Electroactive and Temperature-Sensitive Hydrogel Composites

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ABSTRACT: The composites of the polypyrrole (PPy) and polyelectrolyte copolymers (PE) were prepared by electrochemical polymerization. The various compositions of the polyelectrolyte copolymers were used as a dopant, and were composed of copolymers of water-soluble polymers and 2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS). Thermally sensitive (N-isopropyl acrylamide, NiPAAm) and insensitive (acrylamide, AAm) polymers were used as the water-soluble polymer. The electrochemical activity and mass change during the redox process of the PPy composites were investigated by potentiodynamic voltametry and electrochemical quartz crystal microbalance (EQCM). The mass change during the redox process was mainly concerned with the cation in the electrolyte solution. When the electrochemical activity of the PPy was larger than the amount of the polyelectrolyte anion (AMPS), the insertion/expulsion of the monoanion (ClO_{4}) into/from the PPy composite also occurred to ionically bond with the PPy in the redox process. The PPy/P(NiPAAm/AMPS) shows a significant mass decrease with increasing the temperature compared with the PPy/P(AAm/AMPS). The transition temperature of the PPy/P(NiPAAm/AMPS) is higher in the oxidized state than in the reduced state. The transition temperature of PPy composite increases with the composition of the hydrophilic electrolyte (AMPS). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 311-321, 1999

Key words: PPy/P(NiPAAm/AMPS) composite; polyelectrolyte; thermosensitivity; cyclic voltammogram; EQCM

INTRODUCTION

Polypyrrole (PPy), which was extensively studied for electrical conductivity, shows a higher conductivity and physical property by obtaining the freestanding film using electrochemical polymerization.^{1,2}

The monoanion and polyelectrolyte homopolymer have been used as a dopant in the electrochemical polymerization of pyrrole. The electrochemical activity of a conducting polymer shows considerable difference according to the electrical state of the conducting polymer, and many studies have been reported about factors that affect electrochemical activity of the conducting polymer. Among these factors, electrochemical activity is mainly affected by the dopant.^{3–5} Also, electrochemical activity is affected by the electrode substrate, pH of the solution, temperature, monomer concentration, the current density employed during synthesis.^{6–11}

The polyelectrolyte, protein, and collagen with an anionic group could be used as a dopant in the electrochemical polymerization of pyrrole. These conducting polymer composites have another

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Designation	Description	Source
AAm	acrylamide	Yakuri Chem. Co.
NiPAAm	N-isopropyl acrylamide	Eastman Kodak Co.
AMPS	2-acrylamido-2-methyl- 1-propane sulfonic acid	Aldrich
	potassium persulfate	Shinyl Chem. Co.
	1,4-dioxane pyrrole	Junsei Chem. Co. Aldrich

Table I Chemicals Used for Copolymerization

function, such as the conduction of plastic, membranes, chemical sensors, biosensors, and the electrode substrate of rechargeable batteries according to the kind of dopant, and many studies have recently been reported.^{12–18}

The poly(*N*-isopropyl acrylamide) (P(NiPAAm)) shows a remarkable thermal sensitivity and a low critical solution temperature (LCST) in an aqueous solution. Therefore, many studies concerning the swelling behaviors of P(NiPAAm) have been reported in the field of a drug delivery system (DDS).^{19–21}

In a previous article²² we investigated the electrical properties of PPy/polyelectrolyte composites. The polyelectrolyte was a copolymer of a water-soluble polymer (acrylamide, AAm) and a small portion of electrolytes (2-Acrylamido-2methyl-1-propane sulfonic acid, AMPS), and it was used as a dopant for electrochemical polymerization. This composite showed considerable electroactive behavior. When the thermally sensitive polymer *N*-isopropyl acrylamide (NiPAAm) was used as the water-soluble polymer despite AAm, the PPy composites showed thermal sensitivity as well as the current sensitivity.

