Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ishii, Takao , Kuroda, Shin-Ichi , Kubota, Hitoshi , Kondo, Takashi and Yoshinori, Ikeda(2000) 'EFFECT OF LOCATION OF GRAFTED CHAINS ON pH-RESPONSIVE CHARACTER OF METHACRYLIC ACID-GRAFTED POLYETHYLENE FILM', Journal of Macromolecular Science, Part A, 37: 7, 807 — 814

To link to this Article: DOI: 10.1081/MA-100101124
URL: http://dx.doi.org/10.1081/MA-100101124

J.M.S.—PURE APPL. CHEM., A37(7), pp. 807–814 (2000)

NOTE

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Key Words: Photografting, Methacrylic Acid, Low-Density Polyethylene Film, pH-Responsive Character, Location of Grafted Chains

INTRODUCTION

In previous papers [1-3] photografting on polyolefin films has been performed in liquid- and vapor-phase systems using photoinitiators such as aromatic ketones and quinones, which were coated on the film earlier. The photoinitiators enabled hydrophilic vinyl monomers such as methacrylic acid (MAA) and acrylic acid to graft easily with high yields. It was found that the

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location of MAA-grafted chains introduced into low-density polyethylene film is greatly influenced by polymerization system [4, 5] such as the liquid- and vapor-phase systems. That is, with the liquid-phase system, the grafted chains tended to locate on the film surface. In the vapor-phase system, on the other hand, the grafted chains distributed in the film inside. It was reported in radiation-induced grafting of acrylic acid on polyethylene film by preirradiation method [6] that distribution of the grafted chains in polyethylene film is controlled by the use of Mohr's salt (ferrous ammonium sulfate).

In a previous paper [7], it was observed that *N*-isopropyl acrylamide can be grafted onto ethylene-vinyl alcohol copolymer and polyethylene films by photografting using xanthone-coated films, and the resulting grafted films exhibit a temperature-responsive character, where they swell in water below and shrink above a lower critical solution temperature of poly(*N*-isopropyl acrylamide). Moreover, the extent of the character was largely influenced by location of *N*-isopropyl acrylamide-grafted chains in the grafted films. This paper deals with comparative examinations in a pH-responsive character of MAA-grafted polyethylene films prepared by photografting in the liquid- and vapor-phase systems in order to understand the effect of location of MAA-grafted chains on the character. It is known that MAA-grafted polymer films [8-11] exhibit the pH-responsive character, where the grafted films shrink in acidic media, while they swell in alkaline region.

EXPERIMENTAL

Materials

Commercially available low-density polyethylene (PE) film with a thickness of 25 μm was used as a film sample. The film (3 × 10 cm and 5 × 6 cm) was immersed in acetone solution containing 0.3 wt% xanthone and 0.5 wt% poly(vinyl acetate)($\overline{M}w$=100,000), removed from the solution and then dried under reduced pressure to prepare xanthone-coated film. The quantity of xanthone on the film was too small to determine gravimetrically. MAA was purified by distillation under reduced pressure. Xanthone was a reagent grade and used without further purification.

Preparation of MAA-Grafted PE Films

Liquid-phase photografting was carried out in a Pyrex glass tube containing the xanthone-coated film (3 × 10 cm), 1.5 mL MAA, and 30 mL water under nitrogen atmosphere. Vapor-phase photografting was performed using the Pyrex glass tube as follows: The xanthone-coated film (5 × 6 cm) fixed on a sample holder was set at the center part of the tube, and 1.5 mL MAA monomer was placed in the bottom part. The pressure of the system, after several freeze-thaw cycles, was adjusted to 1 mmHg and then the system was irradiated. 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 Pyrex glass tubes were rotated.

Polymerized films were extracted for 24 hours with hot water and then 3 hours with hot methanol to remove homopolymer of poly(MAA). The MAA-grafted PE films thus obtained in the liquid- and vapor-phase systems were denoted as liquid- and vapor-phase samples, respectively. The percentage of grafting was taken as the percentage of weight increase of the original film. The grafted films with different percentages of grafting were prepared by changing the irradiation time.

