

Photografting of *N*-Isopropylacrylamide and Glycidyl Methacrylate Binary Monomers on Polyethylene Film: Effect of Mixed Solvent Consisting of Water and Organic Solvent

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ABSTRACT: Photografting ($\lambda > 300$ nm) of *N*-isopropylacrylamide (NIPAAm) and glycidyl methacrylate (GMA) binary monomers (NIPAAm/GMA) on low-density polyethylene film (thickness = 30 μm) was investigated at 60°C using mixed solvent consisting of water and an organic solvent such as acetone. Xanthone was used as a photoinitiator by coating it on the film surfaces. A maximum percentage of grafting was observed at a certain concentration of acetone in the mixed solvent, which was commonly observed for both ratios of NIPAAm/GMA, 8/2 and 7/3. Based on the photografting of NIPAAm/GMA on xanthone-coated film, monomer reactivity ratios of NIPAAm (r_1) and GMA (r_2) were calculated using the Fineman–Ross method. The values were 0.31 ± 0.1 and 4.8 ± 0.2 for the water solvent system, while they were 0.96 ± 0.1 and 4.9 ± 0.1 for the mixed solvent system. NIPAAm/GMA-grafted films

with a homogeneous distribution of grafted chains were formed by photografting using water and mixed solvents. The NIPAAm/GMA-grafted films exhibited temperature-responsive characters, whereas the grafted films showed a reversible change in the degree of swelling between 0 and 50°C, respectively. Epoxy groups in the grafted poly(NIPAAm/GMA) chains could be aminated with ethylenediamine in *N,N'*-dimethylformamide at 70°C for 3 h. Complexes of the aminated NIPAAm/GMA-grafted chains with cupric ion exhibited catalytic activity for the decomposition of hydrogen peroxide at 20 to 50°C. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2469–2475, 2005

Key words: photografting; *N*-isopropylacrylamide; glycidyl methacrylate; binary monomers; mixed solvent; temperature-responsive character; polymer catalyst

INTRODUCTION

It was found in our previous papers^{1–3} that mixed solvent consisting of water and organic solvents such as acetone and methanol remarkably accelerated the photografting of methacrylic acid, *N*-isopropylacrylamide (NIPAAm), and glycidyl methacrylate (GMA) on linear low-density polyethylene (LLDPE) film. The accelerated grafting was ascribed to promoting monomer solubility in the system, resulting in the stimulation of monomer supply for the radicals on growing grafted polymer chains, leading to an increase in the percentage of grafting. With photografting using the mixed solvent, moreover, the grafted chains of the MAA-,¹ NIPAAm-² and AA-grafted films⁴ tended to penetrate the inside of the film texture. In the present article, the effect of mixed solvent on photografting of

NIPAAm and GMA binary monomers (NIPAAm/GMA) on LLDPE film was investigated.

Attempts on grafting^{5–18} using mixtures of two or more kinds of monomer have been extensively made for various initiation systems, monomers, and polymer substrates. The advantage of this grafting method is that different types of grafted polymer containing various functional groups can be introduced into the polymer substrate used. NIPAAm and GMA were selected as the two monomer components to be introduced. Poly(NIPAAm) hydrogel with a crosslinked structure^{19–22} is known to swell in water below and shrink above a lower critical solution temperature of poly(NIPAAm), around 32°C. It was observed that NIPAAm-grafted celluloses, which are prepared by photografting of NIPAAm onto wood pulp^{17,23} and regenerated cellulose film,²⁴ exhibit a temperature-responsive character, where the grafted celluloses swell and shrink in water at temperatures lower and higher than around 30°C, respectively. Moreover, metallic ion-absorbing materials having a temperature-responsive character¹⁷ could be prepared by means of

