

# Amidation of Acrylic Acid Grafted Polyethylene Film with Isopropylamine and Temperature-Responsive Character of the Resulting Amidated Film

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**ABSTRACT:** An acrylic acid (AA) grafted polyethylene (PE) film with a homogeneous distribution of grafted chains was prepared by the photografting of AA onto a low-density PE film with a thickness of 30  $\mu\text{m}$ . The AA-grafted PE film was subjected to amidation with isopropylamine (IPA) at 25°C in water as a solvent. Up to 80 mol % of the carboxyl groups of the AA-grafted chains could be successfully converted to *N*-isopropylacrylamide (NIPAAm) residues through the control of the amidation conditions, such as the reaction time, amount of the condensation reagent, and concentration of IPA. The result-

ing amidated PE film exhibited a temperature-responsive character: the film swelled and shrank in water below and above a temperature range of about 40–60°C, respectively. The extent of the character of the amidated PE film was greater than that of NIPAAm- and NIPAAm/AA-grafted PE films prepared by the photografting of NIPAAm monomer and NIPAAm/AA binary monomers, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 685–691, 2009

**Key words:** films; graft copolymers; polyethylene (PE)

## INTRODUCTION

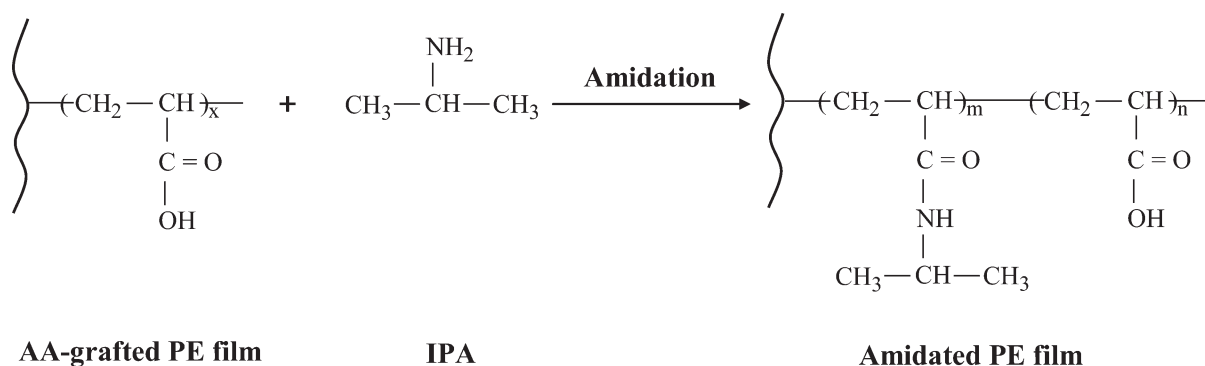
It has been shown in our previous articles<sup>1–16</sup> that photografting is a useful means for the introduction of various functions into polyethylene (PE) film substrates, such as wettability,<sup>1,2</sup> moisture permeability,<sup>3</sup> catalytic activity,<sup>4,5</sup> polymeric peroxides,<sup>6</sup> and stimuli-responsive characteristics.<sup>7–16</sup> The introduced functions were found in these studies to be greatly influenced by the location of the grafted chains in the film substrate. For example, methacrylic acid grafted PE films<sup>8–11</sup> and acrylic acid (AA) grafted PE films<sup>12,13</sup> with a homogeneous distribution of the grafted chains exhibited greater pH-responsive character: the grafted films shrank in acidic media but swelled in alkaline media in comparison with those with the grafted chains mainly located on the film surface.

On the other hand, a temperature-responsive polymer, poly(*N*-isopropylacrylamide) (PNIPAAm), was introduced into a PE film substrate as grafted chains, which were shown to be mainly present near the PE film surface.<sup>14,15</sup> The resultant *N*-isopropylacryla-

midate (NIPAAm)-grafted PE film swelled below and shrank above the lower critical solution temperature (LCST; ca. 32°C) of PNIPAAm in water as the medium, showing a temperature-responsive character. However, the extent of the character was relatively low as a result of the localization of the NIPAAm-grafted chains on the PE film surface. Accordingly, to improve the temperature-responsive character, it is necessary to prepare a NIPAAm-grafted PE film with a homogeneous distribution of the grafted chains. For this purpose, we report here the preparation of such a NIPAAm-grafted PE film by means of amidation of an AA-grafted PE film with isopropylamine (IPA; Scheme 1) because an AA-grafted PE film with a homogeneous distribution of the grafted chains can be prepared by photografting.<sup>12,13</sup> Iizawa and coworkers<sup>17,18</sup> revealed that poly(acrylic acid) (PAA) hydrogels can easily react with IPA and convert to PNIPAAm hydrogels.