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

ATR-IR spectra of the surface layer of grafted film were measured with an infrared spectrometer model MAGNA-IR 750 (Nicolet). The amount of MAA-grafted chains on the surface layer was expressed in terms of the absorbance ratio of the carbonyl (stretching) peak at 1710 cm^{-1} to methylene (scissoring) peak at 1460 cm^{-1}.

Electron Probe Microanalysis (EPMA)

Grafted poly(MAA) was converted to potassium salt by immersing the grafted film in an aqueous solution of 1.0 wt% potassium hydroxide at 25°C for 24 hours. The distribution profile of potassium atoms in the cross section of grafted film was measured with an electron probe microanalyzer model EPM-810 (Shimazu).

Measurement of Dimensional Change

Grafted film (surface area, S_0 mm^2) was immersed in given solution pH at room temperature for 24 hours. To adjust the solution pH, known concentrations of citric acid and dibasic sodium phosphate solution were mixed in a given proportion. After the treatment, an excess solution on the film surface was wiped by filter paper and then the surface area (S_1 mm^2) of the treated film was measured. Dimensional change of the grafted film was defined as follows:

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

RESULTS AND DISCUSSION

In the present study, MAA-grafted PE films were prepared by photografting in the liquid- and vapor-phase systems. The resulting grafted films were subjected to measurements of ATR-IR spectra to confirm location of MAA-grafted chains in the grafted films. The absorbance ratio of the carbonyl (stretching) peak at 1710 cm^{-1} to the methylene (scissoring) peak at 1460 cm^{-1} are shown in Figure 1 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 becomes rich in the MAA-grafted chains compared to the PE components. The magniture of the increase was smaller for the vapor-phase sample than the liquid-phase one. This suggests that MAA-grafted chains of the vapor-phase sample tend to penetrate more inside the film compared to those of the liquid-phase sample. In order to confirm the result by ATR-IR, the distribution of MAA-grafted chains in the cross section of the grafted film was examined by EPMA. Figure 2 shows the distribution profile of potassium atoms in the cross section of MAA-grafted PE films. The observation was done using the grafted films treated with potassium hydroxide. Accordingly, the curve in the figure represents distribution profile of potassium atoms, that is, the MAA-grafted chains, in the cross section of the MAA-grafted PE film. The vertical and horizontal directions in the figure correspond to the relative concentration of potassium atom and the cross section of the films, respectively. The grafted chains of the vapor-phase sample were distributed inside the film, while those of the liquid-phase sample seemed to appear at the film surface. It was thus confirmed that MAA-grafted chains of the vapor-phase sample tend to penetrate more inside the film compared to those of the liquid-phase sample.

Figure 3 shows the dimensional change of MAA-grafted PE film when immersed in various pH solutions at room temperature for 24 hours. The grafted film showed a pH-responsive character, where the grafted film shrinks in acidic medium, while it swells in alkaline region. The dimensional changes at pH=4 and pH=8 are shown in Figure 4 as a function of the percentage of grafting. The

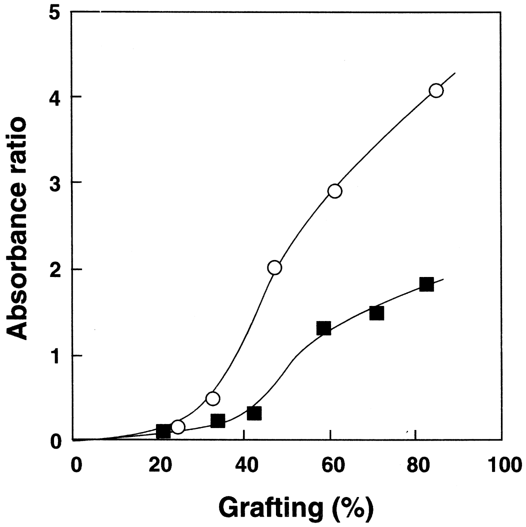

Figure 1. Changes in absorbance ratio of carbonyl peak at 1710 cm^{-1} to methylene peak at 1460 cm^{-1} with percentage of grafting in MAA-grafted PE films. (○) liquid-phase sample, (■) vapor-phase sample.

