

# Characteristics of Acrylic Acid and *N*-Isopropylacrylamide Binary Monomers–Grafted Polyethylene Film Synthesized by Photografting

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**ABSTRACT:** Method for introducing grafted chains consisting of two types of monomer components, acrylic acid (AA) and *N*-isopropylacrylamide (NIPAAm), into low-density polyethylene (PE) film (thickness = 25  $\mu\text{m}$ ) was investigated by two photografting techniques using xanthone photoinitiator at 60°C. In the first method (one-step method), AA and NIPAAm binary monomers were graftcopolymerized onto PE film. In the second method (two-step method), AA was first photografted onto PE film and then NIPAAm was further introduced into the AA-grafted PE film by a second-step photografting. Water absorbencies of the grafted films (one- and two-step samples) prepared by the one- and two-step methods, respectively, decreased in the order of AA-grafted film > one-step sample > two-step sample > NIPAAm-grafted film. The water absorbency steeply decreased at 20 to 40°C with increasing temperature when immersed in water at the temperatures (5–60°C) for 24 h. Thermosensitivity, which was defined as the ratio of water absorbencies of the grafted samples at 5 and 60°C, was higher for the one-step sample than the two-step one. The different extent of the water absorbency and the thermosensitivity between both samples is discussed in terms of location of grafted chains in the film substrate, which was determined by electron probe microanalysis and attenuated total reflection–infrared measurements, and monomer sequence distribution of the grafted chains. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2057–2064, 1998

**Key words:** photografting; *N*-isopropylacrylamide; acrylic acid; low-density polyethylene

## INTRODUCTION

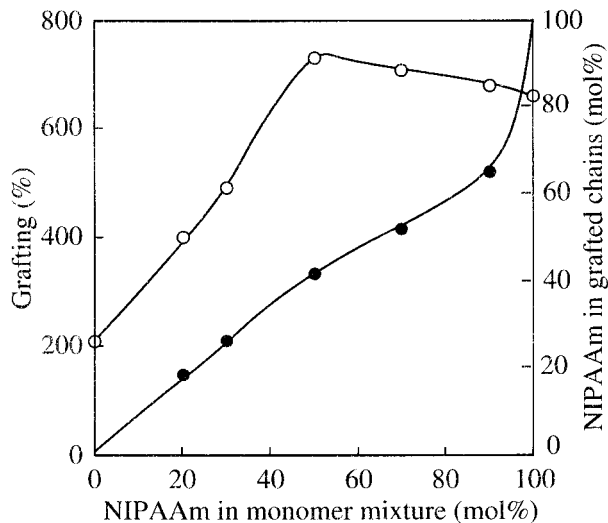
Grafting is known to be useful for the introduction of various functional groups into polymer materials by selecting the type of monomer. It is conceivable that the function of the groups introduced is influenced by monomer sequence distribution of the grafted chains and its location in the polymer substrate, depending on the method of introduction. Accordingly, it is important to investigate

the relationship between the function attached to the polymer materials and the method of introduction of grafted chains. It was found in our previous articles<sup>1–9</sup> that photografting is a useful means for introduction of various functions into polyethylene (PE) film substrate, such as wettability,<sup>1,2</sup> moisture permeability,<sup>3,4</sup> catalytic activity,<sup>5,6</sup> polymer peroxides,<sup>7</sup> and pH- and temperature<sup>9</sup>-responsive characters, which are greatly influenced by the location of grafted chains in the film substrate. This article deals with the method for introducing grafted chains, which consist of two types of monomer component, into polyethylene film by means of photografting.

We selected acrylic acid (AA) and *N*-isopropyl-

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**Figure 1** Photografting of AA-NIPAAm binary monomers onto PE film sensitized with xanthone: (○) grafting (%); (●) NIPAAm content in grafted chains (mol %). Conditions were as follows: irradiation, 60°C; 40 min; [total monomer] = 1.0 mol/L.

lacrylamide (NIPAAm) as the two monomer components to be introduced. Poly(NIPAAm) is well known to exhibit a lower critical solution temperature (LCST) of around 32°C in aqueous solution. Moreover, copolymer<sup>10,11</sup> of AA and NIPAAm is also reported to undergo a discontinuous phase transition in responsive to change in temperature. Therefore, AA-NIPAAm-grafted polyethylene film is expected to exhibit a temperature-responsive character, in which it swells and shrinks in water below and above the LCST of the copolymer, depending on the composition of AA and NIPAAm. It is conceivable that the AA component of the grafted chains can be utilized as a reaction site to introduce various functions through the carboxyl groups.

