

# Photografting of *N*-Isopropylacrylamide on Polyethylene Film in Mixed Solvents Composed of Water and Organic Solvent

Ginting Suka Irwan,<sup>1</sup> Shin-Ichi Kuroda,<sup>1</sup> Hitoshi Kubota,<sup>1</sup> Takashi Kondo<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma, 376-8515, Japan

<sup>2</sup>Gunma Prefectural Industrial Technology Research Laboratory, Maebashi, Gunma, 371-0845, Japan

Received 28 November 2001; revised 30 January 2002; accepted 5 May 2002

**ABSTRACT:** The effects of a mixed solvent consisting of water and organic solvents such as acetone and methanol on the photografting ( $\lambda > 300$  nm) of *N*-isopropylacrylamide (NIPAAm) on linear low-density polyethylene film (thickness = 30  $\mu\text{m}$ ) was investigated at 30°C and 60°C. Xanthone, which had been coated on the film, was used as a photoinitiator. The photografting initiated even in the system at 30°C by using a longer irradiation time. It was found that the maximum percentage of grafting was attained at a certain concentration of organic solvent in the mixed solvent, which shifted to a lower concentration of organic solvent in the system at 60°C compared with the system at 30°C. It was found that the grafted chains of the sample prepared in the system with the higher polymerization temperature and the

use of mixed solvent penetrated into the center of the film compared with the sample prepared in the system with the lower polymerization temperature and use of a water solvent. Moreover, the NIPAAm-grafted films exhibited temperature responsiveness, swelling and shrinking in water at 0°C and 50°C, respectively. The extent of this characteristic was found to be closely related to the location of the grafted chains in film substrate, which was measured by an attenuated total reflection infrared spectroscopy and a scanning electron microscope. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 458–463, 2003

**Key words:** photografting; mixed solvent; polyethylene; graft copolymers; stimuli-responsive polymers

## INTRODUCTION

In a previous article<sup>1</sup> the authors investigated the effect of mixed solvent that consisted of water and organic solvents on the photografting of methacrylic acid (MAA) on linear low-density polyethylene (LLDPE) film. The organic solvents used were acetone, methanol, dioxane, and tetrahydrofuran. It was observed that the component of organic solvent in the mixed solvent remarkably influenced both the grafting behaviors and the location of MAA-grafted chains in the LLDPE film substrate. That is, a maximum percentage of grafting was observed at a certain concentration of organic solvent in the mixed solvent depending on the nature of the organic solvent. The maximum percentage of grafting was supposed to originate in the balance between the two effects of the organic solvent: a positive effect, in which the organic solvent promotes monomer solubility in the system, and a negative effect, in which the organic solvent participates in chain transfer and termination of growing grafted polymer radicals. Moreover, photografting using the mixed solvent resulted in MAA-grafted film

with a homogeneous distribution of grafted chains, exhibiting a larger pH-responsive character, in which the grafted film shrank in an acidic medium and swelled in an alkaline region.

This article deals with application of photografting using a mixed solvent to the introduction of *N*-isopropylacrylamide (NIPAAm)-grafted chains into LLDPE film. Poly(NIPAAm) is well known to exhibit a lower critical solution temperature (LCST) at around 32°C in an aqueous solution, and its hydrogels,<sup>2–4</sup> with a crosslinked structure, are characterized by a temperature-responsive nature, in which they swell in water below the LCST and shrink above it. This behavior may be caused by a balance between the hydrophilicity of the amide group and the hydrophobicity of the isopropyl group in the side chain.<sup>5</sup> The swelling and shrinking characteristics have been applied to the preparation of temperature-responsive membranes<sup>6–9</sup> and adsorbent,<sup>10</sup> in which a grafting technique is used to attach these characteristics to the base materials. In the present study the photografting of NIPAAm on LLDPE film in mixed solvent consisting of water and organic solvents such as acetone and methanol was investigated at 30°C and 60°C for the grafting behavior, the distribution of NIPAAm-grafted chains, and the temperature-responsive character of the resulting NIPAAm-grafted film, which was evaluated by measuring a dimensional change of the grafted film.