In this article, the effects of reaction conditions such as the reaction time, amount of the condensation reagent, concentration of IPA, and percentage of grafting of an AA-grafted PE film on the amidation of an AA-grafted PE film with IPA are examined. Moreover, the temperature-responsive character of the resulting amidated PE films is evaluated and compared with that of NIPAAm- and NIPAAm/AA-grafted PE films prepared by photografting.

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**Scheme 1** Amidation of an AA-grafted PE film with IPA.

## EXPERIMENTAL

### Materials

The PE film was a linear low-density PE film with a thickness of 30  $\mu\text{m}$  (density = 0.927  $\text{g}/\text{cm}^3$ ; Idemitsu Petrochemical Co., Ltd., Tokyo, Japan). Xanthone (XT) as a photoinitiator, 1-ethyl-3-(3-dimethylamino-propyl)-carbodiimide (WSC) as a condensation reagent, and IPA were reagent-grade and were used without further purification. AA was purified by distillation under reduced pressure (4 Torr at 35°C). NIPAAm was purified by recrystallization from a benzene/*n*-hexane mixture. The water used in this study was deionized, and the conductivity was lower than 0.2  $\mu\text{S}/\text{cm}$ .

### Photografting

The PE film (3  $\times$  10 cm) was dipped into an acetone solution containing 0.3 wt % 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 5 h under reduced pressure to prepare the XT-coated film. Photografting of AA was carried out at 60°C for different times (5–60 min) under a nitrogen atmosphere in a Pyrex glass tube containing the XT-coated film and 30 mL of water, in which AA of a given concentration was dissolved. Irradiation with a high-pressure mercury lamp (400 W) was carried out with a Riko rotary photochemical reactor (RH400-10W, Riko Kagaku Sangyo Co., Ltd., Japan), around which the Pyrex glass tubes were rotated. The polymerized film was extracted with deionized water at 80°C for 24 h to remove the homopolymer. The percentage of grafting was calculated with the following equation:

$$\text{Grafting}(\%) = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

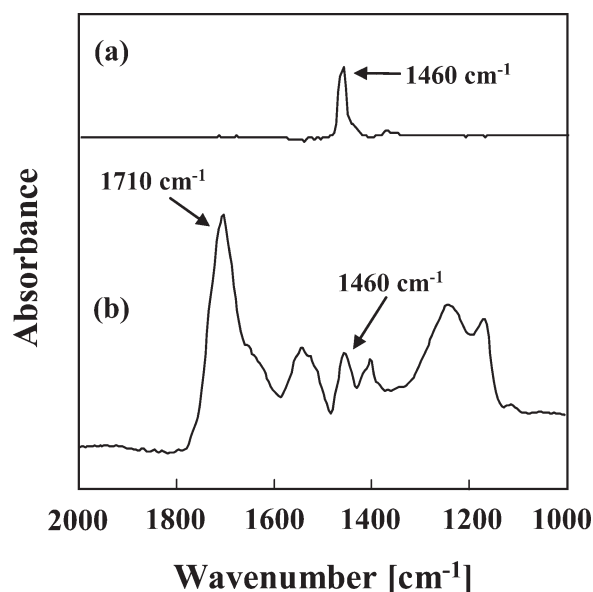
where  $W_g$  is the weight of the grafted PE film and  $W_0$  is the weight of the original PE film.

