Preparation of Thermoresponsive Polymer-Modified Electrodes Having a TEMPO Moiety

Toru UEMUKAI, Tomoya HIOKI, and Manabu ISHIFUNE*

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,
3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

* Corresponding author: ishifune@apch.kindai.ac.jp

ABSTRACT

Thermoresponsive polymers having 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moieties were fixed on the graphite surface by using the reversible addition-fragmentation chain transfer (RAFT) graft polymerization technique. The surface of graphite has been anodically oxidized by using our original electrochemical method, and then modified with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoyloxy groups (RAFT reagents) by esterification with the corresponding acid chlorides. From the resulting RAFT reagent-modified graphite, 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TEMPMA) and *N*-isopropylacrylamide (NIPAAm) monomers were copolymerized stepwise under RAFT polymerization conditions to afford the thermoresponsive block-copolymer-grafted graphite, poly(TEMPMA)-*block*-PNIPAAm-grafted graphite. *N*-Oxylation of tetramethylpiperidyl groups on the resulting graphite successfully afforded the corresponding TEMPO-containing thermoresponsive polymer-grafted graphite. Redox behavior of the resulting graphites was observed by cyclic voltammetry. The potential and intensity of the cathodic current peaks were discontinuously changed below and above the lower critical solution temperature (LCST) of the grafted thermoresponsive polymers. These results indicate that the phase transition of the thermoresponsive polymer on the graphite influences the electron transfer between the TEMPO moieties and the graphite surface.

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Keywords : Graphite Surface, Thermoresponsive Polymer, Graft Polymerization, TEMPO

1. Introduction

Electrochemical reactions of organic molecules are generally performed in organic solvents having high dielectric constants. From the viewpoints of environmental protection alternative solvents such as water,^{1–5} supercritical fluids,^{6,7} and ionic liquids^{8–11} have been actively studied in the field of electrochemical synthesis. Water is an ideal solvent, however, low solubility of organic substrates and electrolysis of water itself restrict the use of water as a solvent of electrochemical reactions of organic compounds. The use of modified electrodes having functional molecules that generate hydrophobic field temporally and locally on the electrode is a promising method for solving these problems. Poly(*N*-isopropylacrylamide) (PNIPAAm) is such a candidate functional macromolecule since PNIPAAm is a typical thermoresponsive polymer which exhibits a distinct phase transition at a lower critical solution temperature (LCST) near 32°C, and is soluble in water below its LCST but becomes hydrophobic above the LCST.^{12,13} We have chosen this thermoresponsive polymer to provide a hydrophobic reaction field on the electrode surface and a graphite rod as a base electrode. Concerning the modification of carbon base electrodes, we have already achieved the introduction of hydroxyl groups on the carbon fiber surface using NO₃ radicals generated by the electro-oxidation of NO₃ anions.^{14,15} Several functional molecules such as β -cyclodextrin were successfully fixed on the carbon fiber by ether bonding of the anodically introduced hydroxyl groups on the carbon fiber with suitable halides or tosylates.^{16,17} For end group control and grafting polymer chains from the solid materials was highly useful the living radical polymerization technique such as reversible addition-fragmentation chain transfer (RAFT) polymerization.^{18–21} In this study new thermoresponsive polymer-grafted graphite electrodes were prepared by grafting the corresponding polymers

from the anodically oxidized graphite electrode using the RAFT polymerization technique. Moreover 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moieties²² as mediatory centers were introduced on the grafted thermoresponsive polymer chains, and redox behaviors of TEMPO moieties were observed by using the resulting modified electrodes as working electrodes at various temperature.

2. Experimental

2.1 General

The constant electrocurrent was supplied with a Takasago GP-050-2 regulated DC power supply. X-ray photoelectron spectroscopy (XPS) measurements were acquired using a Shimadzu AXIS-NOVA with an Al-X-ray source under vacuum of 10^{–7}–10^{–8} Torr. ¹H NMR spectra were measured on a Varian OXFORD NMR 300 (300 MHz) or JEOL JNM-AL 400 (400 MHz) spectrometer, and the chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. The molecular weights of the polymers were determined by using a gel permeation chromatography (GPC). The GPC analyses were performed on a Hitachi L-6000 high performance liquid chromatograph, L3350 RI detector, and Shodex KF-804L column. THF was used eluent at 1.0 mL/min flow rate, and the molecular weights were relative to the polystyrene standard (Shodex STANDARD SM-105). ESR spectra were recorded by JEOL JES-PX1050. Cyclic voltammetry was measured by BAS CV-50.

