

# Examination of the Role of Oxygen in the Photografting of Methacrylic Acid on a Polyethylene Film with a Mixed Solvent Consisting of Water and Organic Solvents

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 13 May 2002; accepted 21 October 2002

**ABSTRACT:** The photografting of methacrylic acid (MAA) on a linear low-density polyethylene film (thickness = 30  $\mu\text{m}$ ) under air and nitrogen atmospheres was investigated at 60°C in mixed solvents consisting of water and an organic solvent, with xanthone as a photoinitiator. The organic solvents used were acetone, methanol, tetrahydrofuran, and dioxane. A maximum percentage of grafting occurred at a certain concentration of the organic solvent in the mixed solvent. This was observed for the systems under both air and nitrogen. The grafting reaction under air exhibited an induction period, but the rate of grafting after the period was greater than that under nitrogen. The formation of poly(ethylene peroxide)s by photoirradiation seemed to

be a factor for the accelerated photografting under air. On the basis of attenuated total reflection infrared spectroscopy and scanning electron microscopy of the grafted film, the MAA-grafted chains of the sample prepared under air tended to penetrate more deeply inside the film than those of the sample prepared under nitrogen. The resulting grafted films exhibited a pH-responsive character: the grafted films shrank in an acidic medium but swelled in alkaline medium. This was evaluated from measurements of dimensional changes in the grafted films. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 992–998, 2003

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

## INTRODUCTION

The photografting of vinyl monomers for the modification of polymeric materials has extensively been investigated by a number of investigators<sup>1–5</sup> since the pioneering work of Oster and Shibata<sup>6</sup> and Stannet et al.<sup>7</sup> Many different methods and procedures have been used to modify various types of polymer substrates to achieve desired functionalities.<sup>4,8–10</sup> In the photografting system, a deaerated system is usually employed for the removal of oxygen; this generally inhibits the radical polymerization of vinyl monomers. However, the photografting of vinyl monomers under air<sup>11–16</sup> has also been investigated. One author<sup>12</sup> reported that the photografting of methacrylic acid (MAA) and acrylonitrile on a benzophenone-coated low-density polyethylene film was successfully performed under air. Efforts have been made to enhance the photografting reaction under air, and various additives, such as hydrazine, metallic ions, riboflavin, and NaIO<sub>4</sub>, have been employed.<sup>12–16</sup> However, it was observed in our previous work<sup>17</sup> for the photografting of MAA on a linear low-density polyethylene (LLDPE) film in mixed solvents consisting of water and an

organic solvent, such as acetone or methanol, that the component of the 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 afforded at a certain concentration of the organic solvent in the mixed solvent. Moreover, photografting with a mixed solvent resulted in an MAA-grafted LLDPE film with a homogeneous distribution of grafted chains. It is interesting to study the characteristics of photografting with a mixed solvent under air. Therefore, this article reports comparative examinations of the polymerization atmosphere (i.e., under air and nitrogen) in the photografting of MAA on an LLDPE film in a mixed solvent in terms of the grafting behavior, the distribution of MAA-grafted chains, and the pH-responsive character of the resulting MAA-grafted films.

## EXPERIMENTAL

### Materials

The polyethylene film used was a commercially available LLDPE film 30  $\mu\text{m}$  thick (density = 0.927 g/cm<sup>3</sup>; Idemitsu Petrochemical Co., Ltd., Tokyo, Japan). The film sample (3 cm  $\times$  10 cm, ca. 0.08 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), was removed from the

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

solution, and was then dried at room temperature for 2 h under a reduced pressure of 5 Torr for the preparation of an XT-coated film. MAA was purified by distillation under reduced pressure (4 Torr at 35°C). XT and hydrophilic organic solvents such as acetone, methanol, tetrahydrofuran, and dioxane, 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 of water or the mixed solvent, in which a given concentration of MAA (0.39M) was dissolved, under air or nitrogen. The reaction mixture was then subjected to UV irradiation with a high-pressure mercury lamp (400 W) at 60°C with a Riko rotary photochemical reactor (RH400-10W, Riko Kagaku Sangyo Co., Ltd., Chiba, Japan), around which the Pyrex glass tubes were rotated.

Polymerized films were extracted for 24 h with hot water for the removal of the homopolymer, poly(methacrylic acid) (PMAA), 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 with various irradiation times. The percentage of grafting and the percentage of the homopolymer were calculated with the following equations:

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

Homopolymer (%)

$$= \frac{\text{Weight of homopolymer}}{\text{Weight of original film}} \times 100$$

### Scanning electron microscopy (SEM)

Carboxylic acid groups in grafted PMAA were converted into potassium salts by the immersion of the grafted film in an aqueous solution of 1.0 wt % potassium hydroxide at 25°C for 24 h and subsequent washing with water. The distribution profile of potassium 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).