For the photografting of NIPAAm or NIPAAm and AA binary monomers onto the PE film substrate, the same system used for the photografting of AA was employed. The total monomer concentration was 1.0 mol/L, and the molar ratio of NIPAAm to AA was 8 : 2 for the binary monomer system. After the photografting, the polymerized film was extracted with deionized water at room temperature for 48 h and then with methanol at 60°C for 24 h to remove the homopolymers. The NIPAAm content of the NIPAAm/AA-grafted PE films (the molar percentage of the NIPAAm component in the NIPAAm/AA-grafted chains) was determined by nitrogen analysis. The synthesis and characteristics of the NIPAAm- and NIPAAm/AA-grafted PE films by photografting was discussed in more detail in our previous articles.<sup>14,15</sup>

### Amidation

A total of 10 mL of an IPA aqueous solution with various IPA concentrations (vol %) was weighed into a 50-mL Erlenmeyer flask. Then, the given amounts of the AA-grafted PE film and WSC were added, and the reaction was carried out at 25°C for the given times. After the reaction, the sample was washed with deionized water and then dried at room temperature under reduced pressure. The amount of the NIPAAm component introduced into the AA-grafted chains was determined by nitrogen analysis. The NIPAAm content was defined as follows:

$$\text{NIPAAm content (mol}\%) = \frac{\text{Amount of NIPAAm component introduced (mol)}}{\text{Amount of AA component in initial AA-grafted film (mol)}} \times 100 \quad (2)$$



**Figure 1** ATR-IR spectra of (a) a PE film and (b) an AA-grafted PE film (grafting = 193%).

#### Attenuated total reflectance/infrared (ATR-IR) analysis

ATR-IR spectra of the surface of the AA-grafted PE film were recorded with an automatic infrared microscope (AIM-800, FTIR-8700) from Shimadzu Co., Ltd. (Kyoto, Japan). The amount of AA-grafted chains on the film surface layer was expressed in terms of the absorbance ratio of the carbonyl band at  $1710\text{ cm}^{-1}$  to the methylene band at  $1460\text{ cm}^{-1}$ .

#### Scanning electron microscopy (SEM)

Carboxyl groups in AA-grafted chains were converted to carboxylate groups by the immersion of the grafted film in an aqueous solution of 1.0 wt % potassium hydroxide at  $25^\circ\text{C}$  for 24 h, and then it was washed with water. 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 cross section of the grafted film was measured with a scanning electron microscope (JSM-5600LV, JED-2200) from JEOL Co., Ltd. (Tokyo, Japan).

#### Measurement of the temperature-responsive character

The grafted film [surface area  $S_0$  ( $\text{mm}^2$ )] was immersed in water at given temperatures ( $0$ – $70^\circ\text{C}$ ) for 24 h. After the treatment, the excess water on the film surface was wiped off with filter paper, and then the surface area of the treated film [ $S_1$  ( $\text{mm}^2$ )] was measured with a ruler equipped with a magni-

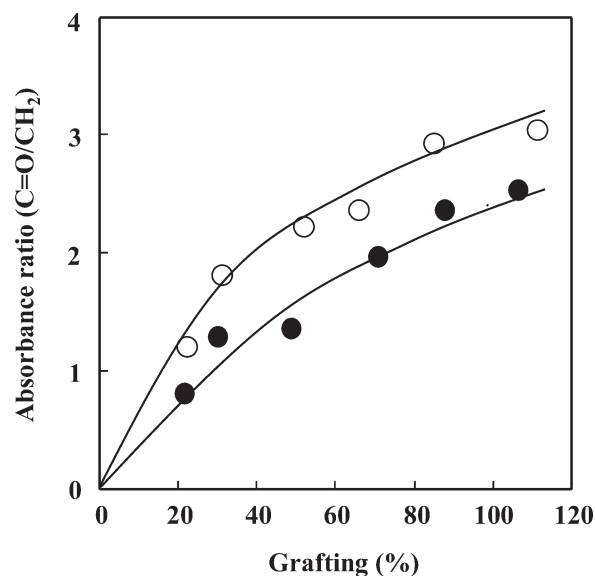
fier. The dimensional change of the grafted film was defined as follows:

$$\text{Dimensional change(\%)} = \frac{S_1 - S_0}{S_0} \times 100 \quad (3)$$

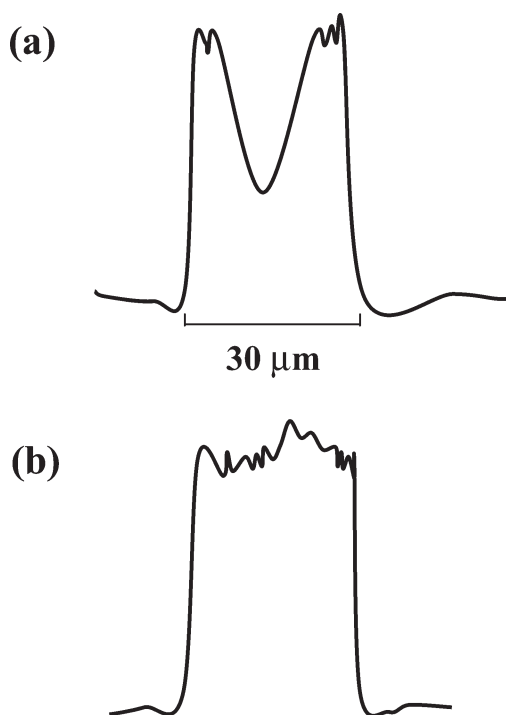
## RESULTS AND DISCUSSION

### Preparation of AA-grafted PE films

AA-grafted PE films with various percentages of grafting were prepared by a photografting technique. The AA monomer concentrations studied in this work were 0.48 and 0.96 mol/L. The obtained AA-grafted films were subjected to ATR-IR and SEM measurements. Figure 1 shows typical ATR-IR spectra of the PE film and AA-grafted PE film. In addition to the characteristic peak of methylene groups at  $1460\text{ cm}^{-1}$  ( $\text{CH}_2$  bending vibration), a sharp peak at  $1710\text{ cm}^{-1}$  due to the carbonyl groups ( $\text{C}=\text{O}$  stretching vibration) of AA-grafted chains was observed in the spectrum of AA-grafted PE films, as shown in Figure 1(b). This indicated that PAA was successfully introduced into the PE film. To investigate the location of the AA-grafted chains in the grafted film, the absorbance ratio of the carbonyl peak at  $1710\text{ cm}^{-1}$  to the methylene peak at  $1460\text{ cm}^{-1}$  of the AA-grafted films has been plotted in Figure 2 as a function of the percentage of grafting. The absorbance ratio increased with the percentage of grafting increasing for grafted films prepared with a 0.48 mol/L monomer concentration (sample I) or a 0.96 mol/L monomer concentration (sample II). However, for the grafted films with almost the



**Figure 2** Changes in the absorbance ratio of the carbonyl peak at  $1710\text{ cm}^{-1}$  to the methylene peak at  $1460\text{ cm}^{-1}$  with the percentage of grafting in AA-grafted PE films. The AA concentration was (○) 0.48 or (●) 0.96 mol/L.



**Figure 3** Distribution profile of potassium atoms in cross sections of AA-grafted PE films measured with SEM: (a) [AA] = 0.48 mol/L and grafting = 84.1% and (b) [AA] = 0.96 mol/L and grafting = 80.7%.

same percentage of grafting, the absorbance ratios of sample I were always higher than those of sample II. This suggests different distributions of AA-grafted chains in the grafted films for the two samples.

To confirm the results by ATR-IR measurements, the distribution of AA-grafted chains in the cross section of the grafted film was examined with SEM measurements. Figure 3 shows the distribution profiles of potassium atoms in the cross sections of AA-grafted films. The observation was made with the grafted films treated with potassium hydroxide. Accordingly, the curve in the figure represents the distribution profile of potassium atoms, that is, AA-grafted chains, in the cross section of the AA-grafted film. The vertical and horizontal directions in the figure correspond to the relative concentration of potassium atoms and the cross section of the film, respectively. It is clear from Figure 3 that more AA-grafted chains in sample II penetrated the film interior in comparison with sample I. It was thus concluded that the AA-grafted film with a homogeneous distribution of grafted chains could be prepared by photografting with the monomer concentration of 0.96 mol/L. Sample II was used for the following amidation with IPA.