2.2 Materials

Graphite (Alfa Aesar, 6.15 mm diameter $\times$ 152 mm long, 99.9995%) was cut into proper length, washed with distilled water and acetone, and dried in vacuo for 3 h before use. *N*-Isopropylacrylamide (NIPAAm) was purified by recrystallization from

hexane-benzene (95:5). 2,2'-Azobis(isobutyronitrile) (AIBN) as a radical initiator was recrystallized from methanol below 40°C. Tetrahydrofuran (THF) was distilled from Na-benzophenoneketyl under an argon atmosphere. Pure water was prepared by purification of distilled water using the Simplicity Personal Ultrapure Water System SIMS 700 0J (Millipore Co., Ltd.). 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid was prepared by reported method¹⁸ and treated with thionyl chloride to form the corresponding acid chloride. Lithium nitrate (LiNO_3), potassium chloride, sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TEMPMA), and the other materials were commercially available and used without further purification.

2.3 Preparation of modified graphite electrodes

2.3.1 Electrooxidation of graphite^{14,15}

A solution of LiNO_3 (2 mmol) as a supporting electrolyte in the mixed solvent ($\text{MeCN}:\text{H}_2\text{O} = 10:1$, 50 mL) was put into an undivided electrolysis cell equipped with a graphite rod (6 mm diameter $\times$ 20 mm long) as an anode and a platinum plate (20 $\times$ 20 mm) as a cathode. The electrooxidation was carried out under the conditions of constant current (50 mA) with cooling by an ice bath. After 0.5 F/mol of electricity based on the supporting electrolyte was passed, the resulting graphite was washed with distilled water under sonication (50 KHz, 10 min $\times$ 3), and then dried in vacuo overnight.

2.3.2 Modification of the oxidized graphite with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoyl group (Preparation of the RAFT reagent-modified graphite)

The oxidized graphite (6 mm diameter $\times$ 20 mm long) was immersed into 7 mL of THF containing triethylamine (3.5 mmol) under an argon atmosphere. A solution of 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoyl chloride (1.0 mmol) in 4 mL of THF was then added dropwise, and the mixture was stirred for 19 h at room temperature. The resulting modified graphite was placed on a Soxhlet type extractor and washed with running THF for 3 h followed by distilled water for 2 h, and then dried in vacuo overnight.

2.3.3 Preparation of PNIPAAm-grafted graphite

The RAFT reagent-modified graphite (prepared in the above section), NIPAAm (84.9 mmol), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (0.90 mmol), AIBN (0.090 mmol), and 9 mL of dry THF were placed in a glass ampoule tube, and the solution was degassed repeatedly by freeze-evacuation-thaw cycles. The polymerization was carried out at 60°C under an argon atmosphere for 12 h. The resulting PNIPAAm-grafted graphite was placed on a Soxhlet type extractor and washed with running methanol for 3 h, and then dried in vacuo overnight. The polymerization solution was poured into a large excess of diethylether to precipitate PNIPAAm having 4-cyano-4-[(sulfanylthiocarbonyl)sulfanyl]pentanoic acid structure at its terminus [RAFT reagent-terminated PNIPAAm, $\overline{M}_{n\text{GPC}} = 6750$, $\overline{M}_w/\overline{M}_n = 1.24$ (estimated by GPC); $\overline{M}_{n\text{NMR}} = 6760$ (calculated based on ^1H NMR signals intensity of a methine proton of isopropyl group of PNIPAAm side chain and methylene protons of the end group)].

Poly(TEMPMA-*co*-NIPAAm)-grafted graphite was also prepared by the same procedure using NIPAAm and TEMPMA as monomers.

2.3.4 Preparation of PTEMPMA-*block*-PNIPAAm-grafted graphite

The RAFT reagent-modified graphite, RAFT reagent-terminated PNIPAAm (prepared in the above section), TEMPMA (880 mmol), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (0.90 mmol), AIBN (0.090 mmol), and 6 mL of dry THF were placed in a glass ampoule tube, and the solution was degassed repeatedly by freeze-evacuation-thaw cycles. The polymerization was carried out at 60°C under an argon atmosphere for 60 h. The

resulting PTEMPMA-*block*-PNIPAAm-grafted graphite was placed on a Soxhlet type extractor and washed with running methanol for 3 h, and then dried in vacuo overnight.

2.3.5 Preparation of PTEMPOMA-*block*-PNIPAAm-grafted graphite

PTEMPMA-*block*-PNIPAAm-grafted graphite (prepared in the above section) was immersed into 40 mL of distilled water and treated with 30% H_2O_2 (16 mL) in the presence of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (2.2 mmol). After stirring for 24 h at 24°C, K_2CO_3 was added to be saturated. The resulting PTEMPOMA-*block*-PNIPAAm-grafted graphite was placed on a Soxhlet type extractor and washed with running water at 5°C for 3 h, and then dried in vacuo overnight.