Correspondence to: H. Kubota (kubota@chem.gunma-u.ac.jp).

## EXPERIMENTAL

### Materials

Commercially available LLDPE film 30  $\mu\text{m}$  thickness (density 0.927  $\text{g}/\text{cm}^3$ , Idemitsu Petrochemical Co., Ltd., Tokyo, Japan) was used as a film sample. The film sample ( $3 \times 10$  cm, ca. 0.08 g) was immersed in an acetone solution containing 0.5 wt % xanthone (XT) and 0.5 wt % PVAc [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 to prepare a XT-coated film. XT and hydrophilic organic solvents such as acetone and methanol (MeOH), all of which were reagent grade, were used without further purification. NIPAAm was purified by recrystallization from a benzene/*n*-hexane mixture.

### Photografting

Photografting was carried out in a Pyrex glass tube containing the XT-coated film sample and 30 mL of water or mixed solvent, in which a given concentration of NIPAAm (0.79M) was dissolved under a nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was performed at the given temperatures using a Riko Rotary Photochemical Reactor (RH400-10W, Riko Kagaku Sangyo Co., Ltd., Chiba, Japan), around which the Pyrex glass tubes were rotated. After the reaction, polymerized films were extracted with water for 48 h to remove the homopolymer of poly(NIPAAm) and then were dried at room temperature for 24 h under a reduced pressure of 5 torr. Grafted samples with different percentages of grafting in each system were prepared by varying the irradiation time. The percentage of grafting was calculated by the following equation:

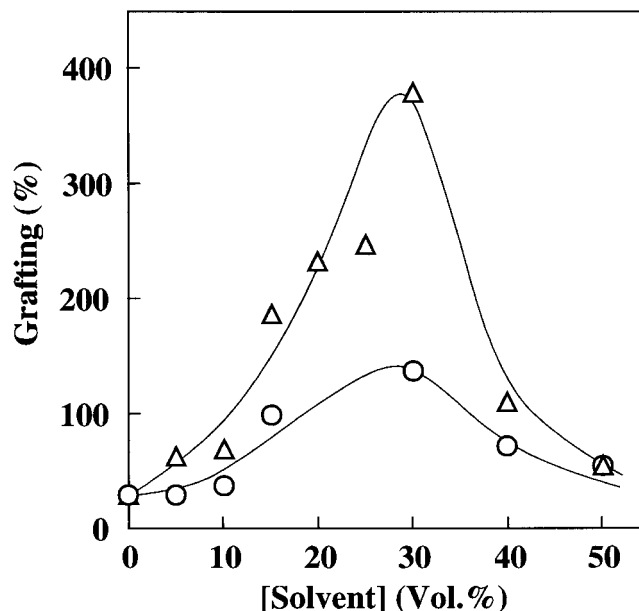
$$\text{Grafting (\%)} = \frac{\text{Weight of grafts}}{\text{Weight of original film}} \times 100$$

### Scanning electron microscope

NIPAAm-grafted film was immersed in a saturated aqueous palladium chloride solution at room temperature for 24 h and then washed with water. The distribution profile of the palladium atoms in a cross section of the grafted film was measured with a scanning electron microscope (SEM; JSM-5600LV, JED-2200, JEOL Co., Ltd. Tokyo, Japan).

### Measurements of ATR-IR spectra

The ATR-IR spectra of the surface layer of grafted film were measured with an automatic infrared microscope (AIM-800, FTIR-8700, Shimadzu Co., Ltd.,



**Figure 1** Photografting of NIPAAm on XT-coated LLDPE film in mixed solvent. [NIPAAm] = 0.79 mol/L. Irradiation at 30°C for 4 h: (○) acetone, (△) methanol.