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

ATR-IR spectra of the surface layer of the grafted film were measured with an automatic infrared microscope (AIM-800, FTIR-8700) from Shimadzu Co., Ltd. (Kyoto, Japan). The amount of MAA-grafted chains on the film surface layer was expressed in terms of the

absorbance ratio of the carbonyl (stretching) band at 1710  $\text{cm}^{-1}$  to the methylene (scissoring) band at 1460  $\text{cm}^{-1}$ .

### Measurements of the dimensional changes

The grafted film was immersed in pH 4 and pH 8 solutions at 25°C for 24 h, alternately. After the treatment, any excess water on the film surface was removed with 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 the surface areas ( $\text{mm}^2$ ) of the grafted films before and after the treatment, respectively. The surface area was calculated from the length and width of the grafted film measured with a standard ruler.

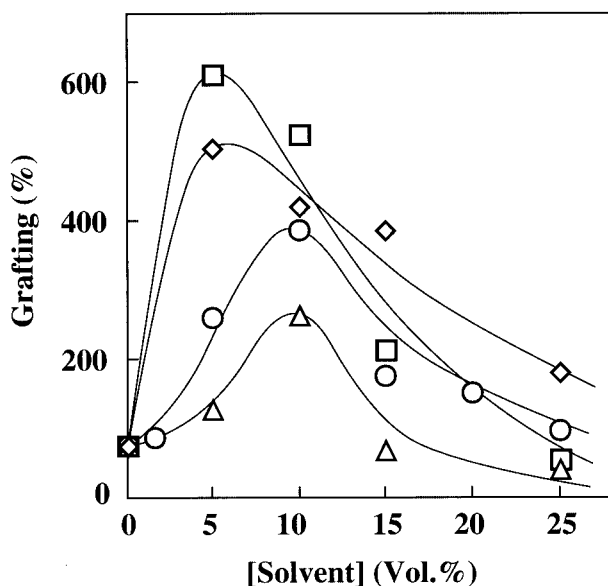
### Formation of peroxide

The photoinduced formation of peroxides on the LLDPE film was carried out in the same system as that of the photografting without the monomer. After the irradiation of the system at 60°C for a given duration under air, the film part was separated from the water, and the amount of peroxide on the film was determined with the following procedures. A flask containing the irradiated film and 20 mL of isopropyl alcohol, to which 5 mL of an isopropyl alcohol solution with saturated sodium iodide and 2 mL of glacial acetic acid were added, was refluxed at 85°C for 15 min. After a period of cooling at room temperature, the liberated iodine was titrated with a 0.01N sodium thiosulfate solution.