The introduction of AA and NIPAAm monomer components into PE film was performed by two photografting methods. In the first method (one-step method), AA and NIPAAm binary monomers were graft-copolymerized onto polyethylene substrate. In the second method (two-step method), AA was first photografted onto polyethylene film, and then NIPAAm was further grafted onto the AA-grafted polyethylene film. In this study, the methods for introducing grafted chains, which consist of two types of monomer component, AA and NIPAAm, into polyethylene film were investigated in terms of grafting behaviors, location of the grafted chains, and properties such as water

absorbency and temperature-responsive character of the resulting grafted PE films.

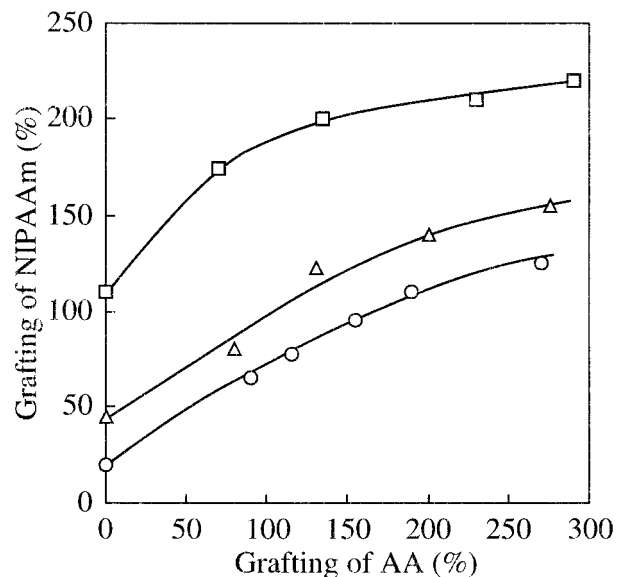
## EXPERIMENTAL

### Materials

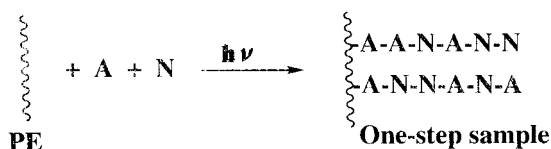
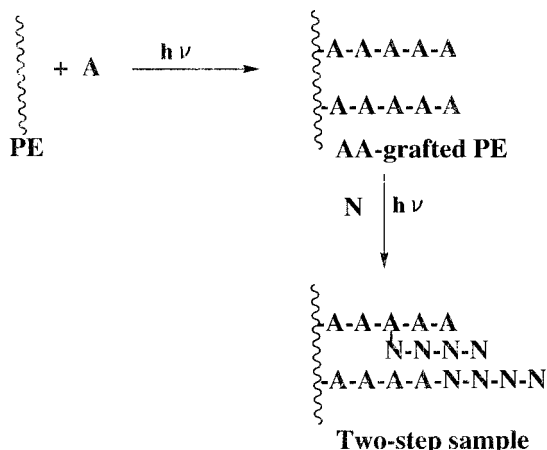
The polyethylene film used was low-density polyethylene (PE) 25  $\mu\text{m}$  thick. The film ( $3 \times 10$  cm) was dipped into acetone solution containing 0.3% by weight xanthone and 0.5% by weight poly(vinyl acetate) ( $M_w = 100,000$ ), removed from the solution, and then dried at room temperature for 5 h under reduced pressure of 5 torr to prepare xanthone-coated film. The quantity of xanthone in the film was too small to determine gravimetrically. However, the existence of xanthone on the film surface was confirmed by attenuated total reflectance-infrared (ATR-IR) measurement, where specific absorption bands due to aromatic ring appeared in the 1600–1700  $\text{cm}^{-1}$  region. Xanthone was of reagent grade and used without further purification. AA and NIPAAm were purified by distillation under reduced pressure (4 torr at 35°C) and by recrystallization from a benzene-*n*-hexane mixture, respectively.