In this article, the effect of the copolymer composition (the water-soluble polymer and the polyelectrolyte) on the electrical properties and the current sensitivity of the PPy/polyelectrolyte composites will be investigated. The potentiodynamic voltametry and electrochemical quartz crystal microbalance (EQCM) was used to measure thermal sensitivity as well as the electrical properties.

EXPERIMENTAL

Materials

Acrylamide (AAm) and *N*-isopropyl acrylamide (NiPAAm) were recrystallized from chloroform and hexane, respectively. 2-Acrylamido-2-methyl-

1-propane sulfonic acid (AMPS) and sodium perchlorate (NaClO₄) (Junsei) were used as received. Potassium persulfate was recrystallized from deionized water before use. 1,4-Dioxane was distilled and stored at room temperature in a dark bottle. Pyrrole monomer was purified by vacuum distillation and stored in a dark, cold place under nitrogen atmosphere before use. The materials of importance used in this study is shown in Table I.

Synthesis of Polyelectrolyte Copolymer

The feed composition in each solution polymerization is shown in Table II. P(AAm/AMPS) and P(NiPAAm/AMPS) random copolymers were synthesized with 1, 3, and 5 mol % of AMPS in 5 wt %, 10 wt % of 1,4-dioxane/deionized water solution (1/2 of 2/1 mixture), respectively. The amount of redox initiator $(K_2S_2O_8)$ was 1 mol % of the total monomer. Reaction mixtures were bubbled with dry nitrogen for 20 min, and polymerization was carried out at 65°C for 36 h. To remove the unreacted monomers and oligomers, the dilute solution of copolymers was dialyzed in deionized water using a 3500 molecular weight cutoff membrane. Copolymers were obtained by freeze drying. The apparent number-average molecular weights of the copolymers are about 35,000, obtained by gel permeation chromatography calibrated by a polyethylene oxide standard.

The composition of a copolymer of a watersoluble polymer and AMPS was confirmed by the elemental analysis of the sulfur content (Table III). The composition of AMPS in the copolymer is smaller than the feed composition. There are no significant differences between the copolymer compositions of P(AAm/AMPS) and P(NiPAAm/ AMPS) when the same feed ratio is used for synthesizing both the copolymers. Thus, these two copolymers of P(AAm/AMPS) and P(NiPAAm/ AMPS) can be used for the comparison of two kinds of PPy composites.

Feed Composition	AMPS (g)	$\begin{array}{c}{K_2S_2O_8}^{\bf a}\\(g)\end{array}$	1,4-Dioxane (g)	Deionized Water (g)
		(a) AAm (5 g)—5 wt %	solution	
99/1	0.147	0.147	33.3	66.7
97/3	0.451	0.150	33.3	66.7
95/5	0.767	0.153	33.3	66.7
	(b) NiPAAm (5 g)—10 wt	t % solution	
99/1	0.092	0.093	33.3	16.7
97/3	0.283	0.094	33.3	16.7
95/5	0.482	0.096	33.3	16.7

Table II Feed Composition for Water-Soluble Polymers and Electrolyte Copolymerization

^a 1 mol % of monomer.

Electrochemical Polymerization of Pyrrole and the Redox Process

A schematic diagram of the electrochemical measurement and cell are shown in Figure 1. Polypyrrole/polyelectrolyte copolymer composites were prepared on a gold-coated quartz crystal at a constant-current density of 0.02 mA/cm² for 1000 s. All electrochemical polymerizations were carried out in an aqueous solution of a 0.1 M pyrrole monomer and a 2 wt % polyelectrolyte copolymer at 22°C.