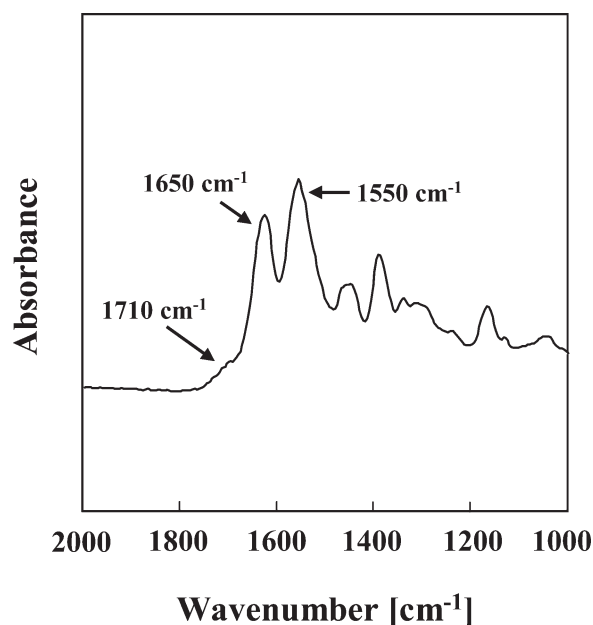
#### Amidation of AA-grafted PE films with IPA

The amidation of AA-grafted films with IPA was carried out at 25°C in water under various condi-

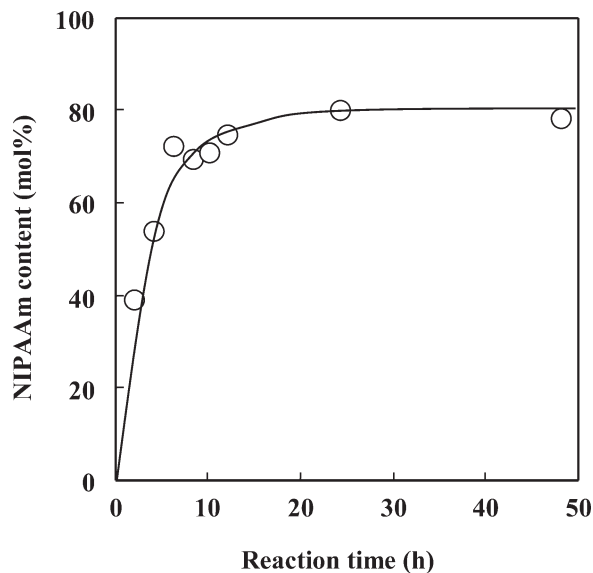
tions. The resulting PE films were analyzed with ATR-IR measurements. A representative ATR-IR spectrum is given in Figure 4. Two sharp peaks were obviously observed at 1650 and 1550  $\text{cm}^{-1}$ , which could be assigned to the amide I band (mainly due to the C=O stretching vibration) and amide II band (a combination of the C-N-H bending vibration and C-N stretching vibration), respectively.<sup>19,20</sup> At the same time, the peak due to the carbonyl groups of AA-grafted chains at 1710  $\text{cm}^{-1}$  became extremely weaker, and this indicated that the most of the carboxyl groups in AA-grafted chains were successfully converted to *N*-isopropylamide groups by amidation with IPA.

The amidation of AA-grafted films with IPA was investigated in detail through the control of the reaction time, amount of the condensation reagent, and concentration of IPA. Figure 5 shows the effect of the reaction time on the amidation. The NIPAAm content increased with the increase in the reaction time and appeared to level off beyond the reaction time of about 24 h. The NIPAAm content at 24 h reached about 80 mol %.

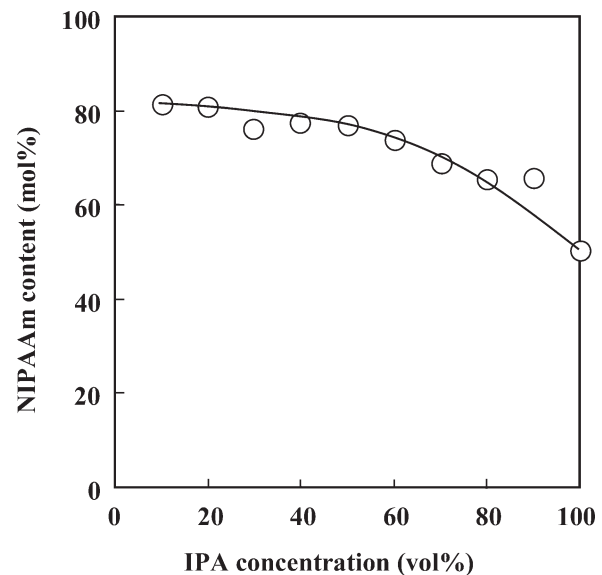
Figure 6 shows the effect of the amount of WSC on the amidation. The horizontal axis represents the amount of WSC, which is expressed in terms of the molar ratio of WSC to the AA component in AA-grafted chains. The amidation proceeded even in the system without any WSC, and about 38 mol % of the carboxyl groups of the AA-grafted chains participated in the amidation. The addition of WSC facilitated the amidation, and the NIPAAm content increased to about 80 mol % when the amount of



