# Studies on Synthetic-Polymer Plates with High Surface Energy. II. Diethylene Glycol Bis(allyl Carbonate)–Unsaturated Carboxylic Acid System

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## Synopsis

Polymer plates with high surface energy were prepared by the procedure described in the previous paper, using diethylene glycol bis(allyl carbonate) as a substrate polymer and acrylic acid or methacrylic acid as a hydrophilic monomer. By the alkali treatment (immersing in an aqueous $0.1N$ NaOH solution for 2 h), the resulting polymer plates had good water wettability (contact angle for water = 10°) and sufficient mar resistance (the scratching hardness = 45–50 g) in a dry state, and their clarities were higher than those for DAP systems previously reported. The surface densities of carboxyl groups on the polymer plate estimated by use of the McBain's equation were 0.18–0.46 molecule/$Å^2$.

## INTRODUCTION

It is very important in practical use to give various surface properties to transparent synthetic polymer materials. In the previous paper,[1] we reported a new modification technique, introducing hydrophilic monomers with a functional group [acrylic acid (AA) and methacrylic acid (MAA)] on the surface of the hydrophobic polymer plate [diallyl phthalate (DAP)]. The resulting gel plates (GPs) had good water wettability and sufficient mar resistance, but had a light yellow green color.

Diethylene glycol bis(allyl carbonate) (CR-39) polymers are colorless, and possess several advantages over other plastics (e.g., abrasion resistance, dimensional stability, and heat resistance).[2] In this paper, CR-39 ($M_1$) was used as the substrate polymer, and the GPs with high surface energy were prepared by the procedure previously reported.[1] The surface properties of the resulting GPs were measured, and the surface density of carboxyl groups on the GP surface was estimated by use of the McBain's equation.[3,4]

## EXPERIMENTAL

### Materials

CR-39, AA, and MAA were purified by distillation (boiling point 130–140°C/0.01–0.03 Torr for CR-39, 43°C/14 Torr for AA and 51°C/6 Torr for MAA). Benzoyl peroxide (BPO) was purified by precipitation from chloroform solution with methanol. Methylene blue trihydrate purchased from Wako Pure Chemical Industries, Ltd., was used without further purification.

## Preparation of the GPs

CR-39 ($M_1$ monomer) containing 6 wt % BPO was filled in a casting cell, then was heated at 90°C for $t_1$ min to obtain a prepolymer gel plate (PGP, the size of 15 mm × 50 mm × 1.5 mm).

In order to clarify a change in compositions of the PGPs with $t_1$, they were fractionated into the following three parts by means of solvent extraction: methanol-soluble part, residual monomer; methanol-insoluble and acetone-soluble part, oligomer and linear polymer; acetone-insoluble part, network polymer.

The PGP taken apart from the casting cell was placed in a glass tube containing 15 g of an aqueous $C$ wt % $M_2$ monomer solution at 90°C for 4 h.  AA and MAA were used as $M_2$ monomer.  In order to completely remove the water-soluble part from the resulting GP, the cycle of alkali treatment (immersing in an aqueous $0.1N$ NaOH solution for 2 h) and acid treatment (immersing in an aqueous $0.1N$ HCl solution for 2 h) was repeated several times until the decrease in the weight of the GP was not recognized.  The value of the weight increment ($\Delta W$) was defined as

$$\Delta W = [(W_1/W_0) - 1] \times 100\%$$

where $W_0$ is the weight of the PGP and $W_1$ is that of the GP after removing the water-soluble part.  It should be noticed that the amount ($\Delta W_{in}$) of $M_2$ diffusing into the PGP is the sum of the observed $\Delta W$ and the amount of CR-39 monomer diffusing out of the PGP.

The CR-39 homopolymer plate (CR-39 HP) was also prepared by placing the PGP in a glass tube, containing 15 g of distilled water, at 90°C for 4 h.

## Measurement of the Properties of the GPs

As a measure of water wettability, the equilibrium contact angles ($\theta$) of distilled water drops on the GP were measured with an Erma Model G-I Contact Angle Meter at 20°C and 65% RH.  Prior to the measurement, the specimens were treated as follows:  The GP after alkali treatment (immersing in an aqueous $0.1N$ NaOH solution for 2 h) or acid treatment (immersing in an aqueous $0.1N$ HCl solution for 2 h) was washed with water and $n$-hexane, followed by drying under reduced pressure.  Contact angles on the alkali- and acid-treated GPs were designated as $\theta_i$ and $\theta_f$, respectively.

