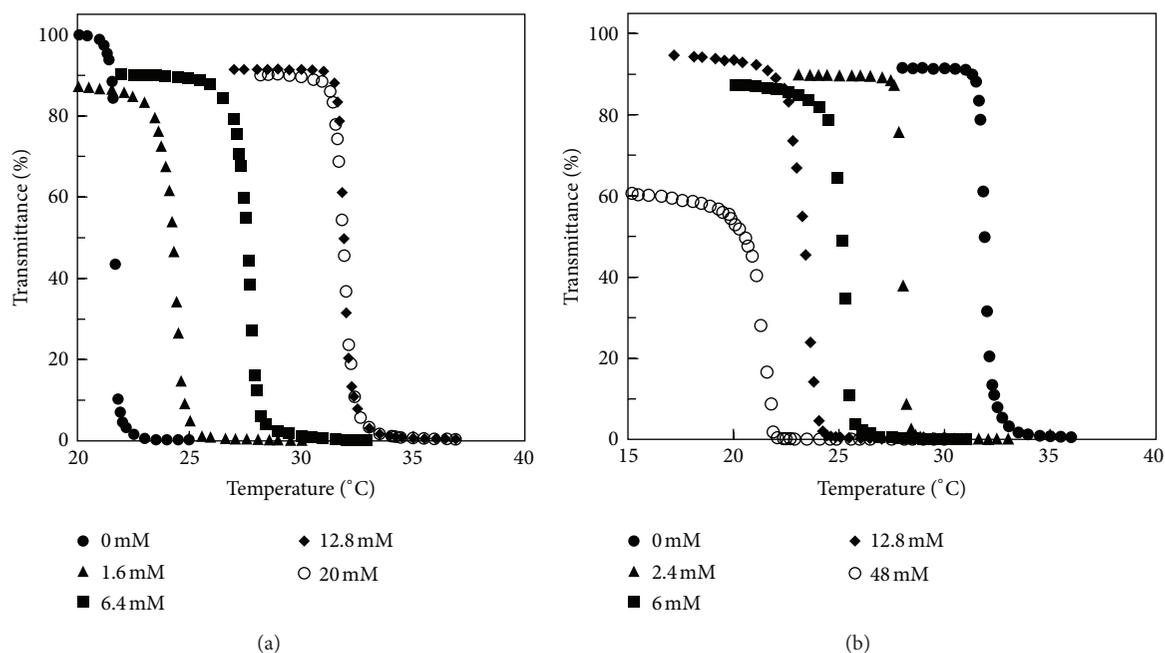


FIGURE 3: (a) Transmittance change of 10 mg/mL solutions of the poly(TEMPOMA-*ran*-NIPAAm) ($1'$) in 0.1 M Na_2SO_4 aq in the presence of various amounts of L-ascorbic acid 0–20.0 mM and (b) transmittance change of the resulting solutions of the corresponding reduced copolymer in the presence of various amounts of $K_3[Fe(CN)_6]$.

