

"poled polymers", may be particularly attractive for electrooptic applications where  $\beta\mu_0$  and the width of the absorption band are critical characteristics.

For this work, the thiazole ring was chosen over other heterocycles because of the availability of starting materials, ease of synthesis, and an anticipated higher stability of intermediates and final products. Presumably other

heterocycles could be used and may result in further red-shifting and hopefully further narrowing of the absorption.

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## Permeability of Methyl Methacrylate Grafted Cellulose Triacetate Membrane

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Methyl methacrylate (MMA) was grafted onto a porous cellulose triacetate membrane by applying the radiation-induced graft polymerization technique in the vapor and liquid phases. Comparison of the pure water flux between the MMA-grafted membrane prepared by vapor-phase or liquid-phase grafting shows that the membrane prepared by vapor-phase grafting exhibited higher flux than the membrane prepared by liquid-phase grafting with the same amount of grafted polymer branches. The apparent specific volume of the graft phase was determined as a function of the degree of grafting from the measurement of the flux and dimensions of the resulting membrane. When vapor-phase grafting is employed, the graft chains are considered to enter the amorphous domain in the trunk polymer, which agrees with the morphological observations of the membrane.

### Introduction

A filtration membrane can be easily modified by radiation-induced graft polymerization.<sup>1</sup> The hydrophilic group<sup>2</sup> and ion-exchange group<sup>3</sup> or chelating group<sup>4</sup> were introduced into existing microfiltration membranes. Since the grafted polymer branches fill the pores of the starting polymer, the introduction of the functional group induces flux decrease. Therefore, the density of the functional group and the water flux are trade-off factors. In a previous paper,<sup>5</sup> vinyl monomers such as acrylonitrile, styrene, vinyl acetate, and acrylic acid were grafted onto a polyethylene microfiltration membrane by the preirradiation grafting technique. The reaction of the monomer vapor with the trapped radical formed in the trunk membranes was found to be a superior method in that the flux decrease was repressed.

The objectives of our study were 2-fold: (1) to prepare the methyl methacrylate grafted membrane by vapor- and liquid-phase grafting; (2) to compare the morphological change and flux of the resulting membranes. In this study, we selected a porous cellulose triacetate membrane as the trunk polymer and examined the permeability change accompanied by radiation-induced grafting by considering the location of the grafted branches.

### Experimental Section

**Materials.** A commercially available porous cellulose triacetate (CTA) membrane (FM22, Fuji Film Co., Ltd., Japan) was used as the trunk polymer for grafting. This flat membrane has been

industrially used for microfiltration. The diameter and thickness of the membrane were 47.4 and 0.179 mm in a wet state, respectively. The membrane has nominally 0.22- $\mu$ m-diameter pore size and 70% porosity. Technical-grade methyl methacrylate (MMA, Wako Pure Chemical Ind., Japan), from which the inhibitor and plasticizer were previously removed, was used.

**Preparation of MMA-Grafted Membrane.** The CTA membrane was irradiated with an accelerator operating at a beam energy of 2.0 MeV and current of 1 mA at room temperature in a nitrogen atmosphere. The dose was 200 kGy. The graft polymerization was performed by introducing MMA vapor or liquid MMA to the reaction ampule. In vapor-phase grafting, irradiated CTA membrane reacted in MMA vapor. In liquid-phase grafting, irradiated CTA membrane was immersed in liquid MMA. After predetermined periods, the membrane was removed from the ampules and washed thoroughly with benzene to remove residual MMA and poly-MMA homopolymer from the membrane. The MMA-grafted membrane was dried under reduced pressure, and the weight was measured.

The degree of grafting (dg), defined in eq 1, ranged from 10

$$dg = [(W_1 - W_0) / W_0]100 \quad (1)$$

to 100%, where  $W_0$  and  $W_1$  are the weights of the starting and MMA-grafted membranes, respectively. The MMA-grafted

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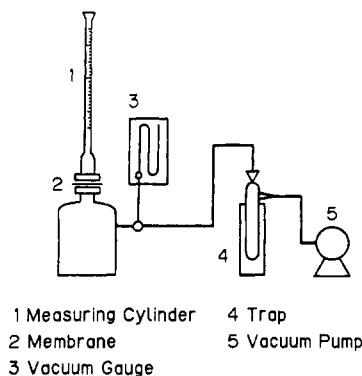
(2) Kim, M.; Saito, K.; Furusaki, S.; Sugo, T.; Okamoto, J. Submitted to *J. Membr. Sci.*

(3) Saito, K.; Kaga, T.; Yamagishi, H.; Furusaki, S.; Sugo, T.; Okamoto, J. *J. Membr. Sci.* 1989, 43, 131.