A slice of the GP about 100 $\mu$m thick, which was prepared by cutting and grinding perpendicular to the GP surface, was alkali treated, and then immersed in an aqueous 0.01-mol/L methylene blue solution at ambient temperature for 48 h.  Because the CR-39 HP was not entirely stained with methylene blue under the above condition, the thickness ($d$) of the stained measured from the micrograph of the slice was regarded as that of the copolymer layer.

The antifogging property was estimated qualitatively from fogging or dewing on the surface of the GP in the same manner as described in the previous paper.[1]
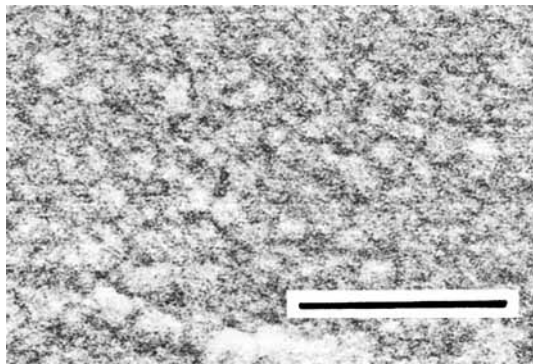
The mar resistance of the GP was estimated by the scratching hardness test using a TYPE-HEIDON-14 Surface Tester at 25°C and 70% RH.  The values of the mar resistance were expressed as the vertical lord against the sapphire needle point.
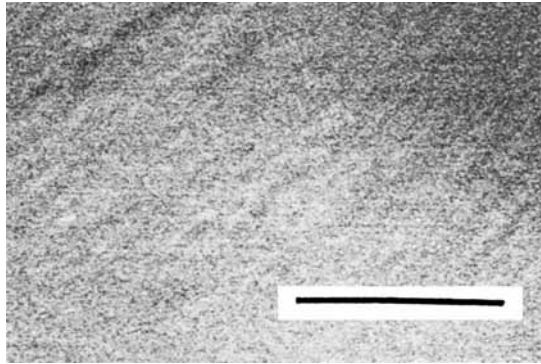
(a)
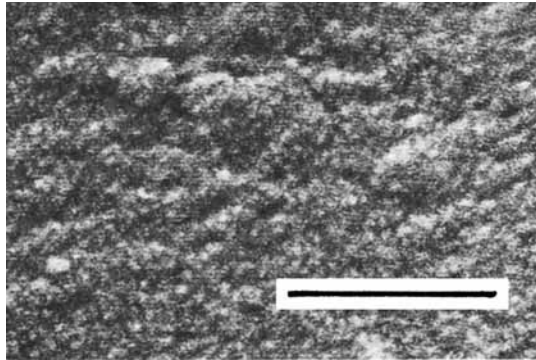


(b)



(c)

Fig. 1. Scanning electron micrographs of the surface structure of the GPs under the condition of 100,000 magnifications: (a) CR-39—HP; (b) CR-39—AA GP prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, $t_2 = 4$ h, and $C = 5$ wt %; (c) CR-39—MAA GP prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, $t_2 = 4$ h, and $C = 1.5$ wt %. The bar represents 0.1 $\mu$m.
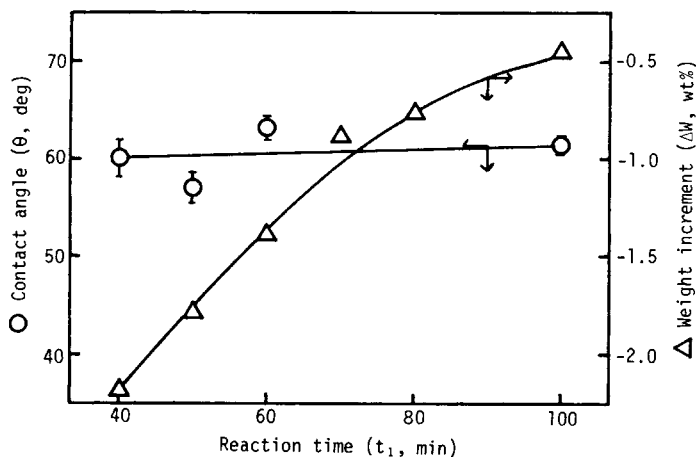
Fig. 2. Effects of reaction time ($t_1$) on contact angle ($\theta$, O) and weight increment ($\Delta W$, $\triangle$) for CR-39 HPs prepared under the condition of $T_1 = T_2 = 90°C$ and $t_2 = 4$ h. Bars on the $\theta$ data point represent one SD.

