

Temperature-Responsive Characteristics of *N*-Isopropylacrylamide-Grafted Polymer Films Prepared by Photografting

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SYNOPSIS

Photografting of *N*-isopropylacrylamide (NIPAAm) on ethylene–vinyl alcohol copolymer films (thickness = 15, 20, and 25 μm) and low- and high-density polyethylene films (thickness = 30 μm) was carried out at 60°C in a water medium. Xanthone was used as a photoinitiator by coating it on the film samples. The resultant NIPAAm-grafted films exhibited a temperature-responsive character, which was evaluated by measuring a dimensional change of the grafted films. The grafted films swelled and shrank in water at temperatures lower and higher than around 30°C, respectively. The character was found to be reversible between 0 and 50°C. It was observed that the extent of the character is largely influenced by film thickness, location of NIPAAm-grafted chains, and crystallinity of film substrate. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In previous papers^{1–4} photografting of acrylic acid and methacrylic acid on low-density polyethylene (LDPE) film in vapor- and liquid-phase systems was investigated together with the relationship between the grafting conditions and the location of grafted chains. It was concluded that the acrylic acid- and methacrylic acid-grafted LDPE films with a homogeneous distribution of the grafted chains can be prepared by proper choice of polymerization system, either vapor- or liquid-phase, and monomer concentration, and polymerization temperature in the liquid-phase system. It was found moreover that the acrylic acid-grafted LDPE films with a homogeneous distribution of the grafted chains exhibit a larger pH-responsive character compared to those with the grafted chains located mainly on the film surface. Thus, the pH-responsive character of the acrylic acid-grafted films was greatly influenced by the location of grafted chains in film substrate.

This article deals with temperature-responsive character of *N*-isopropylacrylamide (NIPAAm)-grafted polymer films prepared by photografting. Poly(NIPAAm) is well known to exhibit a lower critical solution temperature around 32°C in aqueous solution. That is, it swells in water below and shrinks above that temperature. The swelling and shrinking characteristics have been applied to prepare temperature-responsive membranes^{5–7} and adsorbents,^{8,9} where a grafting technique is utilized to attach the characteristics to the base materials. In the present study, temperature-responsive characteristics of NIPAAm-grafted polymer films were investigated together with the location of the grafted chains in film substrates such as ethylene–vinyl alcohol copolymer (EVAL) and polyethylene (PE).

EXPERIMENTAL

Materials

EVAL (ethylene unit/vinyl alcohol unit = 45/55, thickness = 15, 20, and 25 μm) and LDPE and high-density polyethylene (HDPE) (thickness = 30 μm)

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were used as polymer films. The polymer films were dipped in acetone solution containing 0.3 wt % xanthone, taken out of the solution, and then dried under reduced pressure to prepare xanthone-coated films. The quantity of xanthone on the film was too small to determine gravimetrically. Xanthone and NIPAAm were all of reagent grade and used without further purification.

Photografting

Liquid-phase photografting was carried out in a Pyrex glass tube containing the film sample (3×10 cm) and 40-mL aqueous NIPAAm solution with known concentrations under nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 60°C using a Riko rotary photochemical reactor (RH400-10W), around which the Pyrex glass tubes were rotated. After the reaction, the film was extracted for 48 h with water to remove homopolymer. The percent grafting was taken as the percentage of weight increase of the original film.

Electron Probe Microanalysis (EPMA)

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 atom of the grafted film was measured with an electron probe microanalyzer (EPM-8100, Shimadzu Co. Ltd.).

Measurement of Dimensional Change of Grafted Films

NIPAAm-grafted film (surface area, S_0 mm²) was immersed in water at given temperatures for 24 h. After the treatment, excess water on the film surface was wiped by filter paper and then the surface area (S_1 mm²) of the treated film was measured. Dimensional change of the grafted film was defined as follows:

Dimensional change

$$(\%) = \frac{S_1 - S_0}{S_0} \times 100.$$

RESULTS AND DISCUSSION

NIPAAm-Grafted EVAL Films

EVAL is an interesting material composed of both the hydrophilicity of the vinyl alcohol sequences and

the hydrophobicity of the ethylene sequences, resulting in the microphase-separated structure. Grafting on EVAL has been examined in the systems initiated by ceric ion¹⁰ and electron beam irradiation,¹¹ where acrylamide and potassium salt of styrenesulphonic acid were used as monomers, respectively. Photografting of NIPAAm on EVAL film was found to proceed easily by using the xanthone-coated film; the results are shown in Figure 1. The amount of grafts increased with increasing irradiation time and the values were not subjected to a large influence of film thickness within the range of 15–25 μ m. The graft efficiencies, which were taken as the weight percent of grafted polymer relative to total conversion of monomer in a system, were 30 to 40% in each system, showing the predominant formation of homopolymer.