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**Figure 1.** Experimental apparatus for determining pure water flux.

membranes prepared by vapor- and liquid-phase grafting will hereafter be referred to as V-MMA-CTA and L-MMA-CTA membranes, respectively.

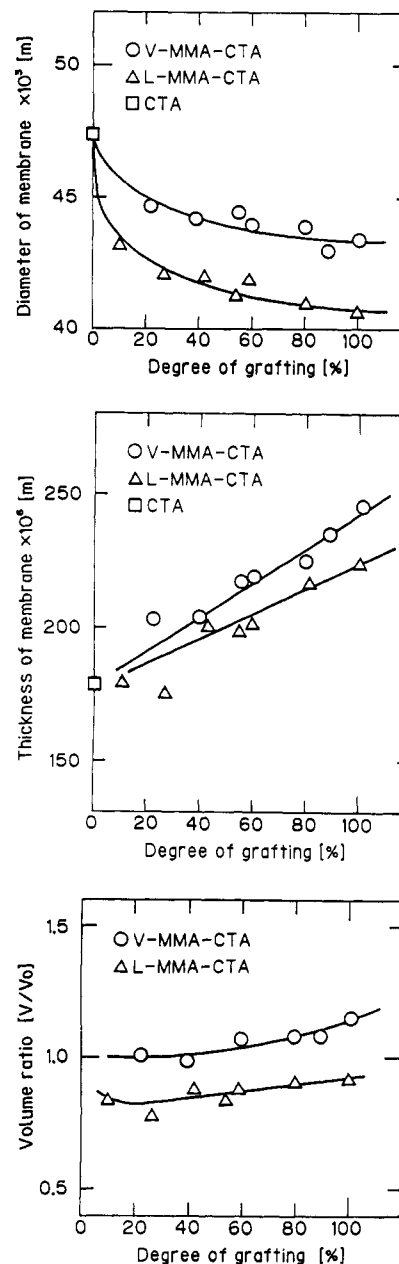
**Properties of MMA-Grafted Membrane.** The diameter and thickness of the resulting membrane were measured with a scale and a thickness meter (Ono Sokki Co., Ltd., Japan) in the wet and dry states. The surfaces of the MMA-grafted membranes ( $dg = 25$  and  $60\%$ ), which were dried under reduced pressure, were observed by means of scanning electron micrography (SEM).

**Flux Measurement.** The experimental apparatus for determining the pure water flux of the flat membrane is schematically shown in Figure 1. Before flux measurement, the MMA-grafted membrane, which was previously dried under reduced pressure, was immersed in methanol for 10 min and replaced with water. The membrane was interposed in the gaskets and the holder. The filtrate side was maintained at a constant pressure of  $10^{-2}$  kg/cm<sup>2</sup> by means of a vacuum pump, while the feed side was open to the atmosphere. The time required for the prescribed amount of pure water to permeate through the membrane was measured. The flow rate was converted into the flux by dividing by the effective surface area of the membrane. The effective surface area is the surface area through which the water permeates.

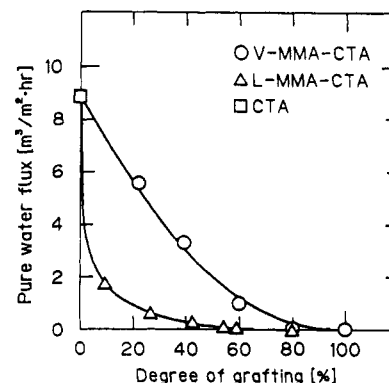
## Results and Discussion

**Properties of MMA-Grafted Membrane.** The diameter and thickness of the L-MMA-CTA and V-MMA-CTA membranes are compared in Figure 2 as a function of the degree of grafting. Both the L-MMA-CTA and V-MMA-CTA membranes shrank in diameter. The thickness of both membranes linearly increased with increasing degree of grafting. This dimensional change can be explained by considering the relaxation of the trunk polymer chains resulting from the following preparation process of the CTA membrane. The CTA dissolved in a solvent was cast in a thin film on a moving belt. The solvent was evaporated gradually and thoroughly from the surface of the film placed on the belt by applying hot air to the moving belt. The resulting membrane shrank in the direction of the membrane thickness, while the membrane stayed at the original dimensions in the direction of the membrane spreading because it was constrained in the direction parallel to the belt. Therefore, the graft polymerization of MMA onto the CTA membrane induced the contrastive relaxation of the trunk polymer chains: swelling and shrinking in the direction of the membrane thickness and spreading, respectively.