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photografting of NIPAAm and acrylic acid binary monomers onto wood pulp. The ability of the grafted samples to absorb cupric ion depended largely on the temperature. On the other hand, poly(GMA) has a reactive epoxy group in the side chain that can react readily with numerous functional groups such as hydroxyl, carboxyl, and amine groups.²⁵⁻³⁴ Therefore, GMA-grafted polymer can be utilized for the introduction of various functions into polymeric materials. The combination of NIPAAm and GMA is useful for the preparation of grafted samples with two different functions. That is, the NIPAAm component in the grafted poly(NIPAAm/GMA) chains acts as a temperature-responsive component, while the GMA component acts as a reaction site to introduce various functions through the epoxy groups. In the present article, the effect of mixed solvent on photografting of NIPAAm/GMA onto LLDPE film was investigated in terms of grafting behavior, distribution of grafted chains, and temperature-responsive characters of the resulting NIPAAm/GMA-grafted film. Moreover, reactivity of the grafted poly(NIPAAm/GMA) chains toward the reaction with ethylenediamine (En) and the catalytic activity of the aminated grafted film/cupric ion complexes toward the decomposition of hydrogen peroxide (H_2O_2) are also examined.

EXPERIMENTAL

Materials

The PE film used was a LLDPE film of density 0.927 g/cm^3 and thickness $30\ \mu\text{m}$ (Idemitsu Petrochemical Co., Ltd., Tokyo, Japan). The film sample was extracted for 24 h with acetone and dried in a vacuum oven before use. The film sample ($3 \times 10\text{ cm}$, $\sim 0.08\text{ g}$) was immersed in an acetone solution containing 0.1 wt % xanthone (XT) and 0.5 wt % poly(vinyl acetate) (weight-average molecular weight = 100,000), removed from the solution, and then dried at room temperature for 2 h under a reduced pressure of 5 Torr for the preparation of an XT-coated film. GMA and NIPAAm were purified by distillation under reduced pressure (4 Torr at 35°C) and by recrystallization from a benzene/*n*-hexane mixture, respectively. XT, En, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Cu^{2+}), H_2O_2 , and acetone, all of which were reagent grade, were used without further purification.

Photografting

Photografting was carried out in a Pyrex glass tube containing the XT-coated film sample and 30 mL water or mixed solvent, in which given molar ratios of NIPAAm/GMA (total monomer concentration = 0.47 mol/L) were dissolved, under a nitrogen atmosphere. Irradiation of UV rays emitted from a high-pressure

mercury lamp (400 W) was performed at 60°C using a Riko Rotary Photochemical Reactor RH400-10W (Riko Kagaku Sangyo Co., Ltd., Chiba, Japan). The Pyrex glass tubes were rotated around the mercury lamp during irradiation. After grafting, polymerized films were extracted with methyl ethyl ketone for 24 and for 48 h with cold water to remove the homopolymers of poly(GMA) and poly(NIPAAm), respectively, and then dried at room temperature for 24 h under a reduced pressure of 5 Torr. The percentage of grafting was taken as the percentage of weight increase of the original film. The NIPAAm component of grafted poly(NIPAAm/GMA) chains was determined by nitrogen analysis. Grafted samples with different percentages of grafting in each system were prepared by varying irradiation times.

Measurements of attenuated total reflection-infrared (ATR-IR) spectra

The ATR-IR spectra of the surface layers of grafted film were measured with an automatic infrared microscope (AIM-800, FTIR-8700) (Shimadzu Co., Ltd., Kyoto, Japan). The density of NIPAAm component in grafted poly(NIPAAm/GMA) chains on the film surface layer was expressed in terms of the absorbance ratio of the amide peak at 1640 cm^{-1} to the methylene peak band at 1460 cm^{-1} .

Scanning electron microscope (SEM)

Grafted film was immersed in a saturated aqueous palladium chloride solution at room temperature for 24 h to form a complex of the NIPAAm component in grafted poly(NIPAAm/GMA) chains with palladium and then washed with water. The distribution profile of palladium atoms in the cross section of the NIPAAm/GMA-grafted film was measured with a SEM (JSM-5600LV, JED-2200) (Jeol Co., Ltd., Tokyo, Japan).