Figure 2 shows dimensional change of NIPAAm-grafted EVAL films when immersed in water at various temperatures (0–50°C) for 24 h. The dimensional change steeply decreased at about 25 to 30°C with increasing the temperature, exhibiting a temperature-responsive character of the NIPAAm-grafted films. The grafted films swelled and shrank in water below and above the temperature, respectively. The extent of the character increased with an increase in the percent grafting. It was found that the temperature-responsive function can be attached to the EVAL film substrate by photografting of NIPAAm.

Figure 3 shows the effect of film thickness on dimensional change of NIPAAm-grafted films. The

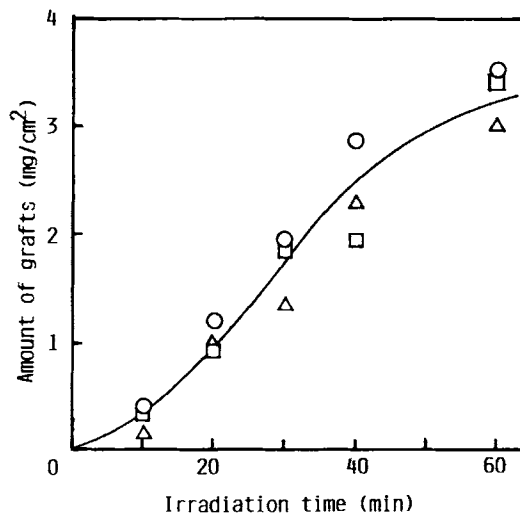


Figure 1 Photografting of NIPAAm on EVAL film sensitized with xanthone. Irradiation temperature, 60°C; concentration of NIPAAm = 0.22 mol/L; film thickness (μ m): (Δ) 15, (\circ) 20, (\square) 25.

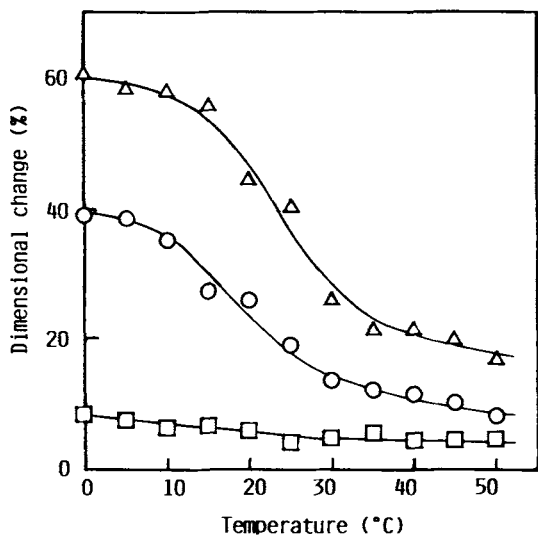


Figure 2 Relationship between dimensional change and temperature in NIPAAm-grafted EVAL films. Film thickness = 15 μm . Grafting (%): (□) 55, (○) 137, (△) 223.

effect was examined using the grafted films with nearly equal amounts of grafts. The vertical axis of the figure represents the dimensional change per unit amount of grafts (g). The dimensional change decreased with increasing film thickness. It was found moreover that the magnitude of the change on dimension between 0 and 40°C was larger in thinner film. It is inferred that NIPAAm-grafted chains of the thinner film are likely to penetrate into the film inside compared to those of the thicker

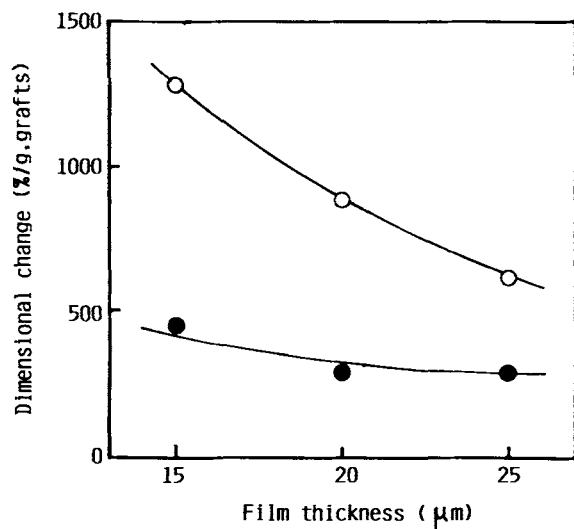


Figure 3 Effect of film thickness on dimensional change in NIPAAm-grafted EVAL films. Amount of grafts = 0.9–1.1 mg/cm^2 . Temperature (°C): (○) 0, (●) 40.

film, resulting in a higher temperature-responsive function.