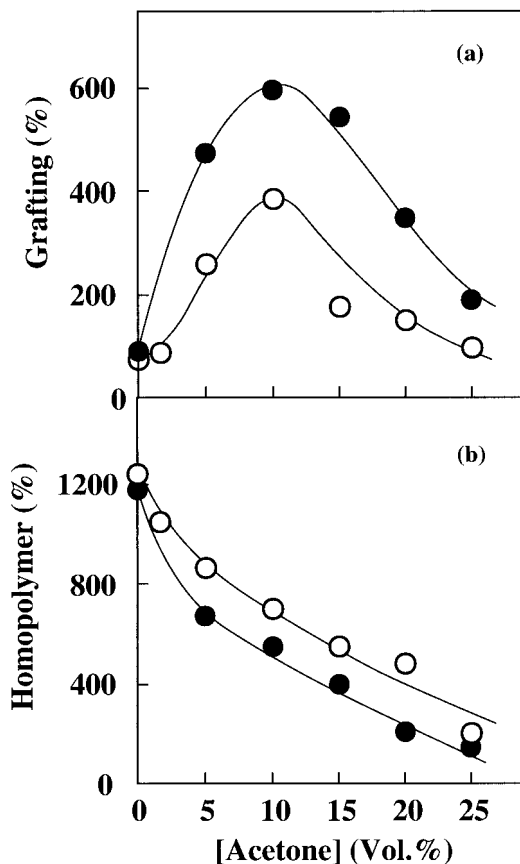
## RESULTS AND DISCUSSION

### Grafting behavior

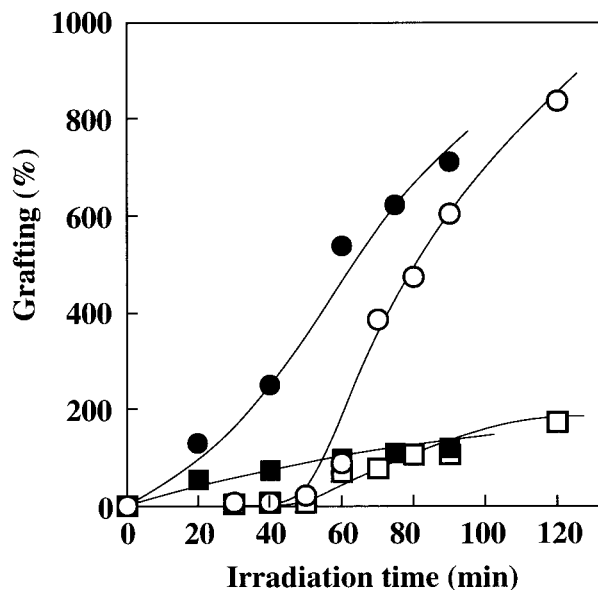
Figure 1 shows the photografting of MAA on an LLDPE film in a mixed solvent under air. The percentage of grafting increased with an increasing concentration of the organic solvent in the mixed solvent, and a maximum percentage of grafting was observed at a certain concentration of the organic solvent in the mixed solvent. The photografting behavior under air and nitrogen was compared, and the results are shown in Figure 2. It was observed that the concentration of acetone affording the maximum percentage of grafting [Fig. 2(a)] was roughly equal in the two systems, although the percentage of grafting under air was lower than that under nitrogen. Accordingly, it was confirmed that the accelerating effect due to the organic solvent in the mixed solvent was a common phenomenon for the air and nitrogen systems. However, a higher percentage of the homopolymer [Fig. 2(b)] was recorded for the system under air. The po-



**Figure 1** Photografting of MAA on an XT-coated LLDPE film in a mixed solvent under air ([MAA] = 0.39 mol/L; [XT] = 0.1 wt %; irradiation at 60°C for 70 min): (□) tetrahydrofuran, (◇) dioxane, (○) acetone, and (△) methanol.



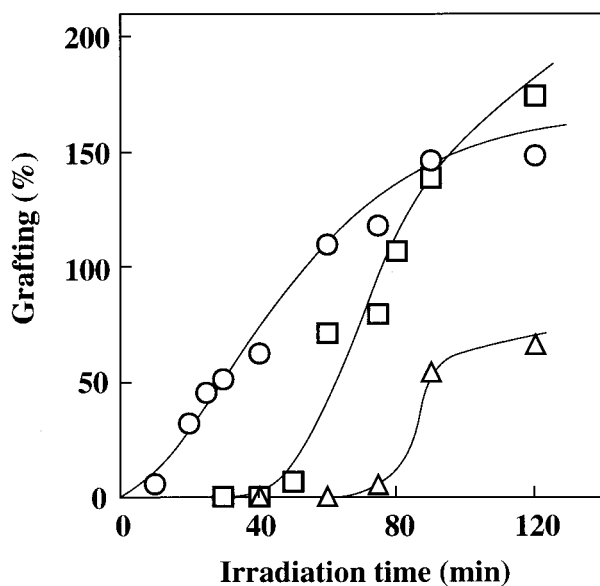
**Figure 2** Photografting of MAA on an XT-coated LLDPE film in a water/acetone mixed solvent ([MAA] = 0.39 mol/L; [XT] = 0.1 wt %) with irradiation at 60°C (●) under nitrogen for 60 min and (○) under air for 70 min.



**Figure 3** Photografting of MAA on an XT-coated LLDPE film ([MAA] = 0.39 mol/L; [XT] = 0.1 wt %) with irradiation at 60°C under nitrogen in (■) water and (●) a water/acetone (10 vol %) mixed solvent and under air in (□) water and (○) a water/acetone (10 vol %) mixed solvent.

lymerization of MAA was also retarded by the organic solvent under air. The explanations for the effect of the mixed solvent consisting of water and an organic solvent on the photografting of MAA<sup>11</sup> under nitrogen have been given in detail previously. It has been proposed that the solubility of monomers in the system increases with an increasing concentration of the organic solvent component in the mixed solvent, and this results in a stimulation of the monomer supply for the radicals on the growing grafted polymer chains, leading to an increase in the percentage of grafting. At a high concentration of the organic solvent, however, the percentage of grafting decreases because of the chain transfer from the growing grafted polymer radicals to the organic solvent and/or the termination of the growing polymer radicals by the solvent radicals formed. An effect similar to the aforementioned effect of the mixed solvent under nitrogen may be applicable to the photografting of MAA under air.