### Photografting

In the one-step method, AA and NIPAAm binary monomers were grafted onto PE film, that is,



**Figure 2** Second-step photografting of NIPAAm onto AA-grafted PE film sensitized with xanthone, with irradiation at 60°C: (○) 5 min, (△) 10 min, and (□) 20 min. [NIPAAm] = 0.50 mol/L.

**(1) One-step method****(2) Two-step method**

A: acrylic acid  
N: N-isopropylacrylamide

Scheme 1

photografting was carried out in a Pyrex glass tube containing the film sample and 30 mL water, in which given molar ratios of AA and NIPAAm binary monomers (total monomer concentration = 1.0 mol/L) were dissolved, at 60°C under a nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was carried out using a Riko rotary photochemical reactor (RH400-10W), around which the Pyrex glass tubes were rotated. The polymerized film was extracted for 2 days with cold water and for 1 day with hot methanol to remove homopolymers and then dried at room temperature for 24 h under reduced pressure of 5 torr. The grafted films thus obtained was denoted as a one-step sample. The percentage of grafting was taken as the percentage of weight increase of the original film. The NIPAAm composition of AA–NIPAAm-grafted chains was determined by nitrogen analysis. With the two-step method, AA was first grafted onto PE film according to the photografting procedures (AA concentration = 0.50 mol/L), as described above. The resulting AA-grafted PE film (first-step sample) was further subjected to photografting of NIPAAm at 60°C using NIPAAm concentration of

0.50 mol/L. The grafted film denoted as a two-step sample. The percentage of grafting of NIPAAm in the second-step photografting was taken as the percentage of weight increase of the AA-grafted PE film. Grafted samples with different percentages of grafting in each system were prepared by varying irradiation time.

**Electron Probe Microanalysis**

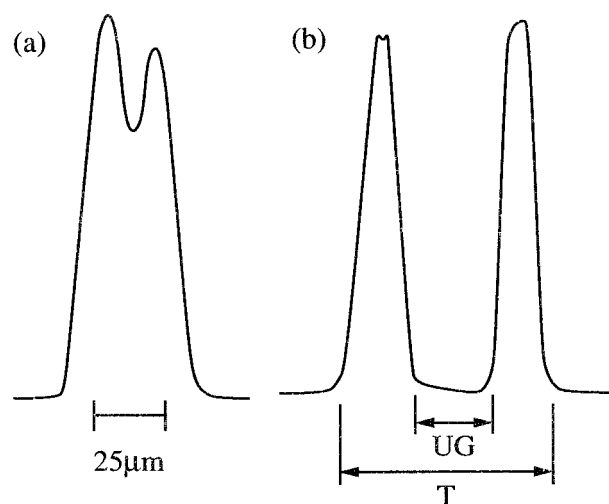
The AA component of AA–NIPAAm-grafted chains was converted to potassium salts by immersing the grafted film into an aqueous solution of 1.0% potassium hydroxide at room temperature for 24 h. A saturated aqueous solution of palladium chloride was used in the case of NIPAAm-grafted chains. The distribution profile of potassium or palladium atoms in the grafted film was measured with an electron probe microanalyzer model EPM-8000 of Shimadzu Co.