**Flux.** The V-MMA-CTA membrane exhibited a higher flux than the L-MMA-CTA membrane with the same amount of grafted branches, as shown in Figure 3. For example, the pure water flux (PWF) of the V-MMA-CTA membrane was 5 times larger than that of the L-MMA-CTA membrane with the same degree of grafting, 20%. This difference, caused by the two grafting techniques,

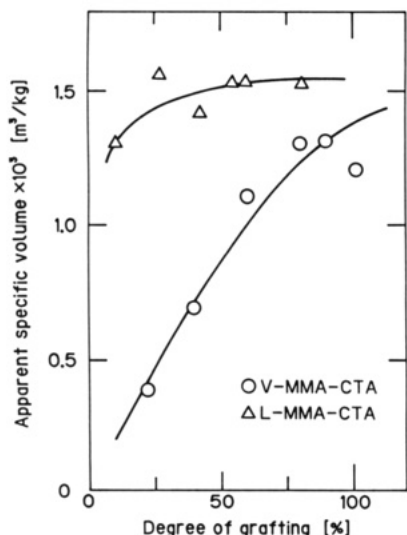


**Figure 2.** Dimensional change: (a) diameter; (b) thickness; (c) volume.



**Figure 3.** Pure water flux vs degree of grafting.

agreed with the results<sup>5</sup> obtained with the polyethylene hollow fiber membrane modified with acrylonitrile, styrene, vinyl acetate, and acrylic acid. The superiority in the water flux of the membrane prepared by vapor-phase grafting



**Figure 4.** Apparent specific volume of graft phase vs degree of grafting.

as compared to liquid-phase grafting was found irrespective of whether the trunk polymer was hydrophobic polyethylene or hydrophilic cellulose triacetate.

**Location of Graft Chain.** Kim et al.<sup>2</sup> prepared the hollow fiber containing an alcoholic hydroxyl or diol group by radiation-induced graft polymerization in the vapor phase of vinyl acetate or glycidyl methacrylate followed by subsequent saponification or acid hydrolysis and proposed a model describing the flux change caused by grafting. Their model can be applied to our system where

the porous flat membrane was modified with MMA by the two grafting techniques. The relationship between the degree of grafting and the apparent specific volume of the graft phase can be determined from the measurement of flux and the dimensions of the resulting membranes. The apparent specific volume of the graft phase,  $v_a$ , gives information on the location of the grafted branches. The derivation of  $v_a$  is described briefly as follows.

The volume change of the membrane can be expressed by

$$v + W_0 G v_a - \Delta V_p = V \quad (2)$$

where  $v$  and  $V$  are the volume including the pore volume of the starting and MMA-grafted membrane, and  $\Delta V_p$  and  $G$  are the pore volume filled with the graft chains and the dimensionless degree of grafting ( $G = (\text{dg})/100\%$ ), respectively. Assuming that the mean pore radius of a cylindrical pore,  $r$ , is formed after grafting, the pore volume is expressed by