Figure 3 presents the relationship between the percentage of grafting and the irradiation time. An induction period was observed for the grafting system under air. Up to 50 min of irradiation, no grafting reaction was observed for the water solvent under air. After that, photografting took place, and the percentages of grafting, 79.6 and 106.9%, were recorded for 70 and 90 min of irradiation time, respectively. These values were higher than those of the system under nitrogen, 51.6 and 70.5% for 20 and 40 min of irradiation, respectively. With the water/acetone (10 vol %) mixed solvent system under air, however, a shortening of the induction period to 40 min was observed. For 60 and 80 min of irradiation, percentages of graft-

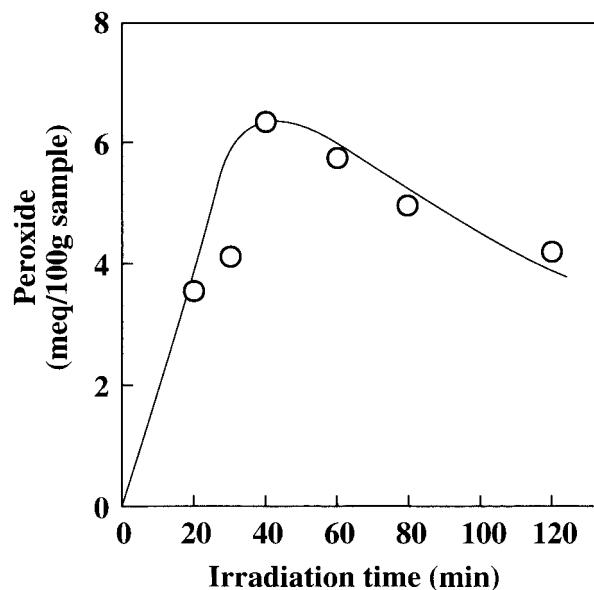


**Figure 4** Photografting of MAA on an XT-coated LLDPE film in a water/acetone (10 vol %) mixed solvent under air ( $[MAA] = 0.39$  mol/L;  $[XT] = 0.1$  wt %): (□) unboiled water, (○) boiled water, and (△) oxygen-bubbled water.

ing of 158.9 and 473.6% were achieved, which were also higher than those of the system under nitrogen, 134.3 and 252.8% for 20 and 40 min of irradiation, respectively. The grafting reaction under air exhibited an induction period, but the use of the mixed solvent in the system led to a shortening of the induction period, and the rate of grafting after the period was greater than that in the system under nitrogen.

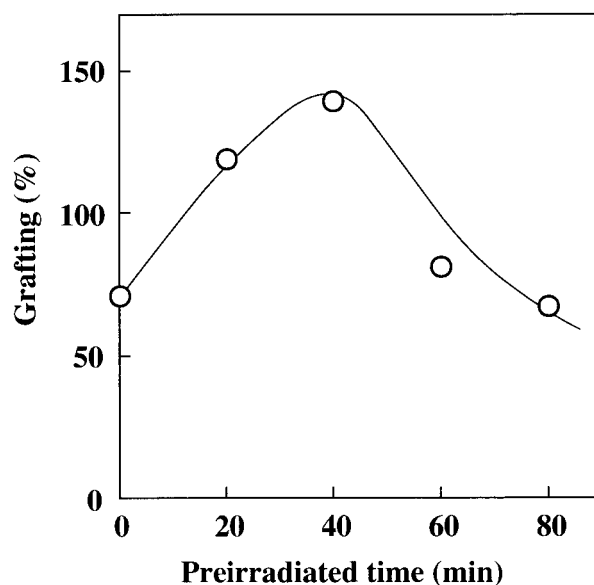
To understand the induction period, we performed photografting with boiled water to exclude dissolved oxygen from the system, and the results are shown in Figure 4. The induction period was shortened by the boiled water. The figure also includes the results of photografting with water into which oxygen was bubbled for 10 min. The induction period was prolonged with the oxygen-bubbled water. These results support the idea that the induction period originated from dissolved oxygen in the grafting system. An induction period due to the presence of oxygen in the photografting was also reported by others.<sup>18-20</sup>