**Measurement of ATR-IR Spectra**

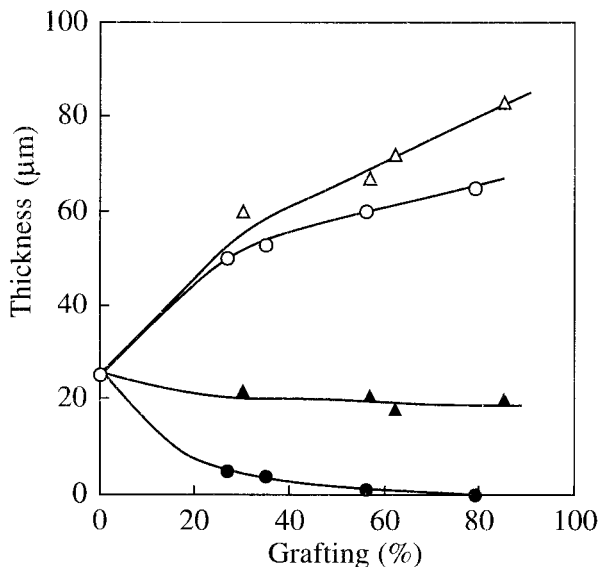
The ATR-IR spectra of the surface layer of grafted film were measured with an IR spectrometer model MAGNA-IR 750 of Nicolet.

**Measurement of Water Absorbency**

Grafted film ( $W_0$ , g) was immersed into water at given temperatures (5–60°C) for 24 h. After the treatment, excess water on the film surface was



**Figure 3** Distribution profiles of potassium and palladium atoms in the cross section of (a) AA- and (b) NIPAAm-grafted films, respectively, measured by EPMA. Grafting (%): (a) 56.0 and (b) 57.1.



**Figure 4** Relationship between the total thickness and the thickness of the ungrafted layer of AA- and NIPAAm-grafted PE films and the percentage of grafting. Total thickness: (○) AA-grafted film; (△) NIPAAm-grafted film. Thickness of the ungrafted layer: (●) AA-grafted film; (▲) NIPAAm-grafted film.

wiped by filter paper, and then the weight ( $W_1$ , g) of the treated film was measured. Water absorbency was defined as follows:

$$\text{Water absorbency (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

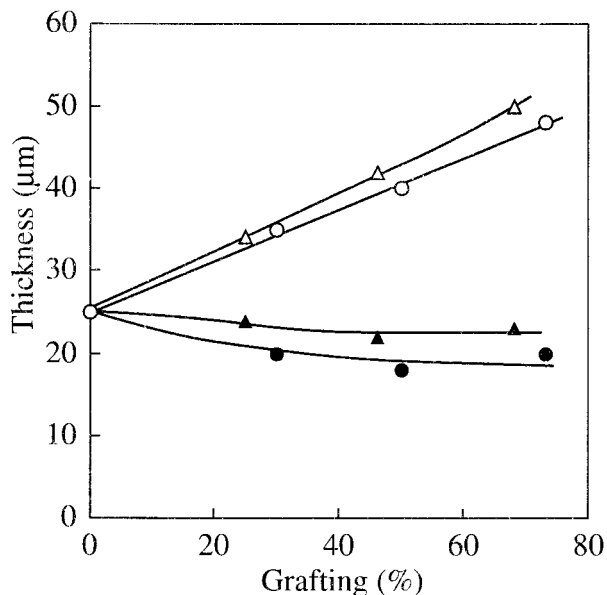
## RESULTS AND DISCUSSION

### Grafting Behavior

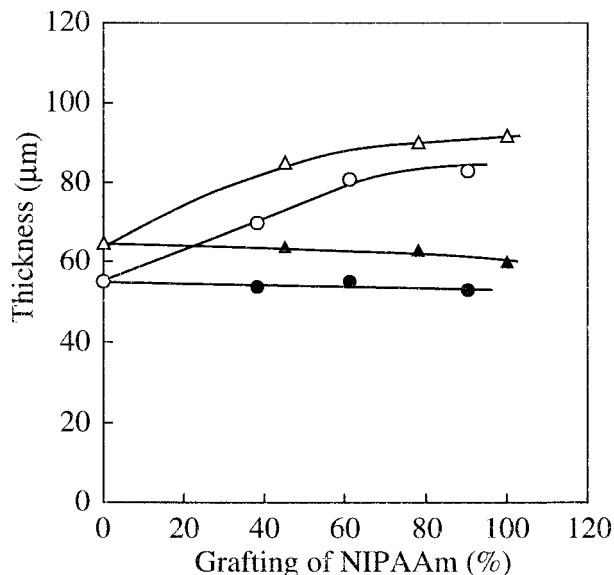
We examined two photografting methods to introduce grafted chains consisting of binary monomer components, AA and NIPAAm, into PE film substrate. With the one-step method, using the monomer mixture of AA and NIPAAm, the two monomer components are copolymerized to introduce into the PE substrate. The photografting results are shown in Figure 1, which also includes NIPAAm composition in the AA–NIPAAm-grafted chains. The percentage of grafting increased with an increase in the NIPAAm composition in binary monomers, but it decreased slightly beyond the NIPAAm component of about 50 mol %. The NIPAAm composition in the grafted chains increased with the NIPAAm composition in binary monomers. Monomer reactivity ratios of NIPAAm