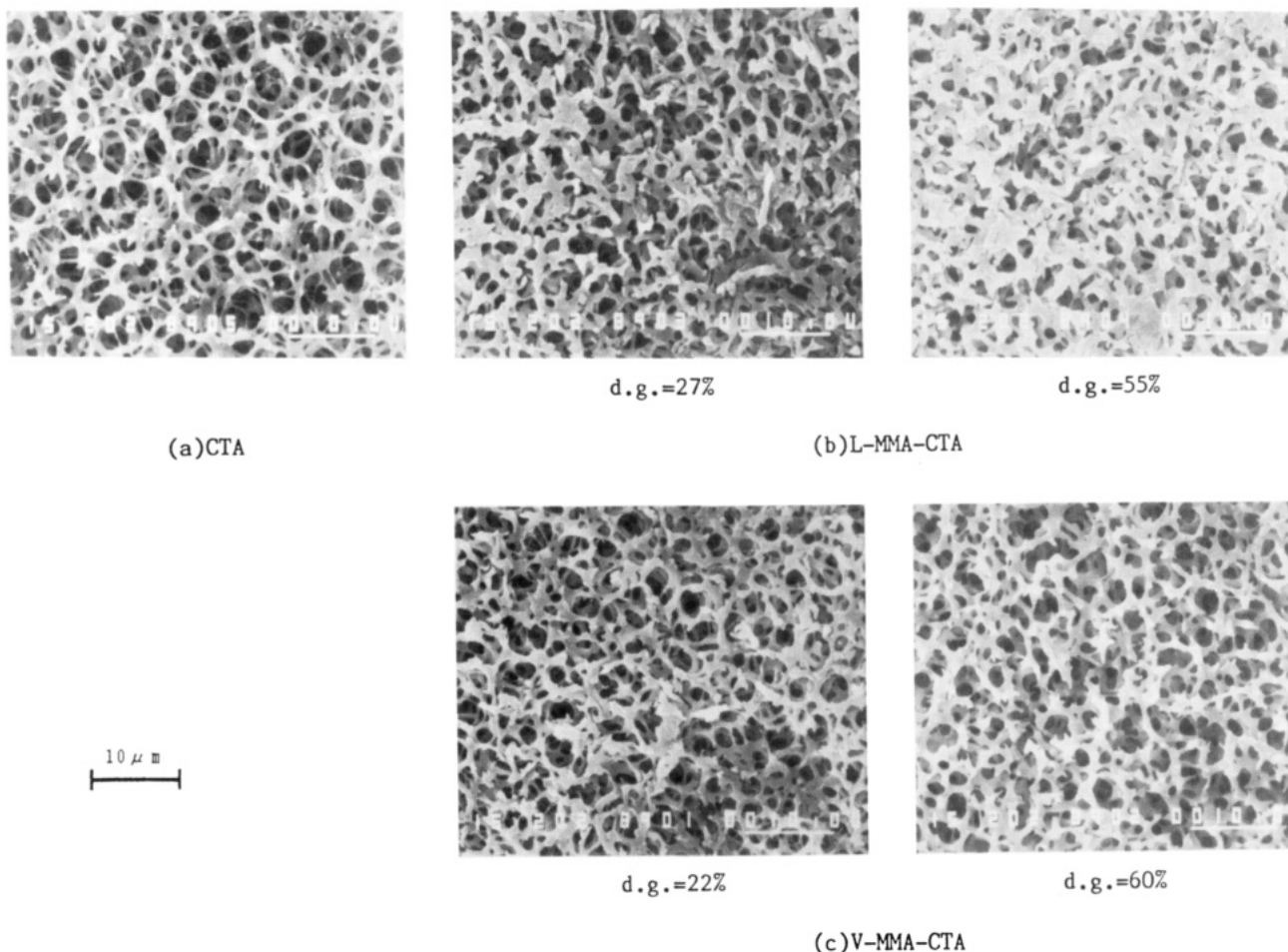
$$n\pi D^2 \pi r^2 L / 4 = v_p - \Delta V_p \quad (3)$$

hence

$$r^2 = 4(v_p - \Delta V_p) / n\pi^2 D^2 L \quad (4)$$

where  $D$  and  $L$  are the diameter and thickness of the MMA-grafted flat membrane, respectively. The number of pores per surface area is expressed by  $n$ . Also,  $v_p$  is the pore volume of the starting membrane.

In general, the water flux of the microfiltration membrane,  $J$ , can be described by the Hagen-Poiseuille equation when it is proportional to the pressure difference across the membrane.<sup>6</sup> A linear relationship between the



**Figure 5.** SEM photograph: (a) CTA; (b) L-MMA-CTA; (c) V-MMA-CTA.

flow rate and the filtration pressure was observed in our system. It is assumed that the pores in the membranes are cylinders with a constant mean radius. The cylindrical pores form a statistical, three-dimensional network in the membrane. Thus, the mean pore radius,  $r$ , includes the tortuous factors:

$$J = n' \pi r^4 \Delta P / 8 \mu L \quad (5)$$

where  $n'$ ,  $\mu$ , and  $\Delta P$  are the pore number of effective surface area, viscosity, and the filtration pressure, respectively. Inserting eqs 2 and 4 into eq 5 yields

$$J = 2n' \{v_p - (v + W_0 G v_a - V)\}^2 \Delta P / \mu n^2 \pi^3 D^4 L^3 \quad (6)$$

Since the dimensions and the flux of the membrane were measured as shown in Figures 2 and 3, respectively, the apparent specific volume of the graft phase can be obtained as a function of the degree of grafting. The grafted polymer branches are formed in two domains of the porous CTA membrane: the pore surface and the amorphous domain in the matrix. The apparent specific volume of the graft phase is defined by (the volume of the graft phase which is assumed to be formed exclusively on the pore surface)/(the weight increase calculated from the degree of grafting). Therefore, the higher volume ratio of the graft phase on the pore surface yields a higher value for  $v_a$ . On the contrary, when most of the graft phase is formed in the amorphous domain of the matrix,  $v_a$  approaches zero.