dimensional changes at pH=4 and pH=8 increased with an increase in the percentage of grafting, indicating that MAA-grafted chains directly contribute to the pH-responsive character of grafted PE films. Moreover, the values at pH=4 and pH=8 were higher for the vapor-phase sample than the liquid-phase one.

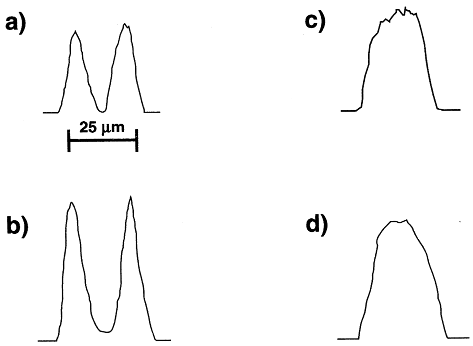

Figure 2. Distribution profile of potassium atoms in the cross section of MAA-grafted PE films measured by EPMA. Liquid-phase sample, grafting (%): (a) 31.9, (b) 60.1, vapor-phase sample, grafting (%): (c) 34.4, (d) 64.8.

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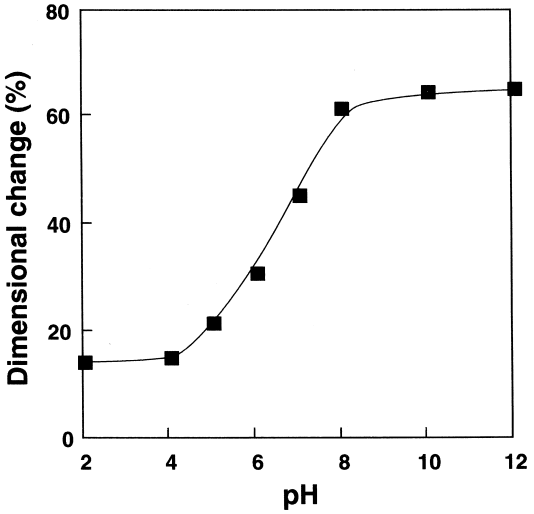

Figure 3. pH-responsive character of MAA-grafted PE film (grafting = 64.8%) prepared in the vapor-phase system.

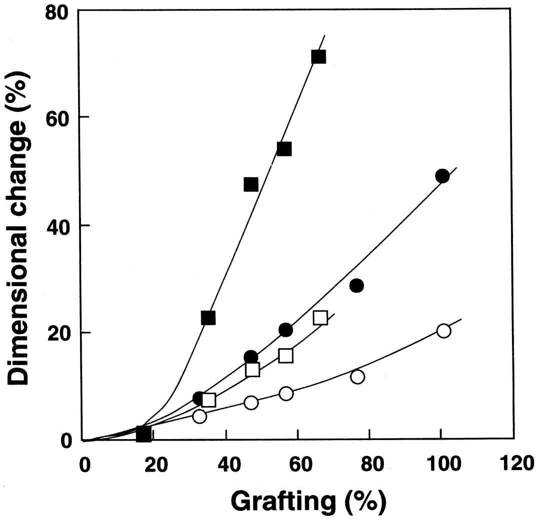

Figure 4. Relationship between dimensional change and percentage of grafting in MAA-grafted PE films. Liquid-phase sample: (○) pH=4, (●) pH=8, vapor-phase sample: (□) pH=4, (■) pH=8.