Kyoto, Japan). The amount of NIPAAm-grafted chains on the film surface layer was expressed in terms of the absorbance ratio of the amide peak at 1640  $\text{cm}^{-1}$  to the methylene peak at 1460  $\text{cm}^{-1}$ .

### Measurements of dimensional change

Grafted film was immersed in water alternately at 0°C and 50°C for 24 h. After the treatment excess water on the film surface was wiped by filter paper. The dimensional change of the grafted film was defined as follows:

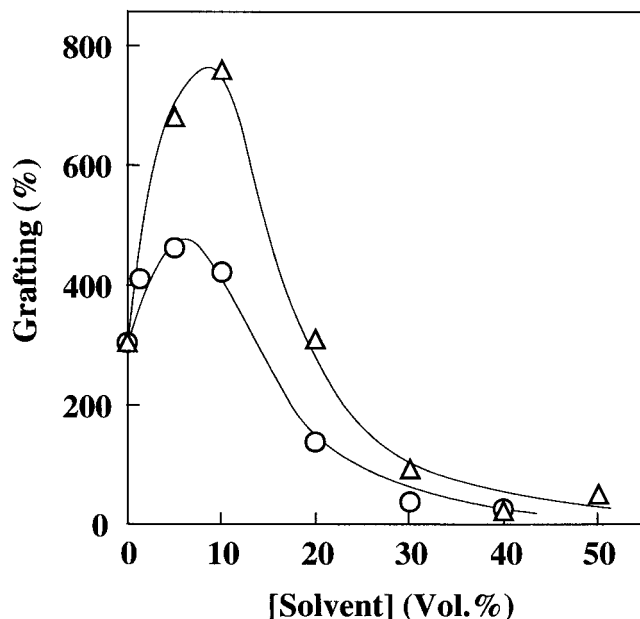
$$\text{Dimensional change (\%)} = \frac{S_1 - S_0}{S_0} \times 100$$

where  $S_0$  and  $S_1$  are surface areas of the grafted films before and after treatment, respectively. The surface area was calculated from the length and width of the grafted film measured with a standard ruler.

## RESULTS AND DISCUSSION

### Grafting behavior

The effect of a mixed solvent consisting of water and organic solvents such as acetone and MeOH on photografting of NIPAAm on LLDPE film was examined at 30°C, and the results are shown in Figure 1. The photografting initiated even in the system at 30°C by using a longer irradiation time. The percentage of grafting increased with an increasing concentration of organic solvent in the mixed solvent, and the maxi-



**Figure 2** Photografting of NIPAAm on XT-coated LLDPE film in mixed solvent. [NIPAAm] = 0.79 mol/L. Irradiation at 60°C for 30 min: (○) acetone, (△) methanol.

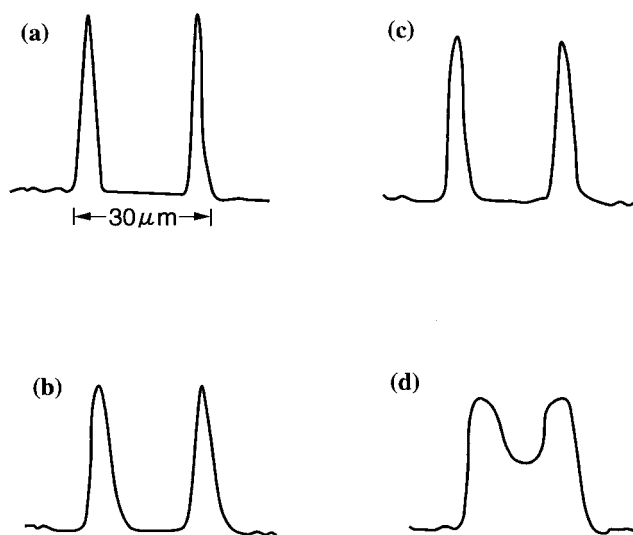
imum percentage of grafting was observed at a certain concentration of organic solvent in the mixed solvent. In our previous article<sup>1</sup> on photografting of MAA on LLDPE film in a mixed solvent, it was supposed that the solubility of MAA monomer in the system increases to stimulate monomer supply for the 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 the 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. Solubility parameters of acetone and MeOH were 9.9 and 14.5 (cal/cc)<sup>0.5,11</sup> respectively, whereas that of poly(NIPAAm) was 11.18 (cal/cc)<sup>0.5,12</sup>. So, it is reasonable to suppose that both solvents promote monomer solubility in the system. As shown in Figure 2, the percentage of grafting at 60°C, which was much higher than that at 30°C, also increased with an increasing concentration of organic solvent, and a maximum value was afforded at a certain concentration of organic solvent in the mixed solvent, which shifted to lower concentration of organic solvent compared with the system at 30°C. As described above, the maximum percentage of grafting was supposed to have originated in the balance between the two effects of the organic solvent—the positive effect of the organic solvent promoting monomer solubility in the system and the negative effect of the organic solvent participating in the chain transfer and

