

# Comparison of Formation Site of Graft Chain between Nonporous and Porous Films Prepared by RIGP

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An epoxy-group-containing vinyl monomer, glycidyl methacrylate (GMA), was grafted onto nonporous and porous polyethylene films which were previously irradiated with an electron beam at a total dose of 200 kGy. The epoxy groups on the poly-GMA chain were ring-opened for the introduction of an iminodiacetate (IDA) group which is capable of transporting protons and chelating metal ions. The formation site of the graft chain can be clarified by comparing the surface and volume resistivities of the resultant IDA-group-containing film (IDA film). A constant volume resistivity of nonporous IDA film irrespective of the degree of GMA grafting (dg) indicated that the central part of the film remained ungrafted. However, both volume and surface resistivities of porous IDA film decreased with increasing dg, indicating that the poly-GMA chains penetrated the porous film thoroughly. The distribution of the IDA group across the IDA film was also verified by XMA determination of copper ions adsorbed onto the film.

## Introduction

Chemical modification of existing polyethylene (PE) films is effective since PE is chemically stable and inexpensive. The PE films are either porous or nonporous. To append new functional groups onto the PE films, graft polymerization is carried out by use of radiation, ultraviolet light, plasma, or chemical initiators. Radiation-induced graft polymerization (RIGP) is a useful technique because it is applicable to various shapes and sizes of existing polymers<sup>1</sup> and it allows a high degree of penetration of graft chains to the polymer matrix due to its ability to produce uniform active radical sites on the polymer during irradiation. RIGP includes (1) a simultaneous irradiation method where the backbone polymer is irradiated in the presence of the monomer,<sup>2</sup> (2) a preirradiation method where the backbone polymer is irradiated in vacuum or nitrogen gas, followed by grafting of monomer by trapped radicals,<sup>3</sup> and (3) a preirradiation method where the backbone polymer is irradiated in the presence of oxygen, followed by grafting of monomer by polymeric peroxides.<sup>4</sup>

Hydrophobicity and hydrophilicity of the polymeric membrane are governed by an interface; therefore, surface modification of the polymer film is required. On

the other hand, collection of proteins and metal ions during permeation of the liquid through the pores of a porous membrane is related to the entire volume of membrane; therefore chemical modification of the entire porous film is necessary to append hydrophilic groups,<sup>5–7</sup> affinity ligands,<sup>8</sup> and chelate-forming groups.<sup>9</sup> For instance, many efforts were made to prepare biocompatible materials by radiation-induced grafting of hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA) onto a strong inert polymeric support, such as nonporous PE film<sup>5</sup> or polyether urethane film.<sup>6,7</sup>

Glycidyl methacrylate (GMA,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{-CHOCH}_2$ ) is a versatile reactive monomer for grafting because its epoxy group can be converted into various kinds of functionality via ring-opening. Here, a chelate-forming group capable of conducting electricity and chelating with metal ions was introduced by ring-opening of the epoxy group. The formation sites of poly-GMA chains as graft chains onto the PE film should be clarified to enable the design of a high-performance membrane.

Gupta et al. studied the morphological changes of ceric ion and preirradiation acrylic-acid-grafted rayon fibers using X-ray diffraction and scanning electron microscopy.<sup>10</sup> In this study, the preirradiation grafting