It is well known that oxygen generally inhibits the radical polymerization of vinyl monomers. It has been reported, however, that during the photoirradiation of a polyethylene film in the presence of oxygen, peroxides capable of initiating grafting reactions are generally formed.<sup>13,21-25</sup> To clarify the effect of oxygen on the photografting of MAA under air, we examined the photoinduced formation of peroxide on an LLDPE film, and the results are shown in Figure 5. Peroxides were also formed on the LLDPE film in this study, and the amount increased with increasing irradiation time and then gave a maximum at a certain irradiation time. To prove that the peroxides on the LLDPE film had the ability to initiate the photografting of MAA,



**Figure 5** Photoinduced formation of peroxides on an XT-coated LLDPE film in water at 60°C under air ( $[XT] = 0.1$  wt %).

we irradiated an XT-coated LLDPE film at 60°C for different times under air, and then the preirradiated films were subjected to the photografting of MAA in the water solvent under nitrogen. The results are shown in Figure 6. The horizontal axis of the figure is the preirradiated time, during which the XT-coated LLDPE films were irradiated at 60°C under air for the preparation of peroxides on the films. The percentage of grafting increased with an increasing preirradiation time, and a maximum percentage of grafting was ob-

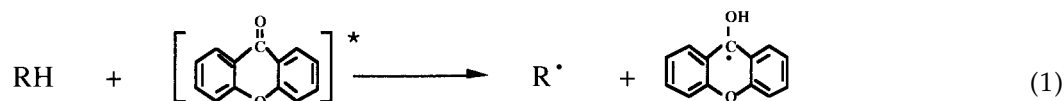


**Figure 6** Photografting of MAA on a preirradiated LLDPE film in water under nitrogen at 60°C ( $[MAA] = 0.39$  mol/L;  $[XT] = 0.1$  wt %). The preirradiation on the XT-coated LLDPE film was carried out under the same conditions used in Figure 5.

served at a certain preirradiation time. It is conceivable that the reaction sites to form the peroxides on the polyethylene film were reduced as the photoirradiation proceeded. Accordingly, the decomposition of peroxide by photoirradiation overcame the formation of peroxides, and this resulted in the maximum amount of peroxide and percentage of grafting at a certain irradiation time. It was confirmed that the

higher rate of grafting in the air system after the induction period was attributable to the initiation due to the peroxides formed on the LLDPE film.

The photografting<sup>11</sup> of MAA on an LLDPE film under nitrogen proceeds according to eqs. (1)–(3). That is, photoexcited XT abstracts hydrogen atoms from the polyethylene substrate to yield polyethylene radicals capable of initiating the grafting:



where RH, R, and G denote LLDPE, its radicals, and growing grafted polymer radicals, respectively. As described previously,<sup>11</sup> it seems that the increased solubility of the MAA monomer due to the organic solvent leads to an enhanced reaction of eqs. (2) and (3), resulting in an increased percentage of grafting. In the grafting system under air, the grafting reaction mainly proceeds according to eqs. (4) and (7). The reaction of oxygen with polyethylene radicals leads to the formation of peroxy radicals<sup>26</sup> [eq. (4)]. The radicals yielded by eq. (4) abstract hydrogen atoms from polyethylene to yield a hydroperoxide and a new polyethylene radical [eq. (5)]. The decomposition of the hydroperoxide according to eq. (6) also participates in the initiation of the grafting reaction of eq. (7). The hydroxy radicals formed by eq. (6) may contribute to the initiation of the homopolymer of eq. (8):