Measurements of swelling

Grafted film (W_0 , g) was immersed in water at 0 and 50°C for 24 h, alternately. After treatment, any excess water on the film surface was removed using a filter paper, and then the weight (W_s , g) of the treated film was measured. Degree of swelling of the grafted film was defined as

$$\text{Swelling (\%)} = 100 \times (W_s - W_0)/W_0$$

Reaction with En

NIPAAm/GMA-grafted film (0.050 g) was added to 30 mL *N,N'*-dimethylformamide, in which known concentrations of En were dissolved, and then the

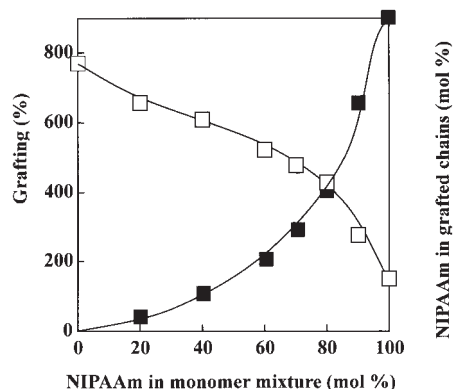


Figure 1 Photografting of NIPAAm/GMA on XT-coated LLDPE film in water solvent. [Total monomer] = 0.47 mol/L, [XT] = 0.1 wt %. Irradiation: 60°C, 60 min. (□) Percentage of grafting, (■) NIPAAm content in grafted poly-(NIPAAm/GMA) chains.

reaction was carried out at 70°C for 3 h. After the reaction, the samples were subjected to measurement of the amount of En residues introduced into the substrate by elemental analysis.

En content (mol %) = $100 \times \text{Amount of En residue introduced} / \text{Initial amount of epoxy group}$

Decomposition of H₂O₂

A given amount of aminated NIPAAm/GMA-grafted film was added to 40 mL aqueous Cu²⁺ solution, [Cu²⁺] = 3.0×10^{-4} mol/L, and the pH was adjusted to 5.5 by Clark-Lubs buffer solution, and then the reaction was carried out at 25°C for 24 h to prepare the complex (Cu²⁺ complex) of the aminated NIPAAm/GMA-grafted film and Cu²⁺. A given amount of the Cu²⁺ complex was allowed to react with 40 mL of aqueous H₂O₂ solution of 3.0×10^{-3} mol/L at 20 to 50°C for 5 h. After the reaction, the Cu²⁺ complex was removed from the solution, and the concentration of H₂O₂ in the filtrate was determined by titration with aqueous 0.1M KMnO₄ solution. The amount of decomposed H₂O₂ was calculated according to the equation:

Amount of decomposed H₂O₂ (%) = $100 \times \text{Amount of decomposed H}_2\text{O}_2 / \text{Initial amount of H}_2\text{O}_2$.

RESULTS AND DISCUSSION

Grafting behavior

Figure 1 shows the results of photografting of NIPAAm/GMA on XT-coated LLDPE film in water solvent. The horizontal axis indicates the NIPAAm composition in the binary monomers. The percentage of grafting decreased with an increase in NIPAAm composition in the binary monomers. On the other hand, NIPAAm composition in the grafted poly-

(NIPAAm/GMA) chains increased with NIPAAm composition in the binary monomers. Monomer reactivity ratios of NIPAAm (r_1) and GMA (r_2) were calculated from the data of Figure 1 using the Fineman-Ross method. The values were 0.31 ± 0.1 and 4.8 ± 0.2 , respectively, which were similar to $r_1 = 0.39$ and $r_2 = 2.69$ determined by copolymerization of NIPAAm/GMA at 70°C in deuterated dioxane.³⁵ Figure 2 shows the photografting of NIPAAm/GMA on XT-coated LLDPE film in a mixed solvent consisting of water and acetone (mixed solvent). The abscissa in Figure 2 represents the concentration of acetone component in the mixed solvent. The percentage of grafting increased with increasing concentration of acetone in the mixed solvent and decreased beyond a certain concentration of acetone, which was commonly observed for both ratios of NIPAAm/GMA, 8/2 and 7/3. The same phenomenon was also observed for photografting of NIPAAm² and GMA³ single monomer on XT-coated LLDPE film in mixed solvent.