After the electrochemical polymerization, PPy composites were thoroughly washed with acetonitrile and deionized water to remove the residual pyrrole monomer. The electrochemical activity of the synthesized PPy composites was evaluated by cyclic voltametry and electrochemical quartz crystal microbalance (EQCM). The redox process was carried out in a monomerfree aqueous solution of 0.1 M sodium perchlorate (monoelectrolyte) from -0.8 to 0.5 V against the reference electrode. The potential sweep rate was 20 mV/s in the redox process of the PPy composites. The temperature of the electro-

chemical cell was controlled by a water bath circulation. The damper was employed to minimize the frequency change due to the vibration induced from the flow of water between the water bath and the electrochemical cell. A three-electrode cell was used in this study. A gold-coated quartz crystal was used as a working electrode. The Pt plate was used as a counter electrode, and the reference electrode was a Ag/AgCl/KCl_(sat). The cyclic voltammogram (CV) was recorded by the AFRDE5 potentiostat-galvanostat from Pine Instrument. At the same time, the mass change was recorded by a EQCN-600 series from ELCHEMA. A EQCN-600 series was completed with a frequency oscillator, a Faraday cage, and a remote probe unit. The working electrode was a keyhole type in shape, which was simultaneously connected to a potentiostat and an oscillator. CV and mass change curves were recorded by a computer, and a home-made program was used for data collections. The crystal oscillates in the shear mode at a nominal 10 MHz frequency. The active area of the gold-coated quartz crystal is 0.78 cm^2 . A frequency decrease of 1 Hz of the

Material	Feed Composition (mol Ratio)	Sulfur Content (wt %)	Copolymer Composition (mol Ratio)
AAm/AMPS	99/1	0.39	99.1/0.9
	97/3	1.03	97.6/2.4
	95/5	1.64	96.1/3.9
NiPAAm/AMPS	99/1	0.26	99.1/0.9
	97/3	0.71	97.4/2.6
	95/5	1.13	95.9/4.1



Figure 1 Schematic diagram of electrochemical synthesis and redox process apparatus (a) and cell (b).

quartz crystal represents a mass increase of about 0.87 ng.

Characteristics of the PPy/PE Composite

Thick polypyrrole/polyelectrolyte composite films were prepared on a stainless steel electrode to measure the electrical conductivity of film. The film was synthesized in an aqueous solution of 0.2 M of pyrrole and 2 wt % of a polyeletrolyte copolymer with respect to the total volume of solution at a constant-current density of 0.2 mA/cm². The film was carefully peeled off from the electrode and thoroughly washed with acetonitrile and deionized water to remove the residual monomer and the polyelectrolyte. Electrical conductivity of the thick film was measured by using van der Pauw's method.²³ Compositions of polyelectrolyte copolymers and PPy contents in the PPy/PE composites was calculated from the sulfur and carbon content obtained by the elemental analysis (Tables III and V).

Transition Temperature of the PPy/PE Composite

The mass change of the PPy/PE composite deposited on the quartz crystal is given by the Sauerbrey equation,²⁴ which was described previously.²²

The frequency of the quartz crystal changes due to the change of property of the quartz crystal with increasing the temperature, and it results in the mass change by the Sauerbrey equation. To consider the temperature effect of the quartz crystal, the mass change of the PPy/P(NiPAAm/AMPS) composite was measured with the PPy/P(AAm/AMPS) composite at fixed potentials [fully oxidized (0.5 V), partially reduced (0 V), and fully reduced state (-0.6 V)] with increasing the temperature with the EQCM.

RESULTS AND DISCUSSION

Electrochemical Polymerization of Pyrrole

The polyelectrolyte copolymers were used as a dopant in the electrochemical polymerization of pyrrole. The PPy composites were synthesized at the constant current (0.02 mA/cm²) for 1000 s. In both PPy/P(AAm/ AMPS) and PPy/P(NiPAAm/ AMPS) composites the polymerization rate during the synthesis was increased with increasing the AMPS composition in the polyelectrolyte copolymer. The potential growth against the reference electrode was decreased with the AMPS composition (Fig. 2 and Table IV).