**Figure 4** Typical ATR-IR spectrum of an amidated PE film (grafting = 266%, NIPAAm content = 63.6 mol %).



**Figure 5** Effect of the reaction time on the amidation of an AA-grafted PE film with IPA (amidation: temperature = 25°C, IPA concentration = 10 vol %, WSC/AA-grafted chain ratio = 20/1 mol/mol, grafting = 230–240%).

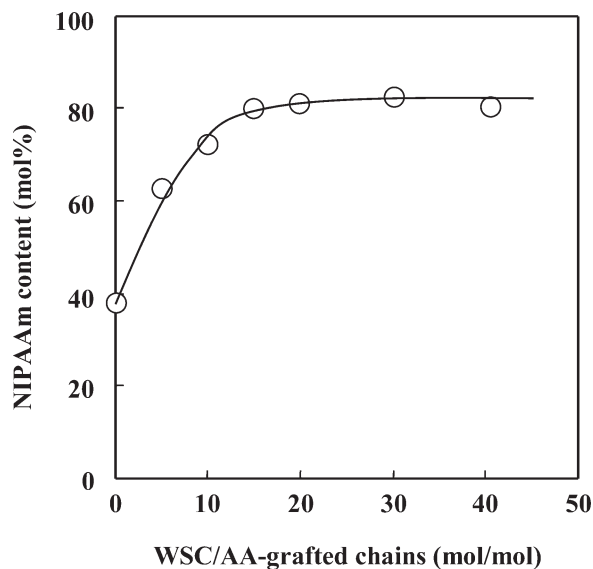


**Figure 7** Effect of the IPA concentration on the amidation of an AA-grafted PE film with IPA (amidation: temperature = 25°C, time = 24 h, WSC/AA-grafted chain ratio = 20/1 mol/mol, grafting = 240.7%).

WSC was about 20 times the molar amount of AA-grafted chains. Figure 7 shows the effect of the IPA concentration on the amidation. In the investigated concentration range, the molar amount of IPA added to the reaction system was in much excess of the amount of the AA component in the AA-grafted chains. As shown in Figure 7, the NIPAAm content tended to decrease when the concentration of IPA exceeded 20 vol %. In the case of 100 vol % IPA (without water), the attained NIPAAm content was

only about 50 mol %. It seems that the presence of water, which can swell hydrophilic AA-grafted chains more efficiently than IPA, contributed to the amidation of AA-grafted PE films in the aqueous solution of IPA.

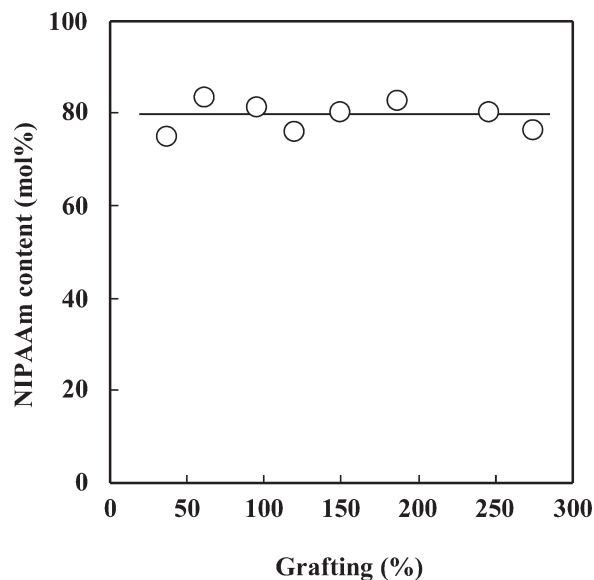
On the basis of the aforementioned investigation, the optimum conditions for the amidation of AA-grafted PE films with IPA at 25°C can be summarized: a reaction time of 24 h, a WSC/AA-grafted chain ratio of 20/1 (mol/mol), and an IPA aqueous solution concentration of 10 vol %. However, the maximum NIPAAm content reached in this study was about 80 mol %, regardless of the percentages of grafting of the AA-grafted films, as shown in Figure 8. This phenomenon was probably caused by the steric hindrance of the bulky isopropyl groups, which were introduced into the grafted films by the amidation of AA-grafted chains.