Poly(TEMPOMA-*co*-NIPAAm)-grafted graphite was also prepared by the same procedure using poly(TEMPMA-*co*-NIPAAm)-grafted graphite (section 2.3.3) as a precursor.

2.4 Electrochemical testing of PMTEMPOMA-*block*-PNIPAAm-grafted graphite

Cyclic voltammograms were measured in 0.1 M KCl aqueous solution after bubbling with nitrogen gas (20 min) by using PTEMPOMA-*block*-PNIPAAm-grafted graphite as a working electrode at various temperatures (5–55°C). As a counter electrode was used a platinum wire (BAS VC-3 cell 5 cm Pt) and a reference electrode consisted of Ag/AgCl (BAS RE-1B). Scan rate was 100 mV/s.

3. Results and Discussion

3.1 Electrooxidation of graphite electrode

It has been already achieved in our previous studies^{14,15} that the phenolic hydroxyl groups are introduced on carbon fiber by the electrooxidation of the LiNO_3 containing electrolyte using the carbon fiber as an anode. In this study, we have first applied our procedure to the oxidation of graphite rod surface (Scheme 1). The graphite rod was found to be readily oxidized under anodic conditions. Figure 1 shows the C 1s peaks of XPS spectra of untreated graphite and oxidized graphite. A sharp peak was observed at 285 eV in the spectrum of the untreated graphite. On the other hand, this peak broadened and shifted to high energy range after 0.5 F/mol of electricity based on LiNO_3 was passed. The peak separation analysis of the C 1s spectrum of the oxidized graphite (Fig. 2) indicates that the spectrum can be characterized as a combination of 4 peaks attributed to C-C ($\text{C}=\text{C}$) at 284.8 ± 0.1 eV, C-O at 286.9 ± 0.3 eV, C=O at 288.5 ± 0.3 eV, and C(=O)O at 289.8 ± 0.2 eV,²³ and the intensity of the peak at 286.9 eV is highest. In our previous study the C 1s peak of the phenolic structure of the anodically oxidized carbon fiber was observed at 286.8 eV.¹⁵ These results indicate that phenolic hydroxyl groups are mainly introduced on the graphite surface under the anodic oxidations.

3.2 Preparation of PTEMPOMA-*block*-PNIPAAm-grafted graphite

The polymerization with reversible addition-fragmentation chain transfer (RAFT) is an extremely versatile process for the synthesis of end-functional polymers and block copolymers.^{18–21} Trithiocarbon-

Scheme 1. Surface oxidation of graphite using anodically generated NO_3 radical.

Figure 1. Photoelectron lines of C 1s of XPS of untreated graphite and oxidized graphite.

Figure 2. Peak separation analysis of C 1s spectrum of the oxidized graphite.

Scheme 2. Preparation of the RAFT reagent-modified graphite.

ate derivatives have been reported to be effective as a chain transfer reagent (RAFT reagent) for polymerization of styrene, acrylates, and acrylamides.¹⁸ In order to graft thermoresponsive PNIPAAm chains from the graphite surface was prepared 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoyl chloride as a RAFT reagent. On the anodically oxidized graphite were then fixed 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoyloxy groups by esterification with the acid chlorides (Scheme 2). From the resulting RAFT reagent-modified graphite, NIPAAm monomers were polymerized under RAFT polymerization conditions to afford PNIPAAm-grafted graphite (Scheme 3). In the mechanism of RAFT polymerization the propagating macroradical species migrate between the RAFT reagents fixed on the graphite and those in the solutions, and it is known that the molecular weights and repeat units sequence structures of the grafted polymers are almost same as those of the polymers recovered from the polymerization solution.^{18,21} Therefore the polymers were recovered from the polymerization solution and characterized. The molecular weight ($\bar{M}_n$) and dispersity index ($\bar{M}_w/\bar{M}_n$) of the grafted PNIPAAm were estimated by GPC to be 6750 and 1.24 respectively. PTEMPMA chains were then inserted between the graphite and PNIPAAm chains by copolymerization of TEMPMA under the same RAFT polymerization conditions. The molecular weight ($\bar{M}_n$) and dispersity index ($\bar{M}_w/\bar{M}_n$) of the grafted block copolymer were 8290 and 1.17 respectively, and the repeat units ratio (NIPAAm units: TEMPMA units) was determined to be 93:7 by ^1H NMR. *N*-Oxylation of tetramethylpiperidyl groups on the resulting PTEMPMA-*block*-PNIPAAm-grafted graphite successfully afforded the corresponding TEMPO-containing PTEMPOMA-*block*-PNIPAAm-grafted graphite. Tetramethylpiperidyl groups were quantitatively con-

verted to the corresponding *N*-oxyl structures, and PTEMPOMA-*block*-PNIPAAm obtained by oxidation of PTEMPMA-*block*-PNIPAAm under same conditions was confirmed to be ESR active. The corresponding random copolymer-grafted graphite, Poly(TEMPOMA-*co*-NIPAAm)-grafted graphite, was also prepared by a graft copolymerization of NIPAAm and TEMPMA monomers under the same RAFT polymerization condition and *N*-oxylation.