When the composition of the AMPS is low, the polymerized mass of the PPy composites is small, and the potential growth during the synthesis is high. When the composition of the AMPS in the copolymer is low, i.e., the charge density of the copolymer is small, the charge to the hydrodynamic volume ratio in the solution is small. This small charge to the hydrodynamic ratio induces the high potential at a constant current. If the



Figure 2 Mass of the composite in pyrrole polymerization in an aqueous solution of (a) 2 wt % P(AAm/AMPS), (b) 2 wt % P(NiPAAm/AMPS) to a constant-current density 0.02 mA/cm², 20 mC/cm² charge consumed); 0.1 mol pyrrole monomer; temperature: $22^{\circ}C$.

polymerization of PPy is linearly dependent on the charge consumed, regardless of the charge density of dopants, the polymerized mass of PPy composites would increase with decreasing the composition of AMPS. However, the polymerized mass of the PPy composite becomes smaller as the composition of AMPS decreases. This indicates that the charge efficiency in the electrochemical polymerization of pyrrole considerably decreases as the composition of AMPS decreases.

The potential growth of PPy/P(NiPAAm/AMPS) is higher than that of PPy/P(AAm/AMPS) during polymerization, and the poly-

Table IVPotential Growth in PyrrolePolymerization in Aqueous Solution of2 wt % PE under Constant-CurrentDensity (0.02 mA/cm²)

	Copolymer	Potential
	Composition	Growth
Material	(mol Ratio)	(V)
AAm/AMPS	99.1/0.9	0.76
	97.6/2.4	0.69
	96.1/3.9	0.64
NiPAAm/AMPS	99.1/0.9	0.79
	97.4/2.6	0.72
	95.9/4.1	0.68

merization rate of PPy/P(NiPAAm/AMPS) is higher than that of PPy/P(AAm/AMPS) in each copolymer composition after polymerization. This is because the charge efficiency of P(NiPAAm/ AMPS) is lower than P(AAm/AMPS) because the hydrodynamic volume of P(NiPAAm/AMPS) is larger than P(AAm/AMPS) due to the higher hydrophilicity at a synthesized temperature (22°C). Although the charge efficiency of P(NiPAAm/AMPS) is lower, the mass of PPy/ P(NiPAAm/AMPS) is larger than that of PPv/ P(AAm/AMPS). The swollen water inside of the composite as well as the molecular weight of a repeat unit of water-soluble polymers can affect the mass increase of PPy composites during electrochemical polymerization. The swelling ratio of P(NiPAAm) in an aqueous solution is larger than P(AAm) at 22°C.^{20–21} The molecular weight of a repeat unit of NiPAAm (113.2) is also larger than that of AAm (71.1). Therefore, the polymerized mass of the PPy/P(NiPAAm/ AMPS) composite is larger than that of the PPy/ P(AAm/ AMPS) composite.

In a previous article,²² the surface morphology of the PPy/PE composite film was studied by scanning electron microscopy and atomic force microscopy, and the smooth surface of the PPy/PE films indicates that the PPy is uniformly dispersed in the composites.



Figure 3 Cyclic voltammogram of (a) PPy/P(AAm/AMPS) and (b) PPy/P(NiPAAm/AMPS) in an aqueous solution of 0.1 mol NaClO₄; sweep rate: 20 mV/s; temperature: 22° C.

Electrical Property of the Polypyrrole Composite

The electrochemical activity and ion behavior during the redox process of PPy/P(AAm/AMPS) and PPy/P(NiPAAm/AMPS) composites results in the monoelectrolyte solution (NaClO₄) as a func-

tion of AMPS composition. The cyclic voltammogram and the mass change during the redox process of the PPy composite is shown in Figures 3 and 4.

As shown in Table IV, the potential growth during the polymerization increases as the com-



Figure 4 Mass change of (a) PPy/P(AAm/AMPS) and (b) PPy/P(NiPAAm/AMPS) in an aqueous solution of 0.1 mol NaClO₄; sweep rate: 20 mV/s; temperature: 22° C.