termination of growing grafted polymer radicals. It seems that the two effects of the organic solvent are more emphasized in the system at 60°C than at 30°C, leading to a shift of the concentration of organic solvent affording a maximum percentage of grafting.

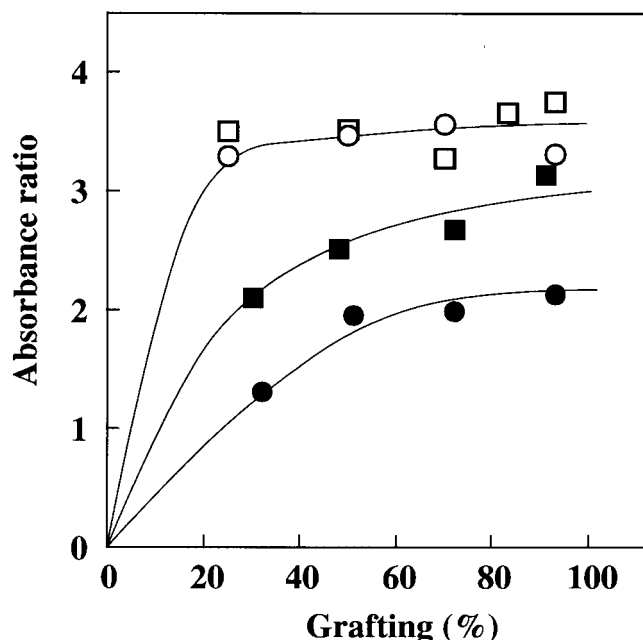
In this study PVAc was used as a polymeric carrier of photoinitiator to hold the photoinitiator homogeneously and tightly on the film surface. An extraction treatment was carried out in order to examine the contribution of PVAc to the grafting. NIPAAm-grafted LLDPE film with 136% grafting was extracted for an additional 24 h with hot MeOH, which is a solvent of both PVAc and poly(NIPAAm).<sup>13</sup> The percentage of grafting recorded after the extraction with MeOH was 132%, indicating only a slight decrease in the percentage of grafting due to the extraction. This suggests that the grafted poly(NIPAAm) is linked directly to the LLDPE substrate, not to the PVAc carrier.

#### Distribution of NIPAAm-grafted chains

Figure 3 shows the distribution profile of palladium atoms in the cross section of NIPAAm-grafted LLDPE films prepared in water and water/acetone mixed solvent, which were measured by SEM to examine the location of the grafted chains. The vertical and horizontal directions in the figure correspond to the relative concentration of the palladium atom and the cross section of the films, respectively. The NIPAAm-grafted chains of the samples prepared in the system at 30°C seemed to locate mainly on the surface layer of the film because they did not penetrate into the center part of the film, which was commonly observed for