( $r_1$ ) and AA ( $r_2$ ) calculated from data of Figure 1 using the Fineman–Ross method were 0.38 and 0.95, respectively. These values are similar to those of AA ( $r_1$ ) and acrylamide ( $r_2$ ),<sup>12</sup> which are 0.36–1.73 and 0.05–1.38, respectively, depending on copolymerization conditions. It is supposed that the monomer combination of AA and NIPAAm is under the influence of a general radical copolymerizability.

In the case of the two-step method, on the other hand, the first-step sample prepared with photografting of AA onto PE film is subjected to second-step photografting of NIPAAm, which is shown in Figure 2. The horizontal axis indicates the percentage of grafting of AA in the first-step sample. The percentage of grafting of NIPAAm in the second-step photografting increased with increasing the percentage of grafting of AA on the first-step sample. In a previous article,<sup>13</sup> photoirradiated AA-grafted PE film showed an electron spin resonance (ESR) spectrum originated from radicals of AA-grafted chains. These results suggest that the second-step photografting of NIPAAm is mainly initiated by radicals on AA-grafted chains, not PE radicals. It is inferred, accordingly, that the monomer sequence distribution of the grafted chains is of block type with



**Figure 5** Relationship between the total thickness and the thickness of the ungrafted layer of the one-step sample and the percentage of grafting. Total thickness: (○) AA–NIPAAm = 60/40; (△) AA–NIPAAm = 40/60. Thickness of the ungrafted layer: (●) AA–NIPAAm = 60/40; (▲) AA–NIPAAm = 40/60.



**Figure 6** Relationship between the total thickness and the thickness of the ungrafted layer of the two-step sample and the percentage of grafting. Total thickness: (○) grafting of AA = 40%; (△) grafting of AA = 85%. Thickness of the ungrafted layer: (●) grafting of AA = 40%; (▲) grafting of AA = 85%.

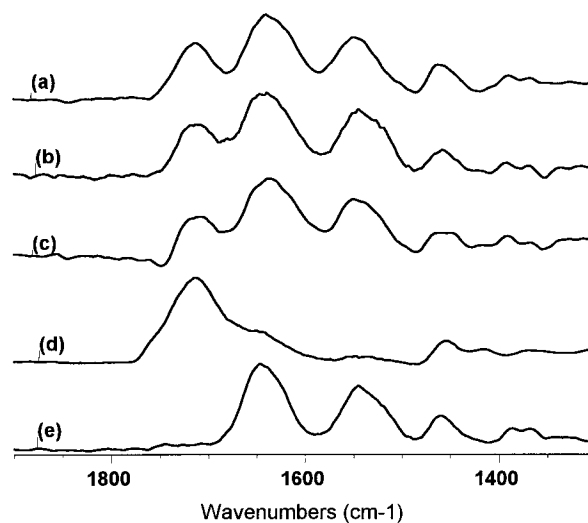
respect to each monomer component. Thus, it was found that grafted PE films with grafted chains consisting of two types of monomer component, such as AA and NIPAAm, can be prepared by using the one- and two-step methods. The structure of grafted chains is schematically shown in Scheme 1.