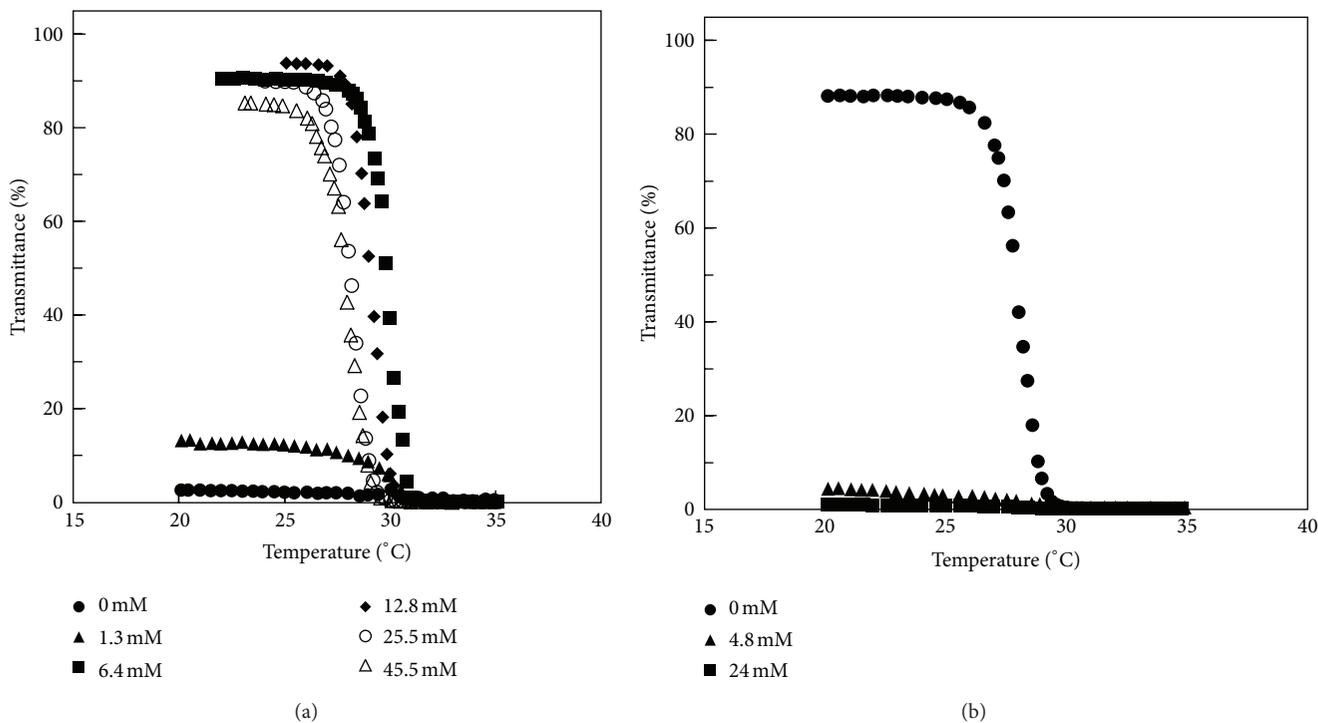


FIGURE 4: (a) Transmittance change of 10 mg/mL solutions of the PNIPAAm-*block*-PTEMPOMA ($2'$) in 0.1 M Na_2SO_4 aq in the presence of various amounts of L-ascorbic acid 0–45.5 mM and (b) transmittance change of the resulting solutions of the corresponding reduced copolymer in the presence of various amounts of $K_3[Fe(CN)_6]$.

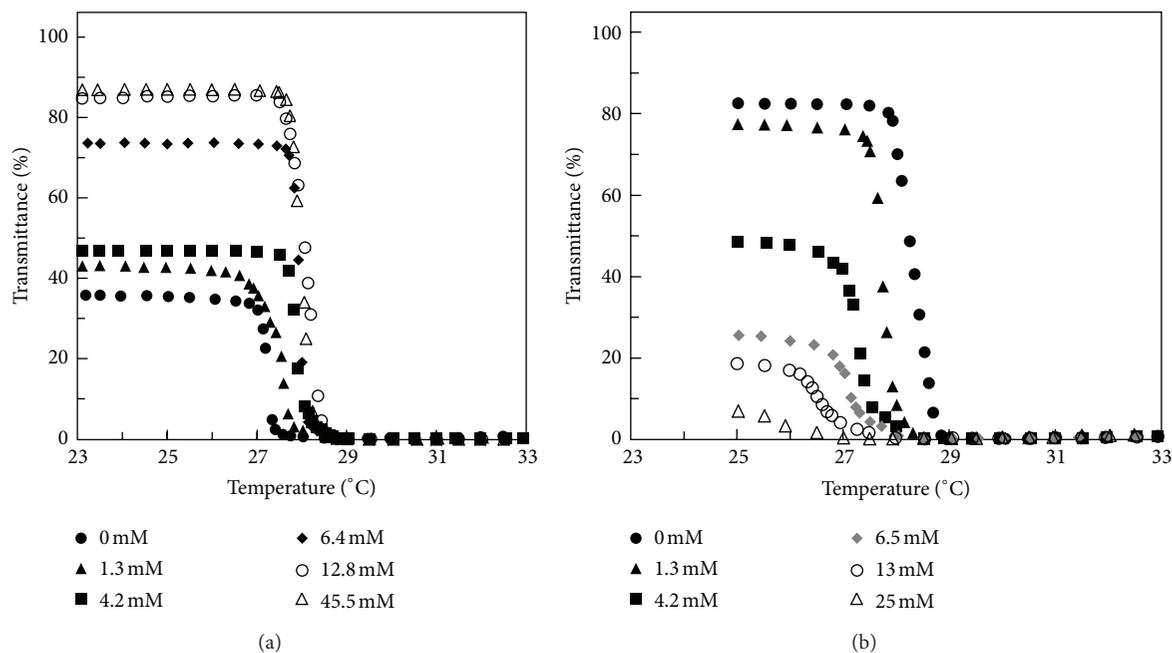


FIGURE 5: (a) Transmittance change of 10 mg/mL solutions of the PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm (3') in 0.1 M Na₂SO₄ aq in the presence of various amounts of L-ascorbic acid 0–45.5 mM and (b) transmittance change of the resulting solutions of the corresponding reduced copolymer in the presence of various amounts of K₃[Fe(CN)₆].

of the diblock and triblock copolymers were less than 2°C. The LCST of PNIPAAm decreases *ca.* 2°C by the addition of ascorbic acid or K₃[Fe(CN)₆] [14]; therefore, the phase transition behavior of the block copolymers seems to be not affected by the redox reactions of the TEMPO moieties. Thus, the TEMPO-containing units sequence and PNIPAAm chains individually function, and thermoresponsivity of the PNIPAAm chains predominantly appears in the block copolymers [19].