Material	Composition of Electrolyte Copolymer	PPy Content in Composite (wt %)	AMPS/Pyrrole mol Ratio (%)	Conductivity (S/cm)
PPy/P(AAm/AMPS)	99.1/0.9 97.6/2.4 96.1/3.9	14.9 16.8 23.1	3.8 10.1 11.1	$egin{array}{c} 1.1 imes 10^{-2} \ 9.3 imes 10^{-2} \ 1.5 imes 10^{-1} \end{array}$

Table V Doping Level of PPy and Electrical Conductivity in PPy/P(AAm/AMPS) Composite

position of AMPS in the polyelectrolyte copolymer decreases. As the potential growth becomes higher in the electrochemical polymerization of pyrrole, the three-dimensional structure of PPy increases due to the 2,3 coupling reaction of the pyrrole. It causes a decrease in electrochemical activity during the redox process in the NaClO₄ solution when the composition of AMPS in the polyelectrolyte copolymer decreases (Fig. 3 and Table IV).

This mass change (Fig. 4) of the PPy composites in the redox process of PPy was shown by the insertion and expulsion of the cation and anion. The oxidized PPy makes the complex with the AMPS anion (sulfonic group, SO_3^{-}) or the monoanion (ClO_4^-) in the solution. In the oxidation process, the AMPS anion makes the complex first with the oxidized PPy at low potential, and the ClO_4^- in the solution makes the complex with the residual oxidized PPy at high potential. In the reduction process of PPy, the ClO_4^- is released from the PPy composite, but the AMPS anion cannot be released from the PPy composite due to the polymeric nature. Therefore, the cation (Na^+) is inserted into the PPy composite to make the complex with the AMPS anion in the reduction reaction. These two competing processes of insertion-expulsion of Na⁺ and expulsion-insertion of ClO_4^- make the mass change shown in Figure 4. The mass peak in the reduction process depends on the amount of the Na⁺ insertion/expulsion, and the peak in the oxidation process depends on the amount of the ClO_4^- insertion/expulsion. These two processes occur in reverse direction with each other, so that the relative amount of ion insertion/expulsion determines the shape of the mass curve.

However, during the redox process (Fig. 4), the mass change by the insertion/expulsion of monoanion (ClO_4^-) into/from the PPy composite at a high potential increases as the composition of AMPS decreases. When the composition of AMPS in the polyelectrolyte copolymer decreases, the mass change curve mainly depends on the amount of the insertion/expulsion of ClO_4^- , which bonds ionically with the oxidized PPy. This is because the relative amount of the sulfonic group (SO_3^-) of the AMPS to the PPy, i.e., the doping level of PPy, is very small (Table V). This phenomena is especially significant for PPy/P(AAm/AMPS) composites.

In the mass change of the PPy/P(NiPAAm/ AMPS:95.9/4.1) during the redox process of PPv. the mass peak by the insertion-expulsion of the monoanion (ClO_4^-) does not appear. This indicates that the amount of the AMPS anion is sufficient to ionically bond with the oxidized PPy.²² The mass peak by the insertion-expulsion of the $ClO_4^$ increases during the redox process of PPy in the PPy/P(AAm/AMPS) as the composition of the AMPS decreases. Meanwhile, in the mass change of the PPy/P(NiPAAm/AMPS:97.4/2.6) and PPy/ P(NiPAAm/AMPS:99.1/0.9), the mass peak by the insertion–expulsion of ClO₄⁻ does not increase as the composition of the AMPS decreases. The mass change by the ClO_4^- decreases because electrochemical activity of the PPy decreases with decreasing the composition of the AMPS in the polyelectrolyte copolymer. Also, the mass change by the ClO_4^- increases because the relative amount of the SO_3^- of the AMPS to the PPy is small. These two effects countervail, so the change of the mass peak by the ClO_4^- does not appear in Figure 4(b).