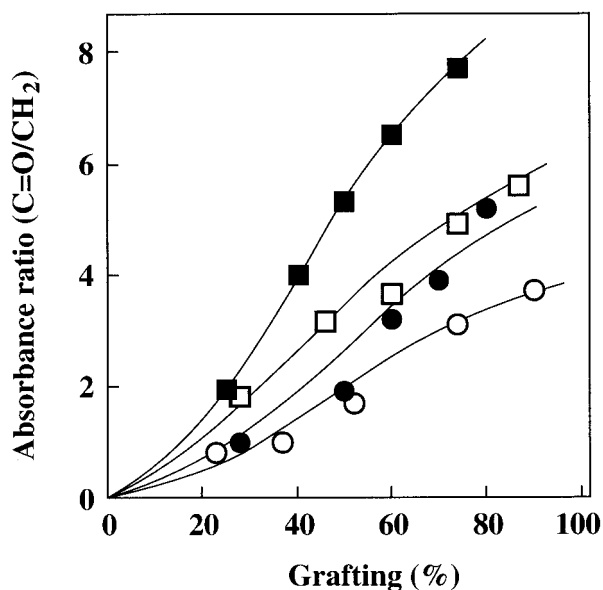


### Distribution of MAA-grafted chains

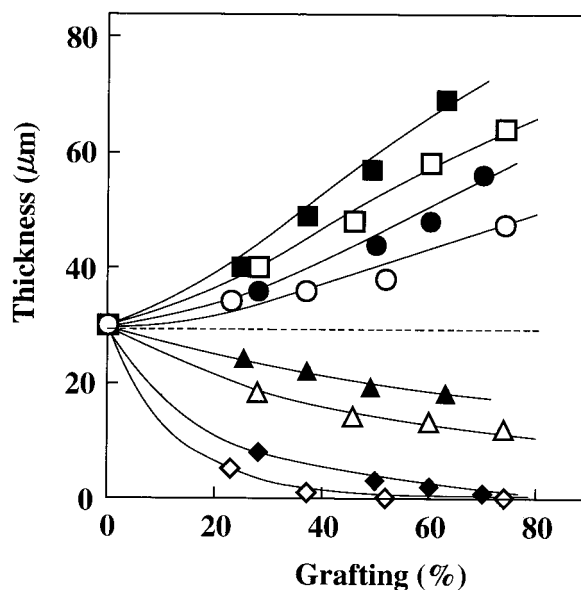
The resulting grafted films were subjected to measurements of ATR-IR spectra to confirm the locations of MAA-grafted chains in the grafted films. The grafted films showed a peak at  $1710\text{ cm}^{-1}$  due to the carbonyl (C=O) groups of the MAA-grafted chains and a peak at  $1460\text{ cm}^{-1}$  due to the methylene ( $\text{CH}_2$ ) of the LLDPE film. The amount of MAA-grafted chains on the

film surface layer was expressed in terms of the absorbance ratio of the C=O (stretching) peak to the  $\text{CH}_2$  (bending) peak, and the results are shown in Figure 7 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 MAA-grafted chains than LLDPE components. The magnitude of the increase was smaller for the samples prepared under air (and this was commonly observed for the systems of both water and mixed solvents) than that of the samples prepared in a nitrogen system. This suggests that MAA-grafted chains prepared under air tended to penetrate more deeply inside the films than those prepared under nitrogen.

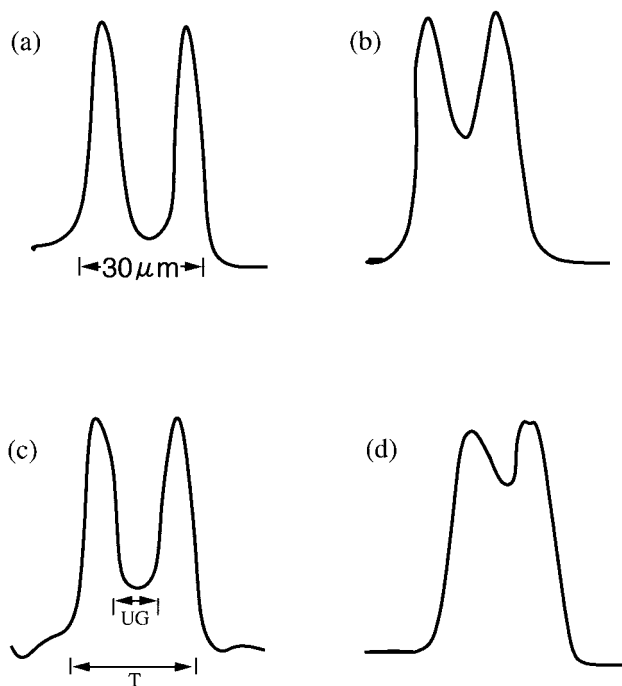
To confirm the results by ATR-IR, we examined by SEM the distribution of MAA-grafted chains in the cross section of the grafted film. Figure 8 shows the distribution profile of potassium atoms in the cross section of MAA-grafted LLDPE films. The observation was performed with the grafted films treated with potassium hydroxide. Accordingly, the curve in the figure represents the distribution profile of potassium atoms, that is, the MAA-grafted chains, in the cross section of the MAA-grafted LLDPE film. The vertical and horizontal directions in the figure correspond to the relative concentrations of potassium atoms and the cross section of the films, respectively. The same tendency was observed for the distribution of grafted chains for samples prepared under air and nitrogen. That is, the grafted chains of the samples prepared in the mixed solvent located inside the film compared with those of the sample with the water solvent; this was commonly observed for each system. The total thickness of the film and the thickness of the ungrafted layer (T and UG, respectively, in Fig. 8) were measured from the distribution profile, and the results are shown in Figure 9 as a function of the percentage of grafting. The dotted line represents the thickness of



**Figure 7** Changes in the absorbance ratio of a carbonyl peak at  $1710\text{ cm}^{-1}$  to a methylene peak at  $1460\text{ cm}^{-1}$  with the percentage of grafting in MAA-grafted LLDPE films: under nitrogen in (■) water and (●) a water/acetone (10 vol %) mixed solvent and under air in (□) water and (○) a water/acetone (10 vol %) mixed solvent.