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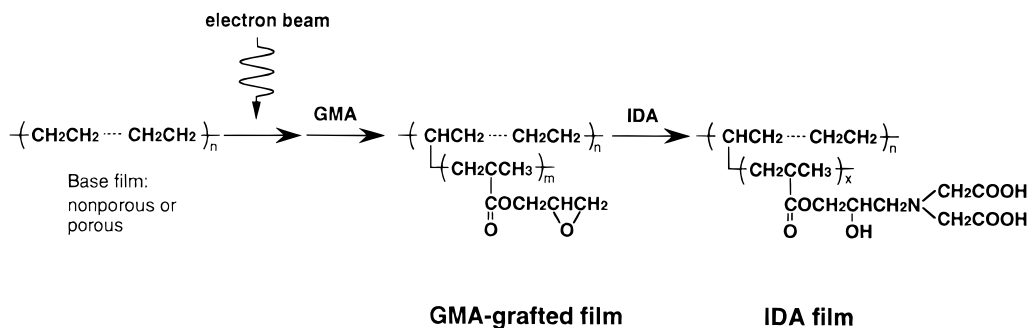
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**Figure 1.** Reaction scheme of the introduction of iminodiacetate group into polyethylene films.

method in the presence of nitrogen gas was used to synthesize a metal-ion-chelating film. The objective of our study was to compare the formation site of the graft chains on the nonporous and porous PE films using two independent techniques of (a) electrical-resistivity measurement and (b) X-ray microanalysis.

### Experimental Section

**Materials.** Nonporous and porous polyethylene (PE) films were used as trunk polymers for grafting. Both high-density PE films were supplied by Asahi Chemical Industry Co., Ltd., Japan. The thickness of the nonporous film was 50  $\mu\text{m}$ . The porous film had a thickness of 100  $\mu\text{m}$  with a pore diameter of 0.2  $\mu\text{m}$  and a porosity of 70%.

Glycidyl methacrylate (GMA,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CHOCH}_2$ ) was purchased from Tokyo Kasei Co., Ltd., and used without further purification. All other reagents were of analytical grade or higher.

**Electron Spin Resonance Spectroscopy.** The initial radical concentration of both nonporous and porous films after irradiation with electron beam was measured by an electron spin resonance (ESR) spectrometer (JEOL JES-RE series spectrometer), operating at 9.2 GHz at 77 K in liquid nitrogen. The samples were cut in stripes of 1 mm  $\times$  10 mm and introduced into a Pyrex tube (5 mm i.d.) sealed at one end with a silicon stopper. The tube was placed in a cylindrical cavity. Spectra were recorded using the following instrumental parameters: sweep width,  $\pm 25$  mT; modulation width, 0.1 mT; sweep time, 2.0 min; time constant, 0.1 s; and microwave power,  $10^{-3}$  mW. The radical concentration per gram of the irradiated films was determined by the double-integration method. Carbon and  $\text{Mn}^{2+}$  were used as standard samples for radical concentration and position of the spectra, respectively.

**Introduction of Functional Group.** A reaction scheme of the introduction of a chelate-forming group, i.e., chelating group, into the PE film is shown in Figure 1. The experimental procedures of GMA grafting and subsequent functionalization were the same for both nonporous and porous films. Irradiation was performed at ambient temperature by means of a cascade electron accelerator (Dynamitron, IEA-3000-25-2, Radiation Dynamics Inc.) which was operated at a voltage of 2.0 MeV and current of 1 mA. The PE film was irradiated with an electron beam at a total exposed dose set to 200 kGy (Gy (gray) equals joules per kilogram) under a nitrogen atmosphere. Then the PE film was immersed in 10 v/v % GMA/methanol previously deaerated by bubbling nitrogen gas and reacted at 313 K. The PE film was reacted for a specific time ranging from 0.1 to 7 h. After grafting, the PE film was soaked in dimethylformamide and methanol for 1 h each to remove the residual monomer and homopolymer and then dried under reduced pressure. The degree of GMA grafting is defined as

$$\text{degree of GMA grafting (dg)} = 100 (W_1 - W_0) / W_0 [\%] \quad (1)$$

where  $W_0$  and  $W_1$  are the weights of the base film and GMA-grafted film, respectively. The resultant film will be referred to as an NP- or a P-GMA-grafted film, where NP and P