**Figure 6** Effect of the amount of WSC on the amidation of an AA-grafted PE film with IPA (amidation: temperature = 25°C, time = 24 h, IPA concentration = 10 vol %, grafting = 266.4%).

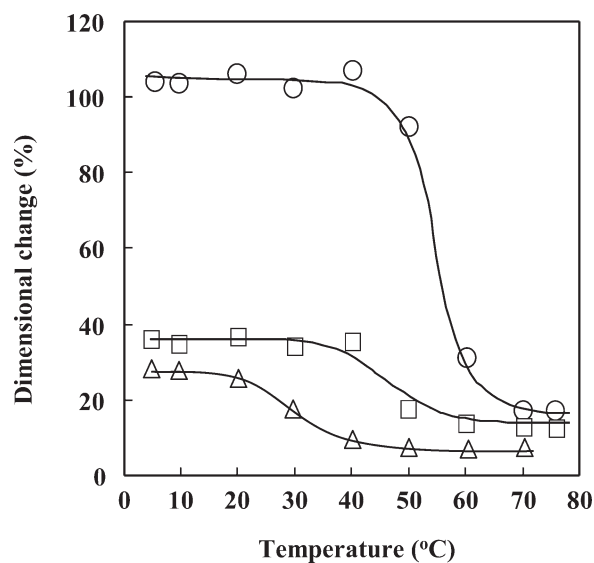
### Temperature-responsive character

Figure 9 shows the dimensional changes of amidated, NIPAAm-grafted, and NIPAAm/AA-grafted films when immersed in water at various temperatures for 24 h. The dimensional change of the amidated film abruptly decreased at about 40–60°C with increasing temperature, and it exhibited a temperature-responsive character. The amidated film swelled and shrank in water below and above the temperature range, respectively. The temperature at which the dimensional change steeply decreased was considerably higher than the LCST of PNIPAAm (ca. 32°C). It has been reported that a copolymer of



**Figure 8** Effect of the percentage of grafting on the amidation of an AA-grafted PE film with IPA (amidation: temperature = 25°C, time = 24 h, WSC/AA-grafted chain ratio = 20/1 mol/mol, IPA concentration = 10 vol %).

NIPAAm and AA undergoes a discontinuous phase transition in response to the change in temperature.<sup>21,22</sup> Moreover, the LCST of PNIPAAm is known to shift to a higher temperature with the introduction of a hydrophilic comonomer component<sup>23</sup> into PNIPAAm main chains. There were AA components in grafted chains of the amidated film that did not participate in the amidation. The AA components were supposed to act as hydrophilic components,