As shown in Figure 4, the  $v_a$  for the V-MMA-CTA membrane increased with an increasing degree of grafting, whereas the value of  $v_a$  for the L-MMA-CTA membrane slightly increased until the degree of grafting was 30% and approximately leveled off at about 1.5 cm<sup>3</sup>/g. These results indicated that the grafted branches are located in the amorphous region of the trunk polymer in vapor-phase grafting but in the pore surface in liquid-phase grafting at a lower degree of grafting.

**Morphological Change of Pore Structure.** SEM photographs of the surfaces of the starting, V-MMA-CTA,

and L-MMA-CTA membranes are shown in Figure 5. The reduction in porosity of the MMA-grafted membranes was observed in comparison with the starting membrane. The above discussion of the location of the grafted branches agreed fairly well with the morphology of the surfaces of the membranes whose degree of grafting were 25 and 60%. As shown in Figure 5b, the white part, indicating the CTA-MMA graft copolymer network, swelled in the L-MMA-CTA membrane due to the formation of grafted branches on the pore surface. Also, the pore diameter decreased with an increasing degree of grafting. In contrast, Figure 5c shows that the porous structure of the V-MMA-CTA membrane was almost identical with that of the starting membrane even with an increasing degree of grafting. The graft chains prepared by vapor-phase grafting entered the amorphous domain in the trunk polymer and allowed the volume of the membrane to increase, as also shown in Figure 2c.

#### Notation

|              |   |
|--------------|---|
| $D$          | diameter of MMA-grafted flat membrane, m                                |
| $G$          | dimensionless degree of grafting  |
| $J$          | pure water flux, m <sup>3</sup> /(m <sup>2</sup> h)                     |
| $L$          | thickness of MMA-grafted membrane, m                                    |
| $n$          | number of pores per surface area of membrane, m <sup>-2</sup>           |
| $n'$         | number of pores per effective surface area of membrane, m <sup>-2</sup> |
| $\Delta P$   | filtration pressure, Pa   |
| $r$          | mean pore radius of MMA-grafted membrane, m                             |
| $v$          | volume of starting membrane (including pore volume), m <sup>3</sup>     |
| $v_a$        | apparent specific volume of graft phase, m <sup>3</sup> /kg             |
| $v_p$        | pore volume of starting flat membrane, m <sup>3</sup>                   |
| $V$          | volume of MMA-grafted membrane (including pore volume), m <sup>3</sup>  |
| $\Delta V_p$ | pore volume filled by grafted branches, m <sup>3</sup>                  |
| $W_0$        | weight of starting membrane, kg   |
| $W_1$        | weight of MMA-grafted membrane, kg                                      |
| $\mu$        | viscosity, Pa h   |

**Acknowledgment.** Helpful discussions with Min Kim are gratefully acknowledged. We are also grateful to Hiroshi Ito of the Japan Atomic Energy Research Institute for performing the SEM measurements.

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## Alkali-Metal-Free Carbonate Coprecipitation: An Effective Synthetic Route to Bismuth-Based Oxide Superconductors

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Bismuth lead strontium calcium copper oxide superconductors are conveniently synthesized via coprecipitation by means of a tetraalkylammonium carbonate. This technique has the advantage over solid-state methods of placing the metal ions in close proximity prior to calcination. Precipitation pH has been optimized by monitoring its effect on metal concentrations in the filtrate, crystallinity of the precipitate, filtering times, and properties of the calcined, superconducting material. The sample initially precipitated at pH 8 produces the most phase-pure -2223 material.

### Introduction

Coprecipitation of oxide precursors such as hydroxides or carbonates is a widely used technique in the synthesis of many mixed metal oxides.<sup>1</sup> It has the significant advantage over solid-state synthesis ("grind-and-fire" meth-

ods) of potentially placing the component metal ions within atomic distances of each other, greatly facilitating solid-state diffusion and minimizing the risk of unwanted phase formation. Furthermore, coprecipitation avoids the grinding steps inherent in solid-state synthesis, which can ultimately lower phase purity by the incorporation of grinding media. Complications arise, however, when the conditions for precipitation of the individual component

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