designate nonporous and porous, respectively. Second, the produced epoxy group was converted into an iminodiacetate (IDA) group ( $-\text{N}(\text{CH}_2\text{COOH})_2$ ) as a chelating group by immersing the GMA-grafted film to a 0.425 M sodium iminodiacetate solution at 353 K.<sup>11</sup> Both the NP- and P-GMA-grafted films were reacted for a specific time ranging from 1 to 24 h. The conversions of the epoxy group to IDA group were calculated from the weight change as follows:

$$\text{conversion} = 100 \{ [(W_2 - W_1) / 133] / [(W_1 - W_0) / 142] \} [\%] \quad (2)$$

where  $W_2$  is the weight of IDA-introduced film. The values 142 and 133 correspond to the molecular weights of GMA and IDA, respectively. The resultant chelating film will be referred to as an NP- or a P-IDA film.

**Electrical Resistivity of Film.** After both IDA films were dried under reduced pressure, they were stored in a desiccator. The surface and volume resistivities of the films were measured with a resistivity cell (Hewlett-Packard Model 16008A) connected to a high-resistance meter (Yokogawa-Hewlett-Packard Model 4329A) at ambient temperature (303–305 K). The surface resistivity ( $\Omega$ ) and volume resistivity ( $\Omega \text{ cm}$ ) are defined as follows:

$$\text{surface resistivity} = \frac{V/d}{I/t} [\Omega]$$

$$\text{volume resistivity} = \frac{Vm}{In} [\Omega \text{ cm}]$$

where  $V$ ,  $I$ ,  $d$ ,  $t$ ,  $m$ , and  $n$  are voltage, current, distance between electrodes, electrode length, film thickness, and electrode area, respectively. The voltage of the high-resistance meter was set at 500 V.

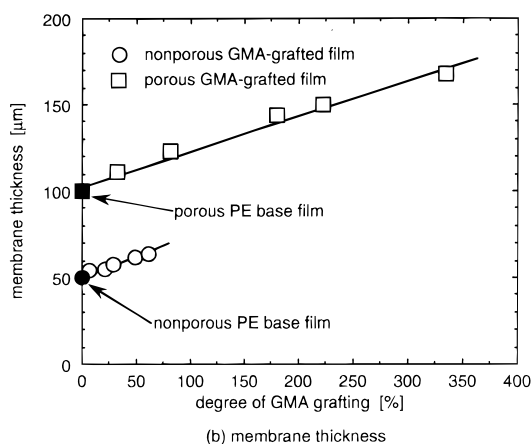
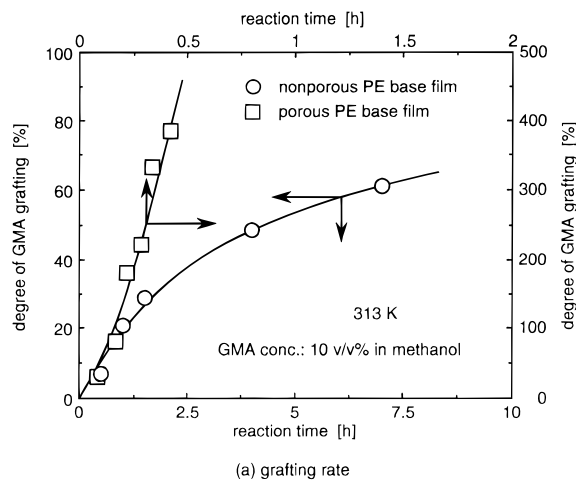
**XMA Analysis of Chelating Film.** To observe the profile of the IDA group in both NP-IDA and P-IDA films, the IDA films were equilibrated in 0.05 M  $\text{CuCl}_2$  solution buffered with acetic acid–sodium acetate solution (pH 5.1) with an excess molar ratio of copper ions in the solution to the IDA group on the film. After equilibration, the film was washed repeatedly with deionized water to remove unbound copper ions and dried under reduced pressure, and the distribution of copper ions adsorbed on the IDA film was determined by measuring the characteristic X-ray profile of copper with an electron probe X-ray microanalyzer (JOEL JXA-733 Model).