It was supposed in previous articles that the solubility of NIPAAm and GMA monomers in the system increases to stimulate the monomer supply for radicals on the growing grafted polymer chains and finally to increase the percentage of grafting, whereas at a high concentration of organic solvent, the percentage of grafting decreases because of the chain transfer from growing grafted polymer radicals to organic solvent and/or termination of the growing polymer radicals by the solvent radicals formed. An effect similar to that of the mixed solvent may be applicable to the photografting of NIPAAm/GMA binary monomers. The solubility parameter of acetone³⁶ is 9.9 (cal/cc)^{0.5}, whereas that of poly(NIPAAm)³⁷ and GMA³⁶ is 11.18 and 7.31 (cal/cc)^{0.5}, respectively. It is reasonable to suppose that acetone promotes solubility of NIPAAm/GMA in this system. So, the maximum percentage of grafting was inferred to have originated in the balance between the two effects of acetone, with the positive effect of acetone

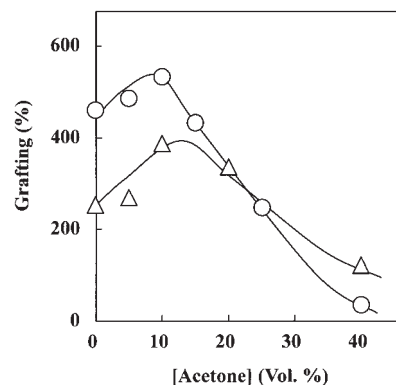


Figure 2 Photografting of NIPAAm/GMA on XT-coated LLDPE film in water/acetone mixed solvent. [Total monomer] = 0.47 mol/L, [XT] = 0.1 wt %. Irradiation: 60°C, 60 min. (○) NIPAAm/GMA = 8/2, (△) NIPAAm/GMA = 7/3.

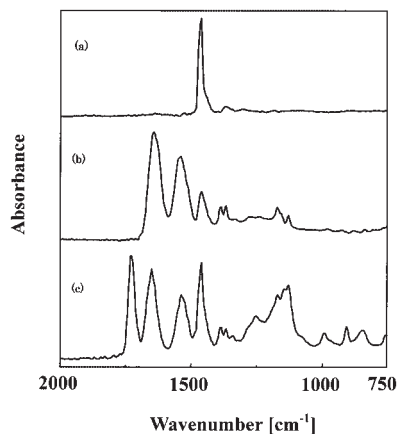


Figure 3 ATR-IR spectra of (a) LLDPE and (b) NIPAAm- and (c) NIPAAm/GMA-grafted LLDPE films. The percentages of grafting are (a) 0, (b) 69%, and (c) 152%, respectively.

promoting NIPAAm/GMA solubility in the system and the negative effect of acetone participating in the chain transfer and termination of growing grafted polymer radicals. As described above, it was confirmed that the accelerating effect due to the organic solvent component in the mixed solvent was a common phenomenon for the systems with single and binary monomers. Monomer reactivity ratios of NIPAAm and GMA calculated from data of photografting of NIPAAm/GMA in a water/acetone (10 vol %) mixed solvent system using the Fineman–Ross method were 0.96 ± 0.1 and 4.9 ± 0.1 . The values were similar to that obtained in the water solvent system (Fig. 1), showing that copolymerizability of NIPAAm/GMA is not largely influenced by the nature of the solvent in the grafting system such as water and mixed solvents.