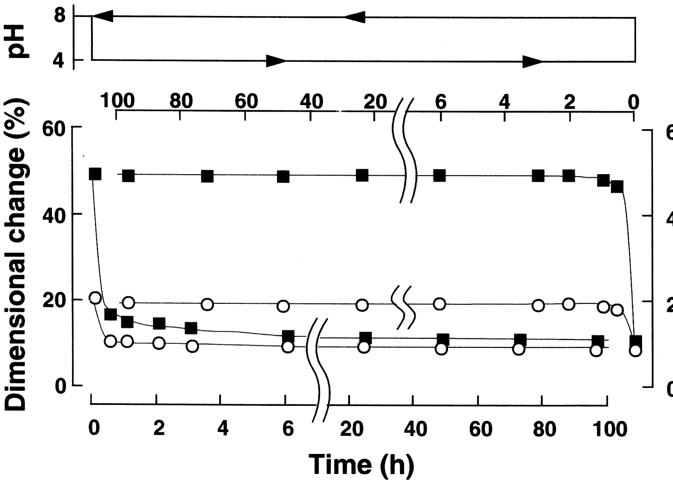

Figure 5. pH-responsive character of MAA-grafted PE films. (○) liquid-phase sample (grafting = 56.1%), (■) vapor-phase sample (grafting = 56.2%).

This might be originated in the MAA-grafted chains located inwards in the vapor-phase sample compared to those of the liquid-phase one. The contribution of MAA-grafted chains on the shrinking and swelling nature of the whole grafted film including the PE substrate may be large for the vapor-phase sample because of a homogeneous distribution of the grafted chains, resulting in a high pH-responsive character. The shrinking-swelling profile between pH=4 and pH=8 at 24-hour intervals was compared among the liquid- and vapor-phase samples, and the results are shown in Figure 5. The solution pH was first kept at pH=4 for 24 hours to shrink the grafted film and then adjusted to pH=8 to swell the grafted film. It was found that shrinking and swelling equilibrium of the grafted film was reached within about 2 hours, and there was no large difference in the profile between the two samples.

CONCLUSION

It is confirmed that MAA-grafted PE films with a homogeneous distribution of grafted chains can be prepared by vapor-phase photo- grafting, while those with the grafted chains located on the film surface are prepared by liquid-phase photogarfting. The resulting grafted films exhibit a pH-responsive character, where the grafted films shrink in acidic medium, while they swell in alkaline region. The extent of pH-responsive character depends on the distribution of grafted chains as well as the percentage of grafting. It is concluded that a high pH-responsive character is available for the vapor-phase sample with a homogeneous distribution of grafted chains.

REFERENCES

[1] Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, *19,* 457 (1981).

[2] H. Kubota, K. Kobayashi, and Y. Ogiwara, *Polym. Photochem.*, *7*, 379 (1986).

[3] Y. Ogiwara, N. Koike, H. Kubota, and Y. Hata, *J. Appl. Polym. Sci.*, *35,* 1473 (1988).

[4] H. Kubota, N. Koike, Y. Ogiwara, and Y. Hata, *J. Polym. Sci. Part C, Polym. Lett.*, *25*, 273 (1987).

[5] H. Kubota and Y. Hata, *J. Appl. Polym. Sci.*, *41,* 689 (1990).

[6] K. Kaji, *J. Appl. Polym. Sci.*, *32*, 4405 (1986).

[7] H. Kubota, N. Nagaoka, R. Katakai, M. Yoshida, H. Omichi, and Y. Hata, *J. Appl. Polym. Sci.*, *51*, 925 (1994).

[8] Y. Osada, K. Honda, and M. Ohta, *J. Membrane Sci.*, *27,* 327 (1986).

[9] M. A. Islam, A. Dimov, and A. L. Maliova, *J. Membrane Sci.*, *66,* 69 (1992).

[10] Y. M. Lee, S. Y. Ihm, J. K. Shim, J. H. Kim, C. S. Cho, and Y. K. Sung, *Polymer*, *36,* 81 (1995).

[11] Y. Ito, Y. S. Park, and Y. Imanishi, *Macromol. Rapid Commun.*, *18*, 221 (1997).

Received November 15, 1999
Revision received February 14, 2000

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