3.4. Redox Behavior of the Resulting Copolymers at Various Temperatures. The resulting copolymers having TEMPO groups were analyzed by cyclic voltammetry in 0.1 M KCl aqueous solution at various temperatures (5–55°C). In the cyclic voltammogram of the random copolymer, poly(TEMPOMA-*ran*-NIPAAm), a pair of anodic and cathodic peaks was observed at around 0.66 V under its LCST (31°C) (Figure 6(a)), but no clear redox waves were observed over its LCST (Figure 6(b)). It was reported that TEMPO and the PNIPAAm having TEMPO groups have a redox potential of 0.63 and 0.66 V versus Ag/AgCl, respectively [14, 20]. The diblock copolymer, PNIPAAm-*block*-PTEMPOMA, showed no redox waves, due to low solubility in water. On the other hand, triblock copolymer, PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm, showed a redox wave at 0.72–0.73 V at lower than its LCST (33°C) (Figure 7(a)). Moreover, the redox behavior of the TEMPO moieties in the triblock copolymer was found to be influenced by the phase transition of the PNIPAAm chains; namely, the anodic peaks were positively shifted to 0.81 V (Figure 7(b)). Below 33°C, the PNIPAAm chains are hydrated and TEMPO

moieties are located in hydrophilic environment. On the other hand, the environment around TEMPO moieties becomes relatively hydrophobic during the phase transition of the PNIPAAm chains above LCST. The positive shift of the anodic peak is probably due to the change of hydrophilicity in the polymer field. Thus, the phase transition of the triblock copolymer having thermoresponsive repeat units was found to influence the redox potential of TEMPO moieties.

4. Conclusion

PNIPAAm-based thermoresponsive random and block copolymers having TEMPO moieties as mediatory centers were successfully synthesized by using the RAFT polymerization technique. Both the random copolymer and the triblock copolymer having TEMPO moieties were found to have LCST at 33°C, but the diblock copolymer was not soluble in water probably due to relatively hydrophobic sequence of TEMPO-containing unit at one side of the polymer chain. All copolymers containing TEMPO moieties exhibited redox sensitive LCST behavior. The observed LCSTs of the random copolymer in aqueous Na₂SO₄ increased from 22°C to 32°C by reduction with ascorbic acid and decreased in reverse by oxidation with K₃[Fe(CN)₆]. On the other hand, the LCST of the triblock copolymer was not so shifted under reduction and oxidation conditions. It is probably due to its block structure consisting of two relatively long PNIPAAm chains connected to the both sides of TEMPO-containing unit sequence. The TEM images of the triblock copolymer aggregates obtained from their aqueous solutions indicate the formation of a polymer micelle. Therefore the oxidation state