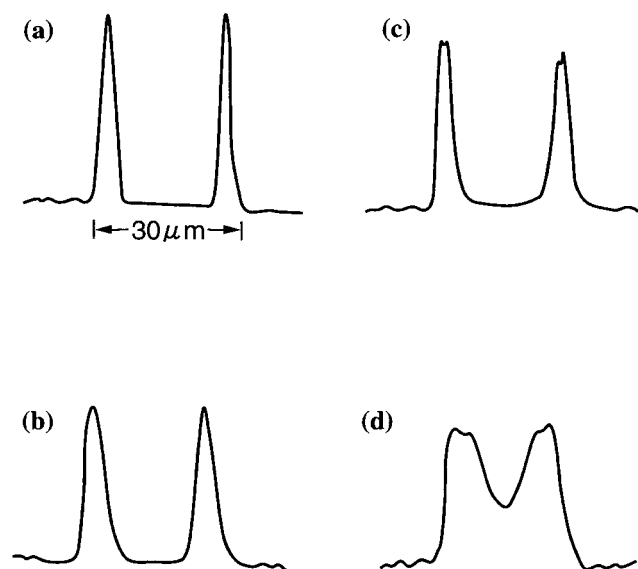
**Figure 3** Distribution profile of palladium atoms in cross section of NIPAAm-grafted LLDPE films prepared in water–acetone mixed solvent, measured by SEM: (a) 30°C, water (grafting = 70%); (b) 60°C, water (grafting = 68%); (c) 30°C, mixed solvent with 15 vol % acetone (grafting = 70%); (d) 60°C, mixed solvent with 15 vol % acetone (grafting = 70%).



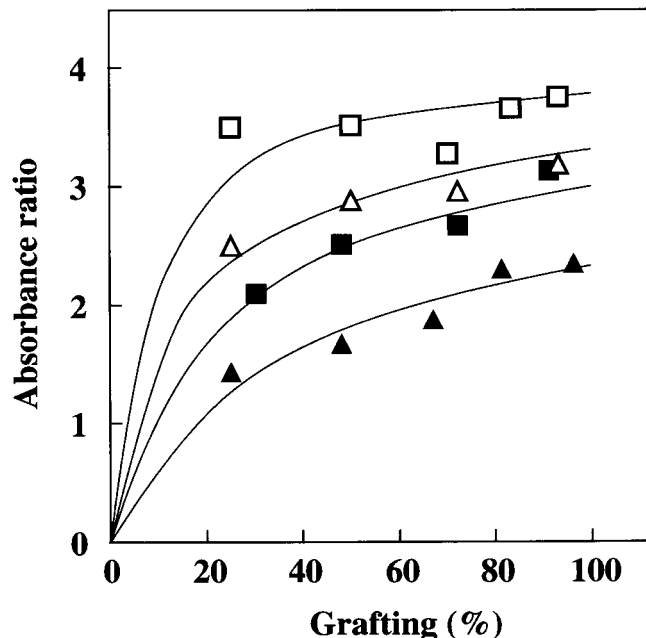
**Figure 4** Changes in absorbance ratio of an amide peak at  $1640\text{ cm}^{-1}$  to a methylene peak at  $1460\text{ cm}^{-1}$  with percentage of grafting in NIPAAm-grafted LLDPE films—for  $30^\circ\text{C}$ : (□) water, (○) mixed solvent with 15 vol % acetone; for  $60^\circ\text{C}$ : (■) water, (●) mixed solvent with 15 vol % acetone.