### Results and Discussion

**Grafting Rate of GMA.** During grafting, GMA monomer molecules react with the radicals formed on the crystalline surface of the existing polymer. Therefore, not all radicals produced in the entire volume of polymer during irradiation involved in the grafting

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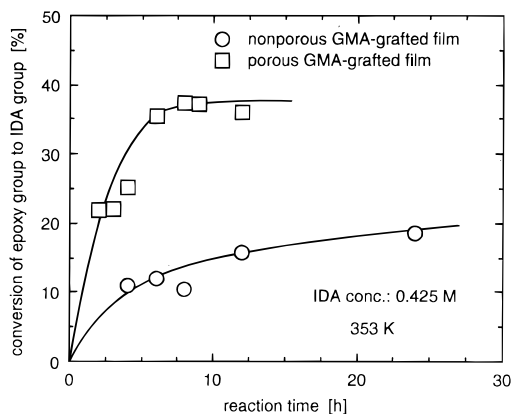


**Figure 2.** Comparison of (a) degree of grafting of GMA onto nonporous and porous polyethylene films and (b) membrane thickness of both GMA-grafted films as functions of degree of GMA grafting.

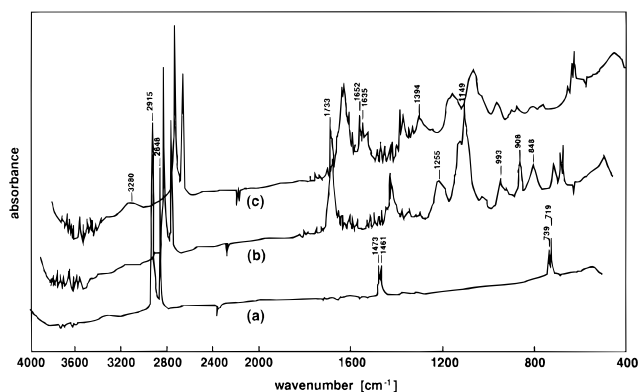
process. The degree of grafting of glycidyl methacrylate (GMA) onto the nonporous and porous PE films is compared in Figure 2a. Although almost the same radical concentrations (radicals formed in the entire volume during irradiation) were observed from ESR measurement ( $1.0 \times 10^{18}$  and  $0.83 \times 10^{18}$  spins/g for nonporous and porous PE films, respectively), a much higher degree of GMA grafting onto the porous PE film was observed here: to achieve a dg of 50%, porous and nonporous PE films required 0.1 and 4 h, respectively. This result is due to the higher specific surface area of the base film: the specific surface area of porous PE film, which is  $22 \text{ m}^2/\text{g}$  of the base film, is 500-fold larger than that of nonporous PE film. The small specific surface area of the nonporous PE film made it difficult for the GMA to diffuse into the nonporous matrix, whereas for the porous PE matrix, its large specific surface area enabled the monomer to permeate well into the reaction sites during grafting. Figure 2b shows the changes of the membrane thickness. The thickness of both membranes increased due to penetration of graft chains during GMA. The high degree of GMA grafting onto the porous PE film also led to a higher increase in membrane thickness. As a result, the selection of an appropriate solvent for grafting and pore size of a base film enables us to control the depth of the graft chain penetrating the film.