The effect of location of NIPAAm-grafted chains in the cross section of the grafted films on dimensional change was examined; the results are shown in Figure 6. The NIPAAm-grafted films with a different location of the grafted chains were prepared by changing the monomer concentration^{2,4} as shown in Figure 4. Figure 5 presents a distribution profile of the palladium atom in the cross section of NIPAAm-grafted films measured by EPMA. It was observed that a considerable amount of grafted chains in the sample prepared by the system of 0.66 mol/L monomer concentration distributes in the film inside compared to that in the sample prepared by the system of 0.22 mol/L monomer concentration, although the grafted chains of both samples still locate on the film surface. Figure 6 shows the dimensional change of NIPAAm-grafted films when immersed in water at 0 and 50°C for 24 h, alternately. Both grafted films exhibited a reversible change on dimension between 0 and 50°C and the magnitude of the change was larger in the sample prepared by the system of 0.66 mol/L monomer concentration. This might be ascribed to the grafted chains located inward in the sample prepared by higher monomer concentration.

NIPAAm-Grafted Polyethylene Films

Figure 7 shows photografting of NIPAAm on LDPE and HDPE films. The percent grafting increased

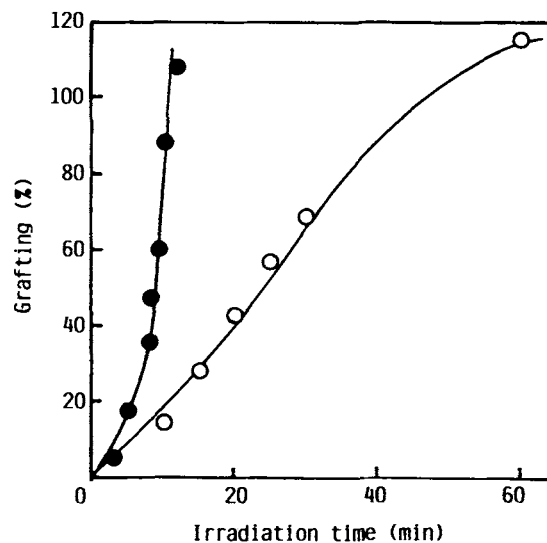


Figure 4 Photografting of NIPAAm on EVAL film (thickness = 25 μm) sensitized with xanthone. Irradiation temperature, 60°C, concentration of NIPAAm (mol/L): (○) 0.22, (●) 0.66.

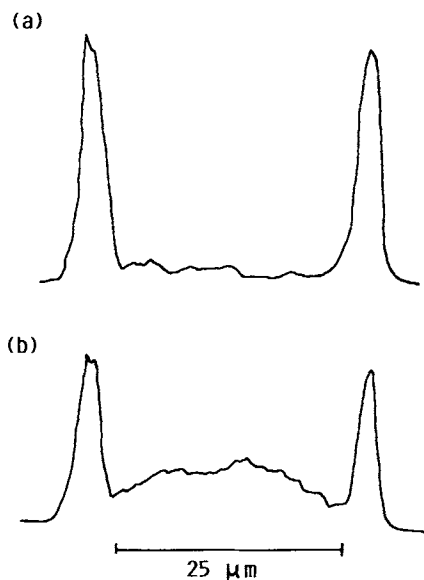


Figure 5 Distribution profile of palladium atom in the cross section of NIPAAm-grafted EVAL film measured by EPMA. Film thickness = 25 μm . (a) concentration of NIPAAm, 0.22 mol/L; grafting (%), 45; (b) concentration of NIPAAm, 0.66 mol/L; grafting (%), 48.

with irradiation time and LDPE showed a higher rate of grafting than HDPE, which was commonly observed for the systems of 0.33 and 0.66 mol/L monomer concentrations. This result may be originated in a lower crystallinity of LDPE¹² compared to HDPE. The activity of LDPE toward vapor-phase photografting¹³⁻¹⁵ of acrylic acid was also found to be higher than that of HDPE. Ishigaki et al.¹⁶ studied grafting of acrylic acid onto polyethylene films preirradiated with electron beam and observed that LDPE gives a higher rate of grafting than HDPE. They explained the result by a higher diffusion rate of monomer due to the lower crystallinity in LDPE.

Figure 8 shows the dimensional change of NIPAAm-grafted LDPE and HDPE films. The film samples prepared by the system of 0.66 mol/L monomer concentration exhibited a larger dimensional change than those prepared by the system of 0.33 mol/L monomer concentration, which was commonly recorded for LDPE and HDPE films. This result was similar to that of EVAL films as shown in Figure 6. It is supposed that the NIPAAm-grafted chains of the sample prepared using the high monomer concentration penetrate into the inside of the film compared to those of the sample prepared using the low monomer concentration, resulting in the larger dimensional change. Moreover, each grafted film showed a reversible change in dimension between 0 and 50°C. The magnitude of the change