Distribution of grafted chains

Figure 3 shows the ATR-IR spectra of LLDPE film and NIPAAm- and NIPAAm/GMA-grafted LLDPE films. In the spectrum of NIPAAm-grafted film, a sharp peak at 1640 cm^{-1} assigned to the amide group of grafted poly(NIPAAm) chains is shown in Figure 3b. With the NIPAAm/GMA-grafted film (Fig. 3c), absorptions due to poly(GMA) component in the grafted poly(NIPAAm/GMA) chains were observed in addition to the amide peak at 1640 cm^{-1} . That is, absorptions at 845 and 906 cm^{-1} are assigned to the contribution of the epoxy group in the poly(GMA) component and a peak at 1728 cm^{-1} corresponds to the carbonyl group in the poly(GMA) component. This is attributable to the fact that both components of NIPAAm/GMA are grafted onto the surface layer of the LLDPE film substrate.

Figures 4 and 5 show the distribution of the grafted poly(NIPAAm) chain component of NIPAAm/GMA-grafted chains on the surface and in the cross section

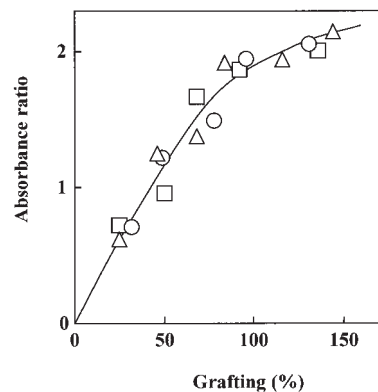


Figure 4 Changes in absorbance ratio of amide peak at 1640 cm^{-1} to the methylene peak at 1460 cm^{-1} with the percentage of grafting in NIPAAm/GMA-grafted LLDPE films prepared in water and water/acetone mixed solvent. NIPAAm/GMA = 8/2. (□) water, (○) water/acetone (5 vol %)-mixed solvent, (△) water/acetone (10 vol %) mixed solvent.

of the grafted films, which were examined by ATR-IR and SEM measurements, respectively. The density of the grafted poly(NIPAAm) chain component in the NIPAAm/GMA-grafted chains on the film surface layer was expressed in terms of the absorbance ratio of the amide peak at 1640 cm^{-1} to the methylene peak at 1460 cm^{-1} , and the results are shown in Figure 4 as a function of the percentage of grafting. The absorbance ratio increased with an increase in the percentage of grafting, indicating that the surface layer of the grafted film became richer in grafted poly(NIPAAm) chains, that is, grafted poly(NIPAAm/GMA) chains, than LLDPE components. The magnitude of the increase was nearly equal among the grafted films prepared in water and mixed solvents. To confirm the above results obtained by ATR-IR measurements, distribution of the grafted poly(NIPAAm) chains component in the cross section of the grafted film was investigated from the distribution profile of palladium atoms in the cross section of NIPAAm/GMA-grafted LLDPE films prepared in water and mixed solvent, which were measured by SEM, and the results are shown in Figure 5. The vertical and horizontal directions in Figure 5 correspond to the relative concentration of palladium atoms and the cross section of the

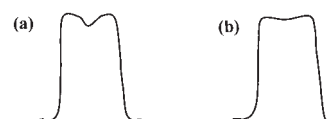


Figure 5 Distribution profiles of palladium atoms in the cross section of NIPAAm/GMA-grafted LLDPE films prepared in water and water/acetone (10 vol %) mixed solvent. NIPAAm/GMA = 8/2. (a) water (grafting = 68%). (b) water/acetone (10 vol %) mixed solvent (grafting = 65%).