#### Introduction of Iminodiacetate Group and Complexation with Copper Ion.

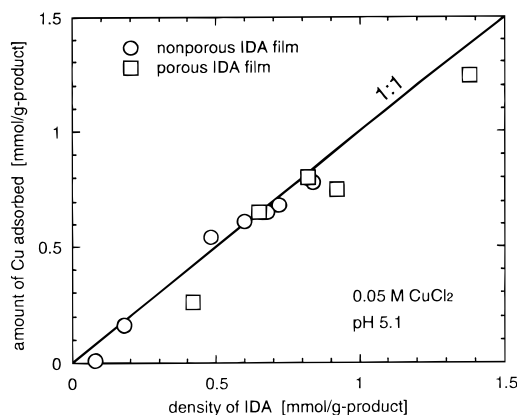
Conversion of the produced



**Figure 3.** Conversion of epoxy group to IDA group vs reaction time.



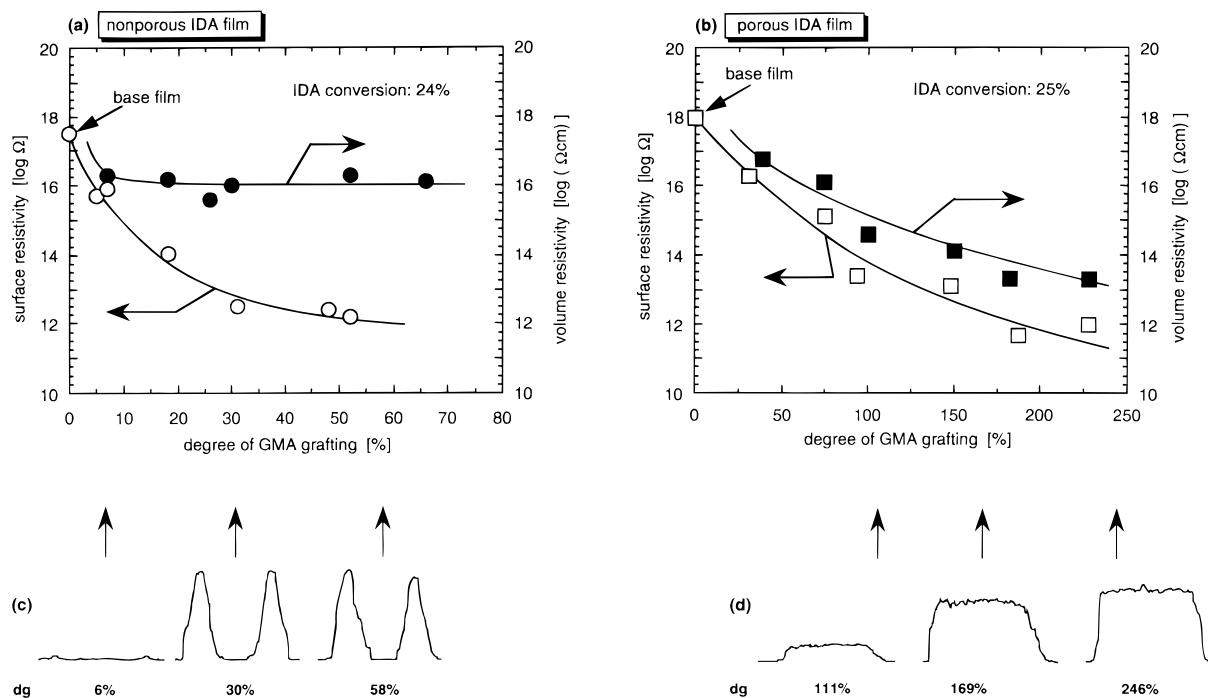
**Figure 4.** FTIR-ATR spectra of (a) porous PE film, (b) P-GMA-grafted film with a degree of GMA grafting of 185%, and (c) P-IDA film (dg 185%) with an IDA group conversion of 25%.



**Figure 5.** Complexation ratio of 1 mol of copper ion to the IDA group on the polymer chain grafted onto nonporous and porous PE films.

epoxy group of the GMA film into the iminodiacetate (IDA) group is shown in Figure 3 as a function of reaction time. The conversions for P-GMA-grafted film leveled off after 12 h at 38%, indicating that the epoxy group to which the iminodiacetate groups were accessible was satisfactorily functionalized. On the other hand, the conversion of the epoxy group in NP-GMA-grafted films increased gradually (20% at 24 h of reaction), again due to the slow penetration of IDA group into the nonporous matrix.