#### Location of Grafted Chains

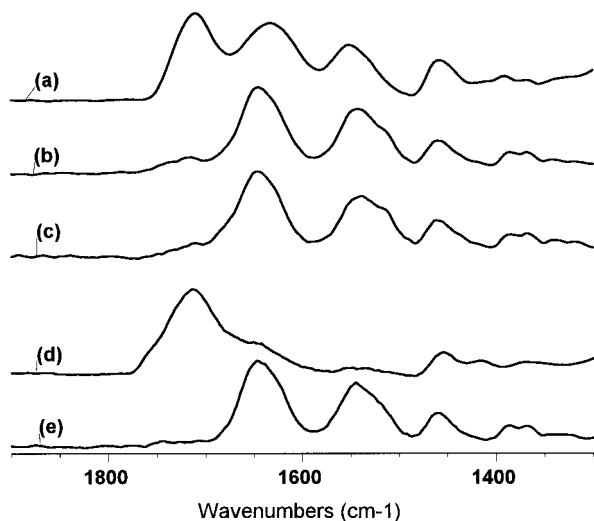
Figure 3 shows the distribution profiles of potassium and palladium atoms in the cross section of AA- and NIPAAm-grafted films, respectively, which were measured by electron probe microanalysis (EPMA) to examine the location of grafted chains. The grafted chains of the AA-grafted film seem to distribute in the inside of the film, while those of the NIPAAm-grafted film locate on the film surface. The total thickness of the film and the thickness of ungrafted layer ( $T$  and  $UG$  in Figure 3, respectively) were measured from the distribution profile, and the results are shown in Figure 4. The NIPAAm-grafted film exhibited a larger increase in the total thickness with an increase in the percentage of grafting than that of the AA-grafted film. The thickness of ungrafted layer decreased with an increase in the percentage of grafting, and the magnitude was very small

in the NIPAAm-grafted film compared to the AA-grafted film. It was found that NIPAAm-grafted chains localize at the film surface, while AA-grafted chains are distributed inside the film. In the present grafting system, photoexcited xanthone may abstract hydrogen atoms from the PE substrate to yield PE radicals on the film surface capable of initiating the grafting reaction. Thus, the grafted layer starts from the film surface. As the grafting reaction proceeds, it is plausible that monomers are supplied to PE substrate through the grafted layer, resulting in the penetration of the grafted layer into the film texture as well as the accumulation of grafted layer on the film surface. This seems to be the case of AA monomer. With the NIPAAm monomer, however, NIPAAm-grafted chains are supposed to shrink in water at 60°C to disturb the diffusion of NIPAAm monomer into the film texture through the grafted layer. This may result in the NIPAAm-grafted film with a localized distribution of the grafted chains due to an emphasized accumulation of grafted layer on the film surface.

Figure 5 shows the results of the one-step sample, which was treated with an aqueous solution of potassium hydroxide. The total thickness largely increased with increasing the percentage of grafting, while a decrease in the thickness of ungrafted layer with the percentage of grafting was small. This tendency was remarkable for the sample with a higher NIPAAm content. The grafted



**Figure 7** ATR-IR spectra of grafted PE films prepared by the one-step method. AA-NIPAAm = 60/40. Grafting (%): (a) 30.1, (b) 50.7, (c) 72.4, (d) AA-grafted PE film (grafting = 121.3%), and (e) NIPAAm-grafted PE film (grafting = 94.7%).



**Figure 8** ATR-IR spectra of grafted PE films prepared by the two-step method. Grafting of AA = 38.4%. Grafting of NIPAAm (%): (a) 34.1, (b) 58.8, (c) 79.2, (d) AA-grafted PE film (grafting = 121.3%), and (e) NIPAAm-grafted PE film (grafting = 94.7%).