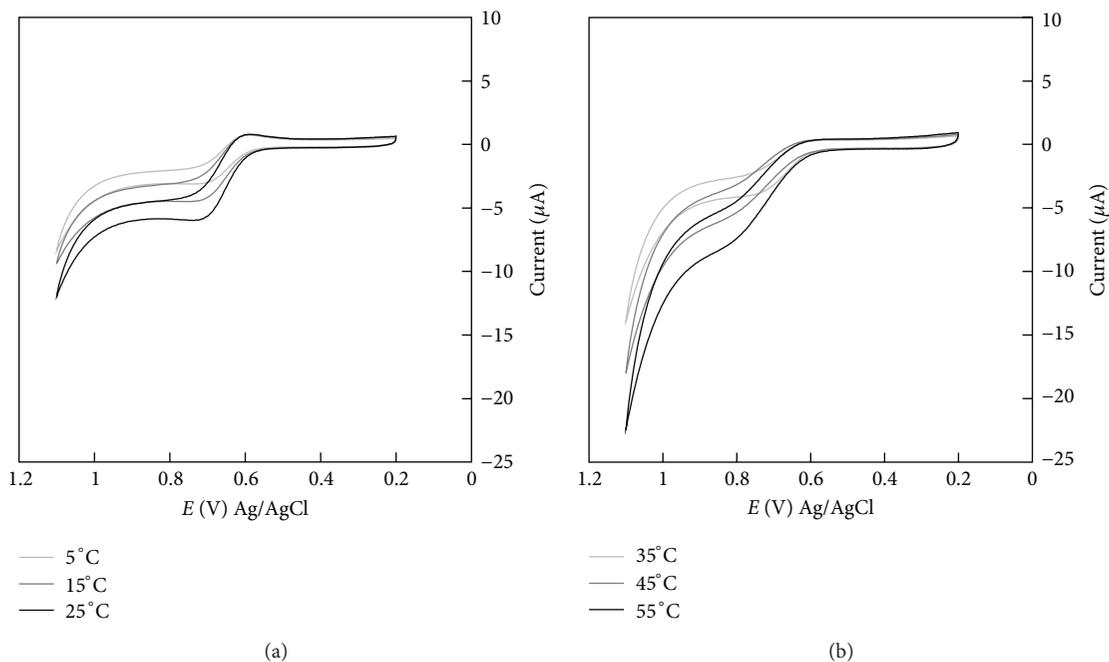


FIGURE 6: Cyclic voltammograms of poly(TEMPOMA-*ran*-NIPAAm) ($1'$) in 0.1 M KCl aqueous solution at (a) 5, 15, and 25°C, (b) 35, 45, and 55°C.

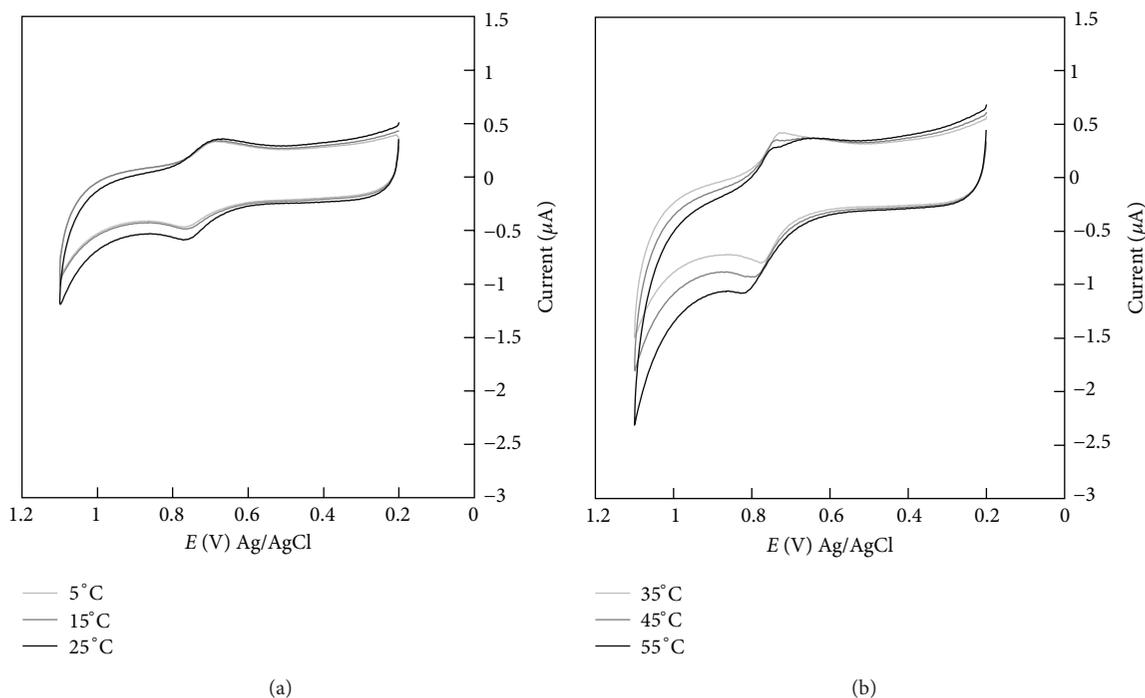


FIGURE 7: Cyclic voltammograms of PNIPAAm-*block*-PTEMPOMA-*block*-PNIPAAm ($3'$) in 0.1 M KCl aqueous solution at (a) 5, 15, and 25°C, (b) 35, 45, and 55°C.

of the TEMPO moieties within the hydrophobic core of the micelle does not influence apparent solubility of the triblock copolymer, but the observed LCST is determined only by the thermoresponsivity of the PNIPAAm chains. The redox behavior of the TEMPO moieties in the triblock copolymer was found to be influenced by the phase transition of the

PNIPAAm chains. The anodic peaks of the TEMPO moieties were positively shifted above the LCST of the copolymers. This potential shift indicates that the TEMPO moieties are surrounded by the PNIPAAm chains and placed on relatively hydrophobic environment during the phase transition at LCST. We have also observed the concentration behavior

of organic substrates into the hydrophobic field generated by PNIPAAm during the phase transition [12, 21]. These phenomena encourage us to perform the TEMPO-mediated oxidation of organic compounds in the thermoresponsive polymer field. Further study on the utilization of the thermoresponsive block copolymers containing TEMPO moieties to organic reactions and also electrochemical reactions in aqueous media is currently in progress [22].

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