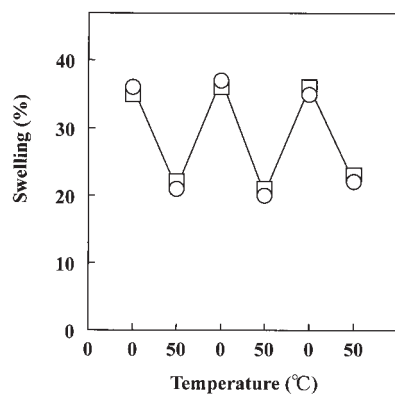


Figure 6 Temperature-responsive character of NIPAAm/GMA-grafted LLDPE films prepared in water and water/acetone mixed solvent. NIPAAm/GMA = 8/2: (□) water, (○) water/acetone (10 vol %) mixed solvent.

films, respectively. The grafted poly(NIPAAm) chains component in the NIPAAm/GMA-grafted films prepared in water (Fig. 5a) and mixed solvent (Fig. 5b) is located inside the film. This indicates that the grafted poly(NIPAAm/GMA) chains are also located inside the film.

Solubility parameters³⁶ of GMA and acetone are 7.31 and 9.9 (cal/cc)^{0.5}, respectively, whereas that³⁷ of poly(NIPAAm) is 11.18 (cal/cc)^{0.5}. Based on the solubility parameters of GMA monomer to that of PE (8.1(cal/cc)^{0.5}), GMA monomer itself has a higher affinity to PE substrate compared to acetone and is also able to dissolve NIPAAm monomer. Accordingly, it is reasonable to suppose that the GMA monomer and acetone solvent increase the solubility of the NIPAAm monomer component in the system and also assist in the penetration of grafted poly(NIPAAm/GMA) chains into the PE substrate. This may lead to formation of NIPAAm/GMA-grafted film with a homogeneous distribution of grafted chains, irrespective of the nature of solvent in the system, water and mixed solvents.

Temperature-responsive characters

The temperature-responsive character of the resulting grafted films prepared in water and water/acetone mixed solvents was evaluated by measuring the degree of swelling of the grafted films when immersed in water at 0 and 50°C for 24 h, alternately. As shown in Figure 6, the grafted film exhibited a reversible change in the degree of swelling between 0 and 50°C. There is no large difference in the temperature-responsive character among the grafted films prepared in water and mixed solvent. This is ascribed to the fact that the distribution of grafted poly(NIPAAm/GMA) chains is similar among the grafted films prepared in water and mixed solvents, as shown in Figure 5. It was found

thus that the NIPAAm/GMA-grafted film shows the temperature-responsive character, in which it swells and shrinks in water at 0 and 50°C, respectively.

Reaction with En

The epoxy groups of the grafted poly(GMA) chains are well known to react with various functional compounds such as amines^{5,28,32,38} that can be utilized in the introduction of functions into polymeric materials. Figure 7 presents the reaction of the epoxy group in grafted poly(NIPAAm/GMA) chains with En, which was carried out in *N,N'*-dimethylformamide at 70°C for 3 h. The horizontal axis of Figure 7 corresponds to the concentration of En in the system, which ranges from 5 to 20 times as much as the epoxy group content of NIPAAm/GMA-grafted film. The En content, the amount of En residues introduced into the grafted poly(NIPAAm/GMA) chains, increased with an increase in the concentration of En used in the system, and the magnitude of the increase was nearly equal among the grafted films prepared in water and water/acetone mixed solvents. The epoxy group of grafted poly(NIPAAm/GMA) chains has the ability to react with En, and there is no great difference in ability among grafted films prepared in water and mixed solvent systems.

Catalytic activity of polymer catalyst

It has been reported that complexes^{39–42} prepared by polymer ligands and Cu²⁺ exhibit higher catalytic activity for decomposition of H₂O₂ than free Cu²⁺. Therefore, the polymer catalyst (Cu²⁺ complex) prepared by reaction of the aminated NIPAAm/GMA-grafted film with Cu²⁺ was subjected to the decomposition reaction of H₂O₂ to examine their catalytic activity. Figure 8 shows the effect of the reaction tem-