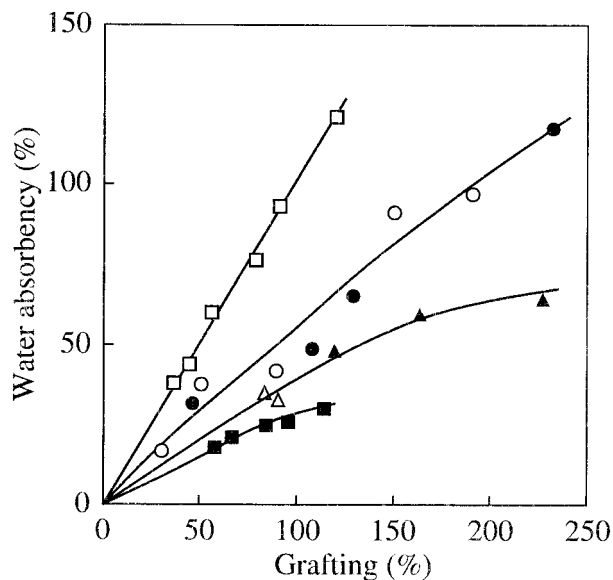
chains of the one-step sample are likely to locate on the film surface. Location of NIPAAm-grafted chains introduced into AA-grafted PE film by the second-step photografting was examined, and the results are shown in Figure 6. The horizontal axis indicates the percentage of grafting of NIPAAm in the second-step photografting. Changes in the thickness of the two-step sample with an increase in the percentage of grafting of NIPAAm was larger for the total thickness than the thickness of ungrafted layer. The NIPAAm-grafted chains are conceivably able to be located on the surface of AA-grafted film.

In order to confirm the above results obtained by EPMA, grafted chains of the surface layer of the one- and two-step samples were examined by ATR-IR, and the spectra are presented in Figure 7. The one-step sample indicated bands at  $1710\text{ cm}^{-1}$  due to carbonyl groups of AA-grafted chains and bands at  $1540$  and  $1640\text{ cm}^{-1}$  due to amide groups of NIPAAm-grafted chains. The grafted chains of the surface layer were found to consist of both AA and NIPAAm components. On the other hand, the two-step sample with a low percentage of grafting of NIPAAm [Fig. 8(a)] also exhibited the same bands originated in both AA- and NIPAAm-grafted chains described above. However, the band at  $1710\text{ cm}^{-1}$  due to AA-grafted chains disappeared in the sample with a high percentage of grafting of NIPAAm [Fig. 8(c)]. This suggests that the surface layer is covered with NIPAAm-

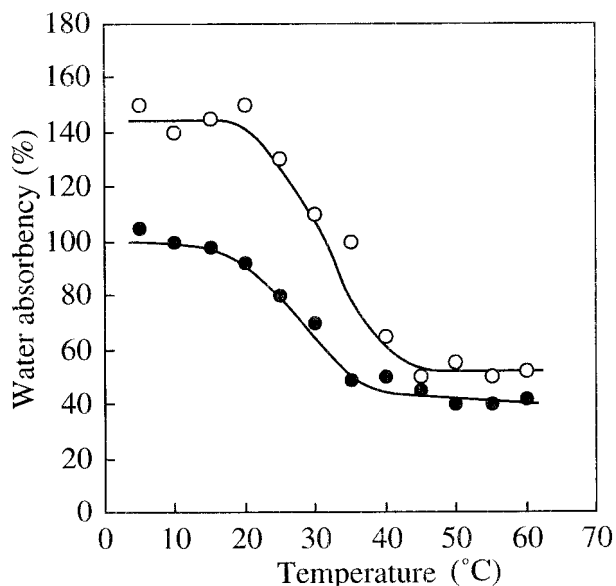
grafted chains. Based on EPMA and ATR-IR studies on the two-step sample, it is concluded that NIPAAm-grafted chains introduced by the second-step photografting locate mainly on the surface of the AA-grafted film.

### Water Absorbency

Figure 9 presents the water absorbency of the grafted PE films, which was measured at  $25^\circ\text{C}$ . The water absorbencies of AA- and NIPAAm-grafted films increased with an increase in the percentage of grafting, and the magnitude was much larger for the former film than for the latter one. This might be ascribed to higher hydrophilicity of the AA-grafted chains compared to the NIPAAm-grafted chains. On the other hand, the water absorbencies of the one- and two-step samples lay between those of the AA- and NIPAAm-grafted films, and the one-step sample showed a higher value than the two-step sample. With the one-step sample, where grafted chains consisting of AA and NIPAAm components localize at the film surface, the AA component is conceivable to contribute to the water absorbency directly. In the case of the two-step sample, the surface of the grafted film is covered with NIPAAm-grafted



**Figure 9** Water absorbency of grafted PE films measured at  $25^\circ\text{C}$ : ( $\square$ ) AA-grafted PE film; ( $\blacksquare$ ) NIPAAm-grafted PE film; ( $\circ$ ) one-step sample, in which AA-NIPAAm = 55-60/40-45; ( $\bullet$ ) one-step sample, in which AA-NIPAAm = 40-45/55-60; ( $\triangle$ ) two-step sample, in which AA-NIPAAm = 55-60/40-45; ( $\blacktriangle$ ) two-step sample, in which AA-NIPAAm = 30-40/60-70.