## Attenuated Total Reflection Infrared Absorption Spectra

Attenuated total reflection infrared absorption spectrum (ATR spectrum) of the surface of the GP (the size of 20 mm × 50 mm × 1.5 mm) was taken with a Hitachi Model 225 Infrared Spectrophotometer and a KRS-5 prism ($n = 2.37$). It should be noted that the penetrating depth of an incident light in the GP was about 1.3 $\mu$m from theoretical calculation in the region of the examined wave numbers.[5] As a measure of the quantity of $M_2$ monomer unit existing in the GP surface, the relative absorption intensity ($Ra$) was calculated from

$$Ra = D_2/D_1 \tag{1}$$

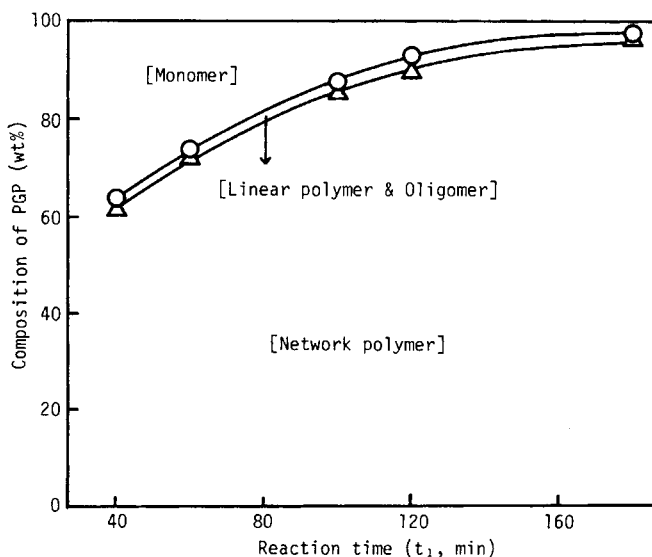where $D_1$ is the absorption intensity at 1740 cm$^{-1}$ due to carbonic ester group



Fig. 3. Change in composition of CR-39 PGP with reaction time ($t_1$) at 90°C. (O) Methanol-insoluble part; ($\triangle$) acetone-insolule part.

of CR-39 monomer unit and $D_2$ is that due to carboxylic ion of AA (1580 cm$^{-1}$) or MAA (1560 cm$^{-1}$) monomer unit.

## Observation of the GP Surface with Scanning Electron Microscope

The GP surface was observed by means of a scanning electron microscope (JEOL Field Emission Scanning Electron Microscope JFSH-30) at a voltage of 30 kV. Pretreatment of the sample was carried out by the same method described in the previous paper.[1]

## Estimation of the Surface-density of Carboxyl Groups on the GP Surface

When the alkali-treated GP is immersed in an excess of aqueous HCl solution, it might be predicted that sodium ion on the GP surface is immediately exchanged with hydrogen ion, but that sodium ion located inside the GP is more slowly ion-exchanged due to requirements of penetration of hydrogen ion into the GP and movement of sodium ion to the surface.

In order to estimate sodium ion on the GP, we carried out an application of the McBain's equation to the latter ion exchange.[3,4] The rate of diffusion of low-molecular-weight species from an aqueous solution into a platelike polymer substrate ($2L$ in thickness) is expressed by the McBain's equation (2), assuming that the concentration of the species in an aqueous phase is constant and the diffusion constant ($D$) is independent of the concentration of the species in the polymer substrate:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[-(2n+1)^2 \pi^2 \frac{Dt}{4L^2}\right] \qquad (2)$$

where $M_t$ and $M_\infty$ are the total amount of the species incorporated into the substrate after time $t$ and at equilibrium, respectively. In the case of $M_t/M_\infty$ = 0–0.6, the value of $M_t/M_\infty$ can be adequately approximated with the first term in the expansion of eq. (2):

$$M_t/M_\infty = 2(Dt/\pi L^2)^{1/2} \qquad (3)$$

This means that $M_t$ is proportional to the square root of $t$.