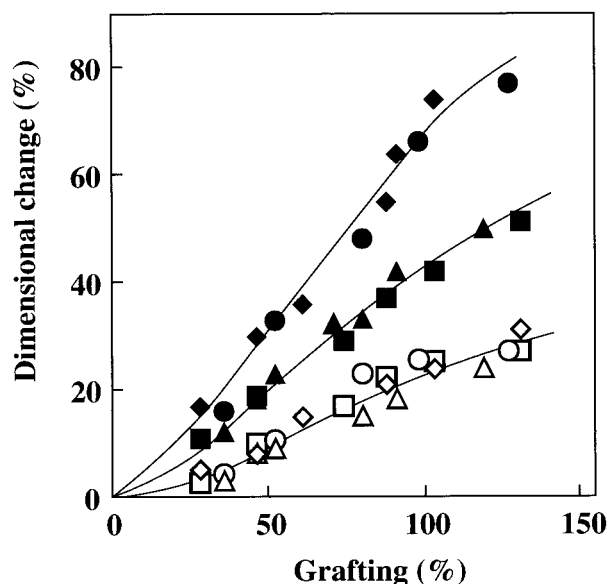


**Figure 9** Relationship between the total thickness and thickness of the ungrafted layer of MAA-grafted LLDPE films and the percentage of grafting: total thickness under nitrogen in (■) water and (●) a water/acetone (10 vol %) mixed solvent, total thickness under air in (□) water and (○) a water/acetone (10 vol %) mixed solvent, thickness of the ungrafted layer under nitrogen in (▲) water and (◆) a water/acetone (10 vol %) mixed solvent, and thickness of the ungrafted layer under air in (△) water and (◇) a water/acetone (10 vol %) mixed solvent.



**Figure 8** Distribution profile of potassium atoms in the cross sections of MAA-grafted LLDPE films measured by SEM: (a) under nitrogen in water (grafting = 65%), (b) under nitrogen in a water/acetone (10 vol %) mixed solvent (grafting = 61%), (c) under air in water (grafting = 54%), and (d) under air in a water/acetone (10 vol %) mixed solvent (grafting = 51%).

the original film. With the grafted films prepared in the water solvent, the sample prepared under air exhibited a smaller increase in the total thickness with an increase in the percentage of grafting than the sample prepared under nitrogen. The thickness of the ungrafted layer decreased with an increase in the percentage of grafting, and the magnitude was larger for the sample prepared under air than for the sample prepared under nitrogen. MAA-grafted chains of the grafted films prepared under air tended to penetrate into a deeper layer of the film surface than those prepared under nitrogen, although the MAA-grafted chains prepared by both methods were still located on the film surface. The same tendency was observed for the grafted films prepared in the mixed solvent system. That is, the total thickness of the grafted films prepared under air exhibited a smaller increase than that of the samples prepared under nitrogen. However, the decrease in the thickness of the ungrafted layer was larger for the sample prepared under air than for that prepared under nitrogen. The different distributions of the grafted chains between the samples prepared under air and nitrogen may be ascribed to the different photografting behaviors for each system, as shown in Figure 3. That is, after the induction period, the rate of the grafting under air was greater than that under nitrogen, and this resulted in the penetration of MAA-grafted chains into a deeper layer



**Figure 10** pH-responsive character of MAA-grafted LLDPE films prepared under nitrogen and air: under nitrogen at pH 4 in ( $\Delta$ ) water and ( $\diamond$ ) a water/acetone (10 vol %) mixed solvent, under nitrogen at pH 8 in ( $\blacktriangle$ ) water and ( $\blacklozenge$ ) a water/acetone (10 vol %) mixed solvent, under air at pH 4 in ( $\square$ ) water and ( $\circ$ ) a water/acetone (10 vol %) mixed solvent, and under air at pH 8 in ( $\blacksquare$ ) water and ( $\bullet$ ) a water/acetone (10 vol %) mixed solvent.

of the film surface than for the system under nitrogen. The polymerization atmosphere influenced both the grafting behaviors and the location of MAA-grafted chains in the LLDPE film substrate.