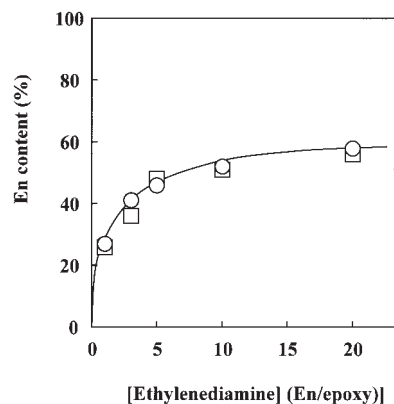


Figure 7 Reaction of grafted poly(NIPAAm/GMA) chains with ethylenediamine at 70°C for 3 h. NIPAAm/GMA = 8/2: (□) water (grafting = 99%), (○) water/acetone (10 vol.%) mixed solvent (grafting = 98%).

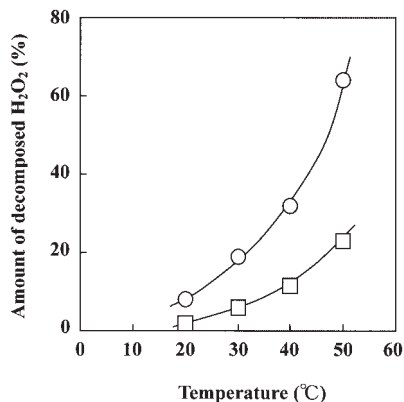


Figure 8 Effect of reaction temperature on decomposition of H₂O₂. [H₂O₂] = 3.0 × 10⁻³ mol/L, [Cu²⁺] = 3.0 × 10⁻⁴ mol/L, time = 6 h: (□) free Cu²⁺ (CuCl₂), (○) Cu²⁺ complex.

perature from 20 to 50°C on the decomposition of H₂O₂. The amount of H₂O₂ decomposed increased with increasing reaction temperature. Moreover, the value was higher for Cu²⁺ complex than for the free Cu²⁺ (CuCl₂), showing that the complexes prepared by reaction of the aminated NIPAAm/GMA-grafted film with Cu²⁺ have catalytic activity for the decomposition of H₂O₂. The ratio of the amount of H₂O₂ decomposed for the complex to that of free Cu²⁺ was calculated as a measure of the extent of enhanced activity for the complex. The ratios were 4.1, 4.0, 2.8, and 2.8 for the complex at 20, 30, 40, and 50°C, respectively. The reduced ratio was observed for the complex at 40 and 50°C. As described above, the NIPAAm/GMA-grafted films shrink at temperatures higher than a lower critical solution temperature of poly(NIPAAm), such as 50°C. Accordingly, it is conceivable that some parts of the Cu²⁺ complex on the grafted poly(NIPAAm/GMA) chains cannot participate in the decomposition reaction of H₂O₂ due to shrinkage of the grafted chains. This may result in a reduced ratio at 40 and 50°C, temperatures that are higher than a lower critical solution temperature of poly(NIPAAm). Thus, it was supposed that the shrinking character of the NIPAAm/GMA-grafted film affects the catalytic activity of the Cu²⁺ complex.

CONCLUSIONS

Photografting of NIPAAm/GMA on polyethylene film is useful for preparation of a grafted sample having two different functions. That is, the grafted poly(NIPAAm) component in the NIPAAm/GMA-grafted chains acts as a temperature-responsive component, while the grafted poly(GMA) component acts as a reaction site to introduce catalytic functions through the epoxy groups. The photografting was accelerated using mixed solvent consisting of water and acetone. The grafted poly(NIPAAm/GMA) chains penetrated

the film substrate, which was commonly observed for grafted films prepared in water and mixed solvents. The NIPAAm/GMA-grafted films exhibited a temperature-responsive character, in which they swelled at 0°C and shrank at 50°C. Moreover, the grafted poly(NIPAAm/GMA) chains have the ability to react with En, and polymer catalyst for the decomposition of H₂O₂ could be prepared by reacting the aminated NIPAAm/GMA-grafted film with Cu²⁺, where its catalytic activity was higher than that of free Cu²⁺.

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