the samples prepared in water and mixed solvent. With the samples prepared in the system at  $60^\circ\text{C}$ , on the other hand, the grafted chains of the sample with mixed solvent located in the film inside compared with those of the sample with water, which located on the surface layer. To confirm the above results obtained by SEM, the surface layer of the grafted films was examined by ATR-IR, and the results are shown in Figure 4. The vertical axis of the figure is the absorbance ratio of the amide peak at  $1640\text{ cm}^{-1}$  to the methylene peak at  $1460\text{ cm}^{-1}$ . The absorbance ratio increased with an increasing percentage of grafting, and the magnitude of the increase decreased in this order:  $30^\circ\text{C}$ , sample with water  $\approx 30^\circ\text{C}$ , sample with mixed solvent  $> 60^\circ\text{C}$ , sample with water  $> 60^\circ\text{C}$ , sample with mixed solvent. This suggests the different distributions of NIPAAm-grafted chains in the surface layer of grafted films among the samples depending on grafting conditions. It is inferred that a higher polymerization temperature enhances the diffusion of the NIPAAm monomer into the film substrate, resulting in penetration of NIPAAm-grafted chains into a deeper layer of the film surface compared with the system at  $30^\circ\text{C}$ . With the grafted film prepared in the system at  $60^\circ\text{C}$ , moreover, the use of water/acetone mixed solvent was found to promote the penetration of the grafted chains into the center part of film substrate. Figure 5 shows the distribution profile of palladium atoms in the cross section of NIPAAm-grafted LLDPE films prepared in the water/MeOH mixed

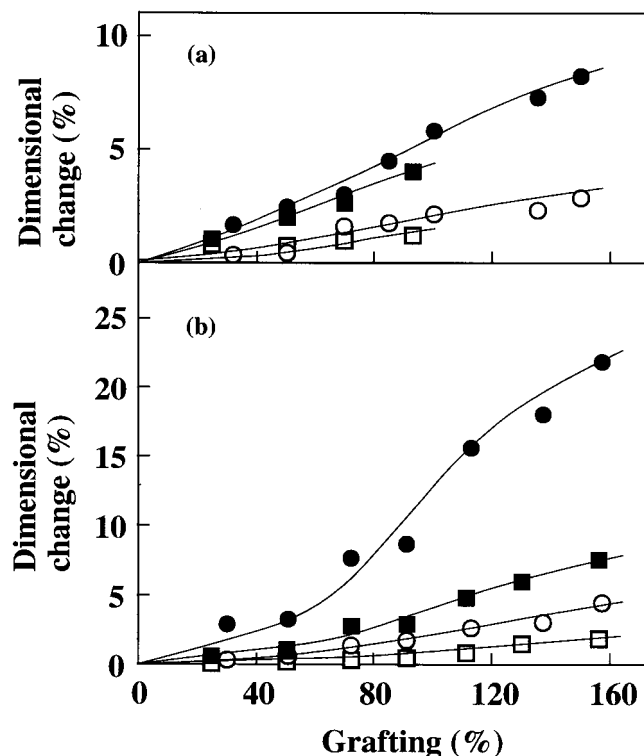
solvent. As with the water/acetone mixed solvent, a tendency for the distribution of grafted chains in the water/MeOH mixed solvent was observed. That is, the grafted chains of the sample prepared in the system with the water/MeOH mixed solvent and a higher polymerization temperature accelerated penetration of NIPAAm-grafted chains into the center part of the film. Figure 6 shows the absorbance ratio of the amide peak to the methylene peak of the grafted films. The absorbance ratio increased with an increase in the percentage of grafting, and the magnitude of the increase decreased in this order:  $30^\circ\text{C}$ , sample with water  $> 30^\circ\text{C}$ , sample with mixed solvent  $> 60^\circ\text{C}$ , sample with water  $> 60^\circ\text{C}$ , sample with mixed solvent. That is, density of NIPAAm-grafted chains in the surface layer of the grafted film was found to decrease with use of the mixed solvent and a higher polymerization temperature. In the photografting of NIPAAm on XT-coated LLDPE film in the water solvent, photoexcited XT may extract the hydrogen atoms from LLDPE substrate to yield LLDPE radicals on the film surface capable of initiating grafting. Therefore, the grafted layers starts from the film surface. As the grafting reaction proceeds, monomers are supplied to the LLDPE substrate through the grafted layer, resulting in the penetration of the grafted layer into the film texture, followed by the expansion of the film texture. Based on the solubility parameters of acetone and MeOH,  $9.9$  and  $14.5$  ( $\text{cal/cc}^{0.5}$ ), respectively, the affinity of the organic solvents to the polyethylene substrate [solubility parameter:  $8.1$  ( $\text{cal/cc}^{0.5}$ )]<sup>11</sup> is higher than water, indicating that the organic solvents also