### pH-responsive character

The pH-responsive character of the resulting grafted film was evaluated by the measurement of the dimensional changes of the grafted films. It is known that MAA-grafted polymer films<sup>27–29</sup> exhibit pH-responsive character: the grafted films shrink in an acidic medium and swell in an alkaline medium. Figure 10 shows the dimensional changes for MAA-grafted films alternately immersed in pH 4 and pH 8 solutions at room temperature for 24 h. The grafted films shrank and swelled in acidic and alkaline media, respectively. The dimensional changes increased with an increasing percentage of grafting. A larger pH-responsive character was observed for the sample prepared in the mixed solvent than for the sample prepared in water, but there was no large difference in the dimensional changes of the grafted films prepared under air and nitrogen atmospheres.

### CONCLUSIONS

The photografting of MAA on LLDPE films easily proceeded under both air and nitrogen in mixed solvents consisting of water and an organic solvent. The maximum percentage of grafting was observed at a certain concentration of the organic solvent in the mixed solvent. Photografting under air was characterized by an induction period, but the rate of grafting after the period was greater than that under nitrogen. The formation of poly(ethylene peroxide)s by photoirradiation seemed to be a factor for the accelerated polymerization under air. Moreover, MAA-grafted chains prepared under air tended to penetrate more deeply inside the film than those prepared under nitrogen; this was commonly observed for grafting systems with water and mixed solvents.

### References

- Davis, N. P.; Garnet, J. L. *J Polym Sci Polym Lett Ed* 1976, 14, 537.
- Kubota, H.; Ogiwara, Y. *J Appl Polym Sci* 1972, 16, 965.
- Tazuke, S.; Kimura, H. *J Polym Sci Polym Lett Ed* 1982, 16, 497.
- Allmer, K.; Hult, A.; Rånby, B. *J Polym Sci Part A: Polym Chem* 1988, 26, 2099.
- Tsubokawa, N.; Shirai, Y.; Tsuchida, H.; Handa, S. *J Polym Sci Part A: Polym Chem* 1994, 32, 2327.
- Oster, G.; Shibata, O. *J Polym Sci* 1957, 26, 233.
- Geacintov, N.; Stannet, V. E.; Abrahamson, W.; Hermans, J. *J Appl Polym Sci* 1960, 3, 54.
- Ogiwara, Y.; Kanda, M.; Takumi, M.; Kubota, H. *J Polym Sci Polym Lett Ed* 1981, 19, 457.
- Ang, C. H.; Garnet, J. L.; Levot, R.; Long, M. A. *J Appl Polym Sci* 1982, 27, 4893.
- Zhang, P. Y.; Rånby, B. *J Appl Polym Sci* 1990, 40, 1647.
- Silna, M. A.; Gil, M. H.; Lapa, E.; Guthrie, J. T. *J Appl Polym Sci* 1987, 34, 871.
- Kubota, H. *J Appl Polym Sci* 1993, 48, 1717.
- Holmstro, B.; Oster, G. *J Am Chem Soc* 1961, 83, 1867.
- Wang, P.; Tan, K. L.; Ho, C. C.; Khew, M. C.; Kang, E. T. *Eur Polym J* 2000, 36, 1323.
- Uchida, E.; Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1990, 41, 677.
- Uchida, E.; Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1993, 47, 417.
- Irwan, G. S.; Kuroda, S.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2002, 83, 2454.
- Tazuke, S.; Kimura, H. *Makromol Chem* 1978, 179, 2603.
- Ruckert, D.; Geuskens, G. *Eur Polym J* 1996, 32, 201.
- Yang, W.; Rånby, B. *J Appl Polym Sci* 1996, 62, 533.
- Geuskens, G.; Kanda, M. N. *Eur Polym J* 1991, 27, 877.
- Geuskens, G.; Thiriaux, P. H. *Eur Polym J* 1993, 29, 351.
- Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1988, 36, 1087.
- Uchida, E.; Uyama, Y.; Ikada, Y. *J Polym Sci Part A: Polym Chem* 1989, 27, 527.
- Chmela, S.; Teissedre, G.; Lacoste, J. *Macromolecules* 1996, 29, 3055.
- Bevington, J. C.; Troth, H. G. *Trans Faraday Soc* 1962, 58, 186.
- Osada, Y.; Honda, K.; Ohta, M. *J Membr Sci* 1986, 27, 327.
- Klier, J.; Seranton, A. B.; Peppas, N. A. *Macromolecules* 1990, 23, 4944.
- Ito, Y.; Park, Y. S.; Imanishi, Y. *Makromol Rapid Commun* 1997, 18, 221.