The existence of GMA and IDA on the P-GMA-grafted and P-IDA films, respectively, was confirmed by FTIR-ATR spectrophotometrically. Figure 4 shows the FTIR-



**Figure 6.** Comparison of surface and volume resistivities in (a) nonporous and (b) porous films with typical XMA profiles of copper ions across both (c) nonporous and (d) porous films.

ATR spectra of (a) porous PE film, (b) P-GMA-grafted film with a degree of GMA grafting of 185%, and (c) P-IDA film (dg 185%) with an IDA group conversion of 25%. The FTIR-ATR spectrum of the P-GMA-grafted film showed a sharp peak at  $1733\text{ cm}^{-1}$  due to C=O stretching in the GMA. New absorption peaks of the epoxy group and ester group of GMA were observed at  $848$ ,  $908$ , and  $993\text{ cm}^{-1}$  and  $1149$  and  $1255\text{ cm}^{-1}$ , respectively. After introduction of the IDA group, the FTIR-ATR spectrum of the P-IDA film showed new absorption peaks for the iminodiacetic acid group at  $1394$ ,  $1635$ ,  $1652$ , and  $3280\text{ cm}^{-1}$ . The absorption peaks of the epoxy group of the P-GMA-grafted film were not observed. These results indicated that the P-GMA-grafted and P-IDA films were successfully prepared.

Complexation ratio of one mole of copper ion to the IDA group on the polymer chain grafted onto the nonporous and porous PE film is shown in Figure 5. The IDA group quantitatively chelated with the copper ion until saturation. Therefore, determination of the distribution of copper ions across the films using XMA agrees with the profile of penetration of poly-GMA chains grafted onto both films.

**Formation Site of Poly-GMA Chain.** Surface and volume resistivities of the NP- and P-IDA films are shown in Figure 6a,b as functions of degree of GMA grafting. Due to the saturation of water to the IDA group of both NP- and P-IDA films, the surface and volume resistivities were measured by means of ion conduction through the IDA group. For the NP-IDA film (Figure 6a), surface resistivity showed a continuous decrease with an increase in the degree of GMA grafting, while volume resistivity showed an initial decrease and remained constant thereafter. In contrast, both surface and volume resistivities of the P-IDA film showed a continuous decrease with an increase in the degree of GMA grafting (Figure 6b).

Both NP- and P-IDA films showed low surface resistivity with increasing degree of GMA grafting because

of an increase in IDA density which is responsible for electric conductance. A constant volume resistivity of the NP-IDA film irrespective of the degree of GMA grafting indicated that the central part of the nonporous film remained ungrafted. In contrast, a gradual decrease in volume resistivity along with surface resistivity of the P-IDA film with an increase in the degree of GMA grafting indicated that the IDA-group-containing graft chain penetrated the porous film and that its density was increased.

By radiation-induced grafting, the surface resistivity of prepared IDA films (particularly based on porous matrix) can be controlled to range from  $10^{12}$  to  $10^{18}\ \Omega$ . The determination of volume resistivity of the membrane after the introduction of chelating and ion-exchange groups is simple and useful for determining the penetration ability of the graft chain.

From XMA, the difference in the formation site of the graft chains between the nonporous and porous IDA films was also observed upon the determination of the distribution of copper ion adsorbed onto the NP- and P-IDA films, as shown in Figure 6c,d. Although sufficient density of the radicals was produced throughout the thickness of the PE films by irradiation with electron beams, the diffusion of GMA monomer into the nonporous PE structure was suppressed (Figure 6c). GMA was grafted only on both sides of the nonporous film. Therefore, a constant volume resistivity of the NP-IDA film was observed. On the other hand, for the porous PE film, GMA was grafted homogeneously across the film because of its porous structure (Figure 6d). As a result, the volume resistivity of the P-IDA film decreased.

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