The RAFT reagent-modified graphite and the copolymer-grafted graphites were analyzed by XPS (Fig. 3). In S 2p spectrum of the RAFT reagent-modified graphite the peak attributed to thiocarbonylsulfanyl group was clearly observed at 163.6 eV. This peak was weakened and slightly shifted to higher energy range in the spectra of PNIPAAm-grafted graphite and PTEMPMA-*block*-PNIPAAm-grafted graphite. Moreover the peaks attributed to the amide groups of PNIPAAm sequence and *N*-oxyl groups of TEMPO moieties were observed at 400.3 eV and 401.5 eV in N 1s spectra of the copolymer-grafted graphites.

3.3 Redox and thermoresponsive behaviours of PTEMPOMA-*block*-PNIPAAm-grafted graphite

In the cyclic voltammogram of a random copolymer, poly-(TEMPOMA-*co*-NIPAAm) ($\bar{M}_n = 4840$, $\bar{M}_w/\bar{M}_n = 1.26$), in 0.1 M KCl aqueous solution, a pair of anodic and cathodic peaks was observed at around 0.63 V under its LCST (33°C). However, no clear redox waves were observed in the cyclic voltammograms using poly(TEMPOMA-*co*-NIPAAm)-grafted graphite (a random copolymer-grafted graphite) as a working electrode [Fig. 4(a)]. In the case of the random copolymer-grafted graphite, NIPAAm units mainly exist near the graphite surface. NIPAAm units probably interrupt the electron transfer between the TEMPO moieties and the graphite

Scheme 3. Preparation of PTEMPOMA-*block*-PNIPAAm-grafted graphite. **Figure 3.** Photoelectron lines of C 1s, O 1s, S 2p, and N 1s in the XPS of the copolymer-grafted graphites.

Figure 4. Cyclic voltammograms of 0.1 M KCl aqueous solution by using (a) poly(TEMPOMA-*co*-NIPAAm)-grafted graphite and (b) PTEMPOMA-*block*-PNIPAAm-grafted graphite as working electrodes.

surface. In the cyclic voltammograms using PTEMPOMA-*block*-PNIPAAm, anodic current peaks were also not clear, but cathodic current peaks were observed at 0.36 V below 35°C and positively shifted to 0.46 V above 45°C. Moreover, the potential and current intensity of these peaks were not changed from 25 to 35°C [Fig. 4(b)]. These cathodic current peaks were also observed by using PTEMPOMA-grafted graphite (TEMPOMA homopolymer-grafted graphite) at around 0.42 V, however, any notable temperature effect on the potential was not observed and the current intensity increased gradually with an increase in temperature. Repeat units sequence having TEMPO moieties of PTEMPOMA-*block*-PNIPAAm-grafted graphite (the diblock copolymer-grafted graphite) is directly fixed on the graphite surface. Below 35°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 cathodic peaks is probably due to the change of hydrophilicity in the polymer field.^{24,25} Thus the phase transition of the thermoresponsive polymer on the graphite electrode was found to influence the electron transfer between the TEMPO moieties and the electrode surface.

4. Conclusion

Graphite rod surface was oxidized by anodically generated NO₃ radicals to introduce phenolic hydroxyl groups, and NIPAAm-based thermoresponsive polymers having TEMPO moieties were successfully grafted from the oxidized graphite surface by using the RAFT polymerization technique. Thermoresponsive character was observed in the redox behaviour of the resulting graphite electrode. The cathodic current peaks of the TEMPO moieties were positively shifted above the LCST of the grafted thermoresponsive PNIPAAm chains. This potential shift indicates that the TEMPO moieties are surrounded by the PNIPAAm chains during the phase transition at LCST. We have also observed the concentration behaviour of organic substrates into the hydrophobic field generated by PNIPAAm during the phase transition in non-electrochemical system.²⁶ This phenomenon encourages us to perform the electrochemical reactions in the polymer field on the electrode surface. Organic substrates are concentrated on the electrode surface by thermoresponsive shrinking of the grafted PNIPAAm chains, and it

possibly enhances the efficiency of the electrochemical reactions mediated by the TEMPO moieties. We are now investigating the redox behaviours of several organic compounds by using the thermoresponsive polymer-grafted graphites as working electrodes.

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