In the mass change of the PPy composites during the redox process (Fig. 4), the mass peak by the insertion-expulsion of ClO_4^- at a high potential is larger in the PPy/P(AAm/AMPS) than in the PPy/P(NiPAAm/AMPS). This is because the electrochemical activity of the PPy/P(AAm/ AMPS) is higer than that of the PPy/P(NiPAAm/ AMPS). Also, the mass change by the insertionexpulsion of Na⁺ at a low potential is larger in the PPy/P(NiPAAm/AMPS) than in the PPy/P(AAm/ AMPS). The mass change by the ClO_4^- is small because electrochemical activity of the PPy/ P(NiPAAm/AMPS) is low. Therefore, the relative



Figure 5 Cyclic voltammogram of (a) PPy/P(AAm/AMPS:99.1/0.9) and (b) PPy/P(NiPAAm/AMPS:99.1/0.9) in an aqueous solution of 0.1 mol NaClO₄; sweep rate: 20 mV/s; temperature: 22, 40, 55°C.

amount of mass change by the insertion–expulsion of the Na^+ to the mass change by the ClO_4^- is larger.

The peak shape in the reduction process is broad, and the peak in the oxidation process is very sharp. This means that the response time for making an Na⁺-AMPS or ClO_4^- -PPy complex is long and short, respectively. It seems that the Na⁺ ion carries the hydration water molecules with its surround, but the ClO_4^- moves without water molecules.

The results of the elemental analysis of PPy/ P(AAm/AMPS) films are shown in Table V. The doping level of P(AAm/AMPS) decreases with the composition of the polyelectrolyte copolymer. The doping level of PPy/P(AAm/AMPS) was calculated from the AMPS/pyrrole mol ratio. The electrical conductivities of the PPy/P(AAm/AMPS) composite films increase with increasing the AMPS composition, as shown in Table V. The conductivity of the PPy film is dependent on not only their compositions, but also their PPy structures arising from the synthesis condition such as the current density and the potential growth during the synthesis.

The electrochemical activity of the PPy/ P(AAm/AMPS) and PPy/P(NiPAAm/AMPS) composites is characterized at various temperatures. The cyclic voltammogram and the mass change during the redox process of the PPy composite is shown in Figures 5 and 6. From Figure 5, the current during the redox process of the PPy composite decreases with increasing the temperature. From Figure 6, the mass peak by the ClO_4 in the oxidation process decreases with increasing the temperature.

In the previous article²² it was illustrated that electrochemical activity of the PPy composite decreases with increasing the temperature. This change makes the current in the redox process decrease (Fig. 5) and the sharp mass peak in the oxidation process at a high potential smaller with increasing the temperature (Fig. 6).

Transition Temperature of the Polypyrrole Composite

The coagulation of P(NiPAAm) with increasing the temperature and the lower critical solution temperature (LCST) of P(NiPAAm) was observed in a water solution. The LCST of P(NiPAAm) was 32° C, as known from the literature.²⁰ The LCST of copolymer [P(NiPAAm/AMPS)] is higher than that of P(NiPAAm), due to the more hydrophilic electrolytes (AMPS). In Figure 8, the swelling ratio (W_s/W_p) of the crosslinked P(NiPAAm) and P(NiPAAm/AMPS) copolymers changes with increasing the temperature.These polymers were crosslinked with 2 mol % (for the NiPAAm and AMPS monomers) of ethylene glycol dimethacrylate. W_s and W_p denote the weight of a solvent in the polymer and the weight of the polymer, re-



Figure 6 Mass change of (a) PPy/P(AAm/AMPS:99.1/0.9) and (b) PPy/P(NiPAAm/AMPS: 99.1/0.9) in an aqueous solution of 0.1 mol NaClO₄; sweep rate: 20 mV/s; temperature: 22, 40, 55° C.

spectively. The swelling ratio of the P(NiPAAm) critically decreases with increasing the temperature, but the swelling ratio of the P(NiPAAm/ AMPS) copolymer shows the smooth decrease different from the behavior of the P(NiPAAm).

In a previous article, the nature of quartz crystal, depending on the temperature, was discussed prior to confirming the mass change of the PPy composite with increasing the temperature.²²

The PPy composite synthesized by the thermally insensitive polyelectrolyte copolymer [P(AAm/ AMPS)] shows the linear mass decrease with increasing the temperature (Fig. 8). The swelling ratio of the crosslinked P(AAm/AMPS) copolymer





Figure 7 Equilibrium swelling ratio of P(NiPAAm), P(NiPAAm/AMPS:99.1/0.9, 95.9/4.1) as a function of temperature.