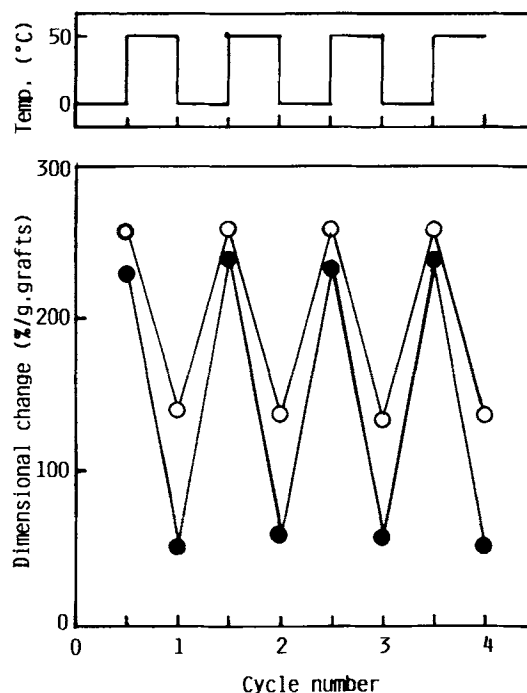


Figure 6 Reversible change in dimension of NIPAAm-grafted EVAL films. Film thickness, 25 μm ; grafting (%), 100-110; concentration of NIPAAm (mol/L): (O) 0.22, (●) 0.66.

between the both temperatures was larger in LDPE than in HDPE. This suggests that the temperature-responsive character of NIPAAm-grafted film may also be influenced by the crystallinity of the film

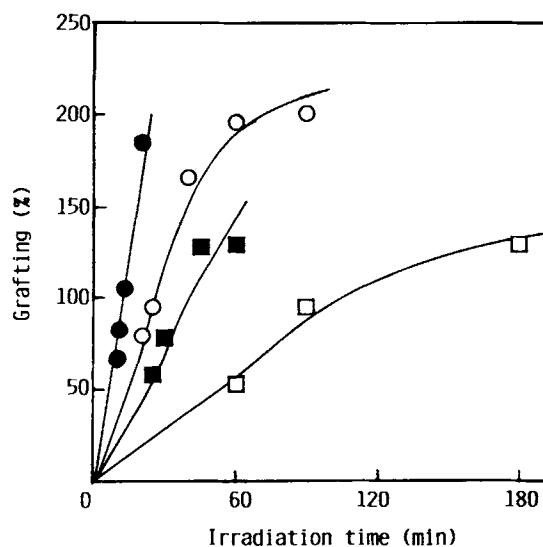


Figure 7 Photografting of NIPAAm on (O, ●) LDPE and (□, ■) HDPE films sensitized with xanthone. Irradiation temperature, 60°C; concentration of NIPAAm (mol/L): (O, □) 0.33, (●, ■) 0.66.

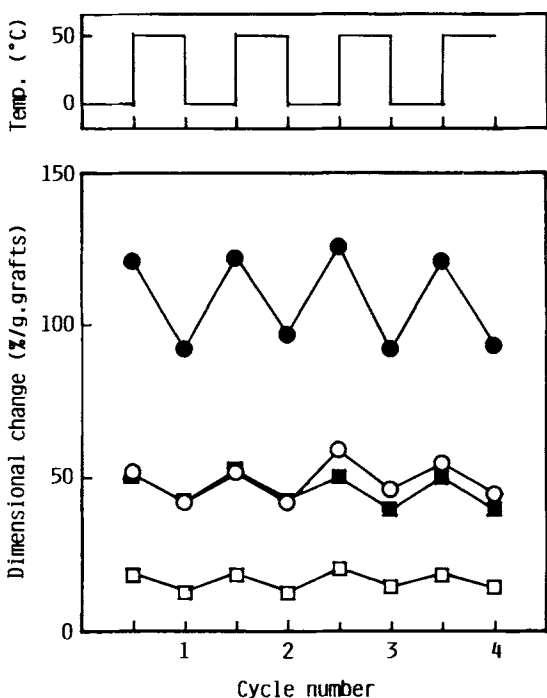


Figure 8 Reversible change in dimension of NIPAAm-grafted (○, ●) LDPE and (□, ■) HDPE films. Concentration of NIPAAm (mol/L): (○, □) 0.33, (●, ■) 0.66.

substrate other than the location of the grafted chains.

Based on the above investigations, it was found that photografting of NIPAAm on polymer films such as EVAL and PE proceeds easily and the resultant NIPAAm-grafted films exhibit a temperature-responsive character, the extent of which is largely influenced by film thickness, location of the grafted chains, and crystallinity of the film substrate. Accordingly, it is concluded that the temperature-responsive function can be attached to the polymer film by means of photografting of NIPAAm and the

extent of the function is closely related to the location of the grafted chains in the film substrate.

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