**Figure 10** Relationship between water absorbency and temperature in (○) one-step and (●) two-step samples. Total grafting = 250%; AA-NIPAAm = 60/40.

chains, as shown in the ATR-IR spectrum [Fig. 8(c)]. This may cause an emphasized contribution of the NIPAAm component to the water absorbency, resulting in a lower value compared to the one-step sample.

#### Temperature-Responsive Character

Figure 10 shows water absorbencies of the one- and two-step samples at various temperatures. The water absorbency steeply decreased at about 20 to 40°C with increasing temperature, which was commonly observed for both samples. Thus, the grafted samples exhibited a temperature-responsive character, in which they swelled and shrank in water below and above the temperature, respectively. The extent of the character was compared between both samples by using thermosensitivity,<sup>14</sup> which was defined as the ratio of water absorbencies of the grafted sample at 5 and 60°C; the results are summarized in Table I. The thermosensitivity was higher for the one-step sample than the two-step sample, though the value depended on both the percentage of grafting and the NIPAAm content in the grafted chains.

It was observed that grafted PE films with grafted chains consisting of two types of monomer component, AA and NIPAAm, exhibit a temperature-responsive character, the extent of which is different, depending on the method used for intro-

ducing the grafted chains. It is supposed that the monomer sequence distribution of grafted chains and its location in the grafted film are main factors affecting the temperature-responsive character. It was found in a previous article<sup>9</sup> on NIPAAm-grafted polymer films that the extent of the temperature-responsive character is influenced largely by location of NIPAAm-grafted chains. That is, the grafted film with the grafted chains located inward in the film exhibited a larger extent of the temperature-responsive character compared to that with the grafted chains located mainly on the film surface. Based on the examinations of location of grafted chains in the one- and two-step samples, the poly(NIPAAm) component of the grafted chains, which is responsible for the temperature-responsive character, was commonly observed to locate on the film surface in the samples. It is inferred, therefore, that the different extent of the character between both samples is ascribed to the monomer sequence distribution of grafted chains rather than the location of grafted chains. As shown in Scheme 1, the monomer sequence distribution of the grafted chains in the two-step sample seems to be of a block type with respect to each monomer component. It is conceivable that only poly(NIPAAm) component of the grafted chains shrinks when immersed in water at a temperature higher than the LCST of poly(NIPAAm). This may cause a small contribution of the poly(NIPAAm) component to the shrinking of the whole grafted chains, including the poly(AA) component. With the one-step sample, on the other hand, the poly(NIPAAm) component is supposed to participate directly in the shrinking of grafted chains because the grafted chains are composed of copolymer of AA and NIPAAm monomers.

**Table I** Thermosensitivity<sup>a</sup> of AA-NIPAAm-Grafted PE Films

Grafting (%)	One-step Sample		Two-step Sample	
	NIPAAm Content (mol %)		NIPAAm Content (mol %)	
	40	60	40	60
250	1.7	2.9	1.5	2.5
500	3.7	5.3	1.7	2.8

<sup>a</sup> Thermosensitivity is defined as the ratio of water absorbencies of the grafted sample at 5 and 60°C.

Based on the above investigations, it is concluded that the introduction of grafted chains, which consist of AA and NIPAAm binary components, into PE film is possible by two photografting methods; that is, one is the photografting of AA and NIPAAm binary monomers onto the PE film, and the other is the photografting of NIPAAm onto the AA-grafted PE film. The resulting grafted PE films are characterized by the monomer sequence distribution of the grafted chains, and its location in the film substrate, depending on the methods, resulting in a different extent of properties, such as water absorbency and the temperature-responsive character between the grafted films prepared by the two methods.

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