Figure 8 Mass change of PPy/P(AAm/AMPS:97.6/2.4) with increasing the temperature (from 25 to 56° C) in an aqueous solution of 0.1 mol NaClO₄.



Figure 9 Mass change of PPy/P(NiPAAm/AMPS: 97.4/2.6) with increasing the temperature (from 25 to 56° C) in an aqueous solution of 0.1 mol NaClO₄.

is known as being independent of the temperature.^{20,21} So, it is considered that the mass decrease with the temperature is due to the change of the physical property of the quartz crystal deposited with the PPy composite.

But, the PPy composite synthesized by the thermally sensitive polyelectrolyte copolymer [P(NiPAAm/AMPS)] shows a considerable mass decrease with increasing the temperature, comparing it with the PPy composite synthesized by P(AAm/AMPS). It decreases linearly, but the

slopes of the mass decrease are changed at around 37°C (Fig. 9). The slope of the mass decrease in the PPy/P(NiPAAm/AMPS) comes from the LCST of the NiPAAm.

In the case of the PPy/P(AAm/AMPS) composite, the mass change of the PPy composite is the same in both the reduced and oxidized state of the PPy. However, in the PPy/P(NiPAAm/AMPS) composite, the transition temperature of the PPy composite at which the slope of the mass decrease changes, is higher in the oxidized state of PPy than in the reduced state of PPy. It is considered that there is a restriction in the coagulation of NiPAAm by the ionic bond of the sulfonic group (SO₃⁻) of AMPS and the oxidized PPy. Therefore, the temperature at which the NiPAAm coagulates is higher in the oxidized state of PPy.

The conformation of the PPy/P(NiPAAm/AMPS) composite in the oxidized and reduced state of PPy with increasing temperature is shown in Figure 10. This schematic diagram shows the conformational changes of the polymer chain induced by the variation of the temperature and the electrical state. The change by the variation of the temperature comes from the temperature sensitivity of NiPAAm. The change from the variation of the electrical states comes from the doping–dedoping behavior of the PPy and AMPS.

The transition temperature of the PPy composite increases from 33 to 39°C in a reduced state, and increase from 36 to 41°C in an oxidized state with changing the composition of AMPS (Fig. 11). This is



Figure 10 Schematic representation for the LCST change of NiPAAm copolymer between the complexation state and the decomplexation state with polypyrrole.



Figure 11 LCST change of PPy/P(NiPAAm/AMPS) composite in an oxidized, partially reduced, reduced state.

due to the amount of hydrophilic electrolytes. These results correspond to the change of transition temperature verified by the swelling ratio with increasing the temperature, as shown in Figure 7. Regardless of the AMPS composition, the difference of the transition temperature between the reduced and oxidized state is the same. This means that the small amount of ionic bond between the polyelectrolyte anion (AMPS) and the oxidized PPy is enough to delay the coagulation of the NiPAAm.

CONCLUSIONS

The temperature-sensitive and electroactive PPy composites have been prepared. The PPy/ P(NiPAAm/AMPS) has the current sensitivity as well as the thermal sensitivity via the composite of the themosensitive polymer and the conducting polymer. These composites have a high electrical conductivity even at a low composition. The mechanical properties of these composites are very good, due to the included polymers in the polyelectrolyte copolymers compared to the PPy film prepared with a monoelectrolyte, even though it was not shown in this article.

The transition temperatures of PPy/P(NiPAAm/ AMPS) was raised with increasing AMPS composition. This is because the hydrophilicity of the NiPAAm copolymer increases with increasing the AMPS composition. Regardless of the AMPS composition, the difference in transition temperature between the reduced and oxidized states is same. Thus, the small amount of ionic bond (0.9 mol % of AMPS) between the SO_3^- and the oxidized PPy is enough to delay the coagulation of P(NiPAAm/AMPS).

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