**Figure 5** Distribution profile of palladium atoms in cross section of NIPAAm-grafted LLDPE films prepared in mixed solvent, measured by SEM: (a)  $30^\circ\text{C}$ , water (grafting = 70%); (b)  $60^\circ\text{C}$ , water (grafting = 68%), (c)  $30^\circ\text{C}$ , mixed solvent with 15 vol % methanol (grafting = 72%); (d)  $60^\circ\text{C}$ , mixed solvent with 15 vol % methanol (grafting = 78%).



**Figure 6** Changes in absorbance ratio of an amide peak at  $1640\text{ cm}^{-1}$  to a methylene peak at  $1460\text{ cm}^{-1}$  with percentage of grafting in NIPAAm-grafted LLDPE films—for  $30^\circ\text{C}$ : ( $\square$ ) water, ( $\triangle$ ) mixed solvent with 15 vol % methanol; for  $60^\circ\text{C}$ : ( $\blacksquare$ ) water, ( $\blacktriangle$ ) mixed solvent with 15 vol % methanol.

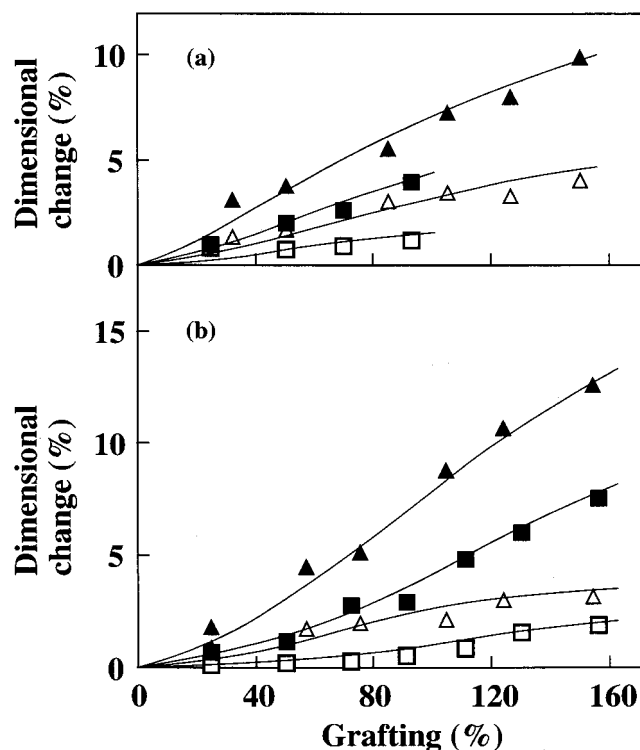


**Figure 7** Dimensional change of NIPAAm-grafted LLDPE films prepared in water–acetone mixed solvent at (a)  $30^\circ\text{C}$  and (b)  $60^\circ\text{C}$ —for  $0^\circ\text{C}$ : ( $\blacksquare$ ) water, ( $\bullet$ ) mixed solvent with 15 vol % acetone; for  $50^\circ\text{C}$ : ( $\square$ ) water, ( $\circ$ ) mixed solvent with 15 vol % acetone.

assist the penetration of NIPAAm-grafted chains into polyethylene substrate. It was thus confirmed that a higher polymerization temperature and use of mixed solvents accelerate the penetration of NIPAAm-grafted chains into the film texture.