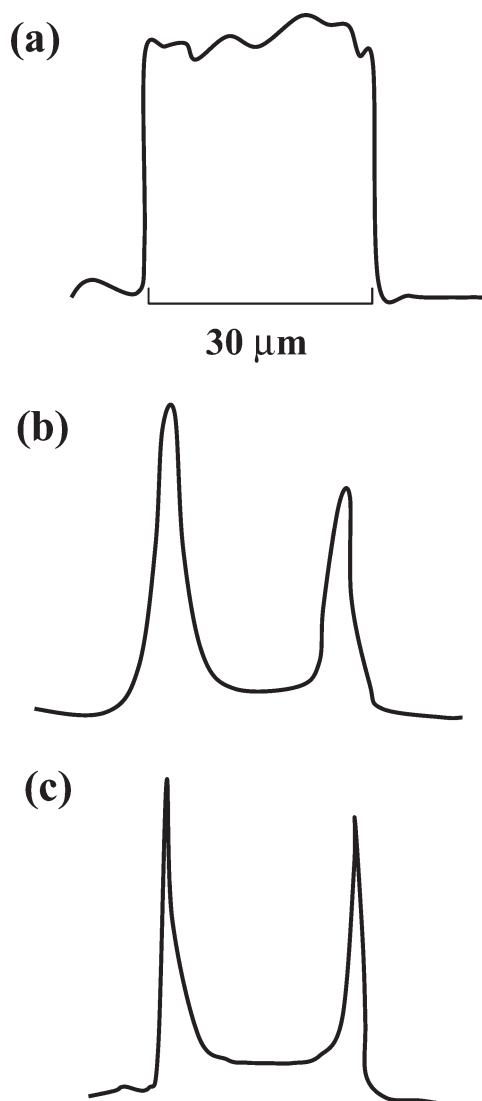


**Figure 9** Temperature-responsive character of grafted PE films: (○) amidated PE film (grafting = 407.2%, NIPAAm content = 61.3 mol %), (□) NIPAAm/AA-grafted PE film (grafting = 452.3%, NIPAAm content = 53.1 mol %), and (△) NIPAAm-grafted PE film (grafting = 422.6%).

**TABLE I**  
Thermosensitivity of the Grafted Films

| Grafted PE film        | Grafting (%) | NIPAAm content (mol %) | Thermosensitivity |
|------------------------|--------------|------------------------|-------------------|
| Amidated film          | 266.4        | 63.6                   | 3.16              |
|                        | 407.2        | 61.3                   | 5.80              |
| NIPAAm/AA-grafted film | 156.0        | 54.9                   | 1.04              |
|                        | 452.3        | 53.1                   | 2.58              |
| NIPAAm-grafted film    | 136.7        | —                      | 1.74              |
|                        | 422.6        | —                      | 4.04              |

resulting in a higher temperature in comparison with the LCST of PNIPAAm, at which the dimensional change decreased steeply.



**Figure 10** Distribution profile of palladium atoms in cross sections of grafted PE films measured by SEM: (a) amidated PE film (grafting = 266.4%, NIPAAm content = 63.6 mol %), (b) NIPAAm/AA-grafted PE film (grafting = 216.1%, NIPAAm content = 41.4 mol %), and (c) NIPAAm-grafted PE film (grafting = 215.3%).

As shown in Figure 9, the dimensional change of the NIPAAm/AA-grafted PE films, which were prepared by the photografting of NIPAAm/AA binary monomers, also decreased at about 40–60°C with increasing temperature. On the other hand, the dimensional change of the NIPAAm-grafted film decreased at about 20–40°C with an increase in the temperature. The extent of the temperature-responsive character was compared among the films with the thermosensitivity,<sup>24</sup> which was defined as the ratio of the dimensional change at 5°C to that at 70°C. The results are summarized in Table I. The thermosensitivity was higher for the amidated film than for the NIPAAm- and NIPAAm/AA-grafted films, although the value depended on the percentage of grafting. The location of grafted chains in the grafted films is believed to be one of the main factors affecting the temperature-responsive character. Figure 10 shows the distribution profiles of palladium atoms in the cross sections of amidated, NIPAAm-grafted, and NIPAAm/AA-grafted films. The grafted chains of the amidated film were distributed homogeneously in the film, whereas those of the NIPAAm- and NIPAAm/AA-grafted films were located predominantly on the film surface. It was thus confirmed that the temperature-responsive character of the grafted films was closely related to the location of the grafted chains in the film substrate.

### CONCLUSIONS

In conclusion, NIPAAm-grafted PE films with a homogeneous distribution of grafted chains could be prepared by the amidation of an AA-grafted PE film, in the film substrate of which the AA-grafted chains were distributed homogeneously. About 80 mol % of the carboxyl groups could be converted to NIPAAm residues; this depended on reaction conditions such as the reaction time, amount of WSC, and concentration of IPA. The resulting amidated film exhibited a temperature-responsive character, the extent of which was greater than that of NIPAAm-

and NIPAAm/AA-grafted PE films prepared by the photografting of NIPAAm and NIPAAm/AA binary monomers, respectively.

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