#### Temperature-responsive characters

Figure 7 shows the dimensional change of NIPAAm-grafted LLDPE films prepared in water/acetone mixed solvent at  $30^\circ\text{C}$  and  $60^\circ\text{C}$  when immersed in water alternately at  $0^\circ\text{C}$  and  $50^\circ\text{C}$  for 24 h. The NIPAAm-grafted films prepared in the system at  $30^\circ\text{C}$  [Fig. 7(a)] swelled at  $0^\circ\text{C}$ , whereas they shrank at  $50^\circ\text{C}$  in water, though the dimensional change was relatively low. The dimensional change increased with an increase in the percentage of grafting, and the magnitude was slightly larger for the sample with mixed solvent compared to the sample with water. The dimensional change was higher for the grafted films prepared in the system at  $60^\circ\text{C}$  [Fig. 7(b)] than those prepared in the system at  $30^\circ\text{C}$ . Moreover, a larger temperature-responsive character was observed for the sample with mixed solvent compared with the sample with water, which was emphasized in the grafted films prepared in the system at  $60^\circ\text{C}$ . This might be ascribed to the grafted chains of the sample



**Figure 8** Dimensional change of NIPAAm-grafted LLDPE films prepared in water–methanol mixed solvent at (a)  $30^\circ\text{C}$  and (b)  $60^\circ\text{C}$ —for  $0^\circ\text{C}$ : ( $\blacksquare$ ) water, ( $\blacktriangle$ ) mixed solvent with 15 vol % methanol; for  $50^\circ\text{C}$ : ( $\square$ ) water, ( $\triangle$ ) mixed solvent with 15 vol % methanol.

with mixed solvent, which penetrated into the center of the film, compared with the sample with water, as shown in Figure 3. Dimensional changes of NIPAAm-grafted LLDPE films prepared in water/methanol mixed solvent at 30°C and 60°C are shown in Figure 8(a,b), respectively. It was confirmed that a higher dimensional change is afforded for the grafted films prepared in the systems with a higher polymerization temperature and use of the water/MeOH mixed solvent.

### CONCLUSIONS

It has been concluded that NIPAAm-grafted chains with a temperature-responsive function can be introduced into LLDPE films by photografting using XT-coated film, which is largely influenced by grafting conditions such as polymerization temperature and use of a mixed solvent consisting of water and organic solvent. The resulting NIPAAm-grafted films were characterized by their temperature responsiveness, how they swelled and shrank in water at 0°C and 50°C, respectively. The extent of this characteristic was closely related to the distribution of grafted chains,

depending on the grafting conditions such as the polymerization temperature and the use of mixed solvent.

### References

1. Irwan, G. S.; Kuroda, S.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2002, 83, 2454.
2. Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1984, 81, 6379.
3. Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1987, 87, 1392.
4. Otake, K.; Inomata, H.; Konno, M.; Saito, S. *Macromolecules* 1990, 23, 2893.
5. Bae, Y. H.; Okano, T.; Kim, S. W. *J Polym Sci, Part B: Polym Phys* 1990, 28, 923.
6. Okahata, Y.; Noguchi, H.; Seki, T. *Macromolecules* 1986, 19, 493.
7. Iwata, H.; Oodate, M.; Uyama, Y.; Amemiya, H.; Ikada, Y. *J Membr Sci* 1991, 55, 119.
8. Lee, Y. M.; Ihm, S. Y.; Shim, J. K.; Kim, J. H.; Cho, C. S.; Sung, Y. K. *Polymer* 1995, 36, 81.
9. Hiroki, A.; Yoshida, M.; Nagaoka, N.; Asano, M.; Reber, N.; Spohr, R.; Kubota, H.; Katakai, R. *Radiat Eff Detects Solids* 1999, 147, 165.
10. Kuwabara, S.; Kubota, H. *J Appl Polym Sci* 1996, 60, 1965.
11. Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1989; pp. IV-4.
12. Ahmad, H. *J Macromol Sci Chem* 1982, A17, 585.
13. Winnik, F. M.; Ottaviani, M. F.; Bossman, S. H.; Garibay, M. G.; Turro, N. J. *Macromolecules* 1992, 25, 6007.