The surface density of carboxyl groups was estimated with the aid of eq. (3) as follows: (1) The GP was immersed in an aqueous 0.1$N$ NaOH solution for 24 h, and followed by washing with water and $n$-hexane and by drying under reduced pressure. (2) Several glass tubes containing 5 mL of an aqueous 0.1$N$ HCl solution were placed in a row. The above-treated GP was placed in one of them, and was transferred in turn into the next glass tube at specified time intervals. The concentrations of sodium ion contained in the glass tubes were determined from the absorbance at 589.0 nm by the flame photometry using a Varian Techtron Model AA-5 Atomic Absorption Spectrophotometer. (3) The amount [$A_t$ (molecules/Å$^2$)] of sodium ion diffusing out of the GP was plotted against the square root of the immersion time ($t$). An intercept of the resulting straight line on $M_t$ axis was regarded as the amount [$A_0$ (molecules/Å$^2$)] of sodium ion (i.e., carboxyl group) on the GP surface.
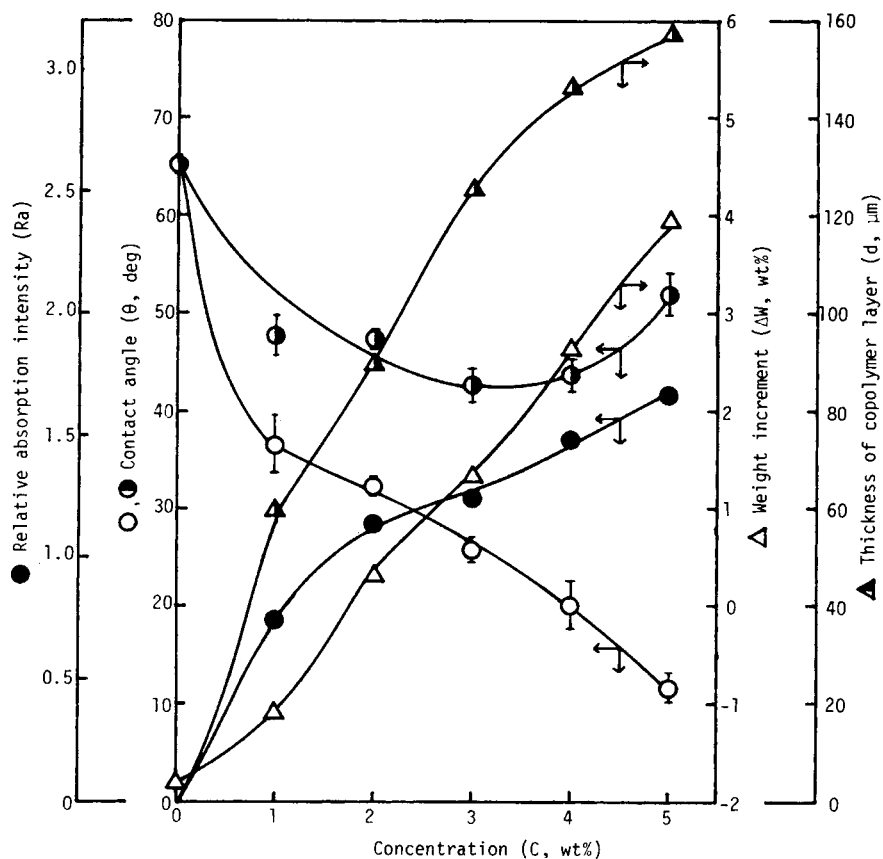
Fig. 4. Effects of concentration $(C)$ of immersion solution on contact angle after alkali treatment $(\theta_i, \bigcirc)$ and after acid treatment $(\theta_f, \mathbf{\Phi})$, weight increment $(\Delta W, \triangle)$, thickness of copolymer layer $(d, \blacktriangle)$, and relative absorption intensity $(RA, \bullet)$ for CR-39—AA GPs prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, and $t_2 = 4$ h.   Bars on the $\theta$ data point represent one SD.

## RESULTS AND DISCUSSION

### Properties of the GP

ATR spectra for the alkali-treated GPs after removing the water-soluble part were of the peak at 1580 cm$^{-1}$ for CR-39—AA GPs and at 1560 cm$^{-1}$ for CR-39—MAA GPs due to the respective carboxylic ion, from which the existence of M$_2$ monomer unit in the surface layer of the GPs was confirmed.

The surface structure of the GPs was clarified from the observation by means of a scanning electron microscope under 100,000 magnification.   As shown in Figure 1, the surface of the CR-39 HP (a) was almost flat, but those of the GPs for CR-39—AA (b) and CR-39—MAA (c) systems exhibited orange-peel surfaces covered all over with grains of about 0.01 $\mu$m size.   These grains are presumably due to a mutual aggregation of the chains predominantly composed of M$_2$ monomer unit on the GP surface.

As shown in Figure 2, the values of $\theta$ for the CR-39 HPs remained almost constant in the range of $t_1$ examined, and the mean value was 60.1°.   The negative values of $\Delta W$ for the CR-39 HPs (designated as $\Delta W_0$) correspond to the
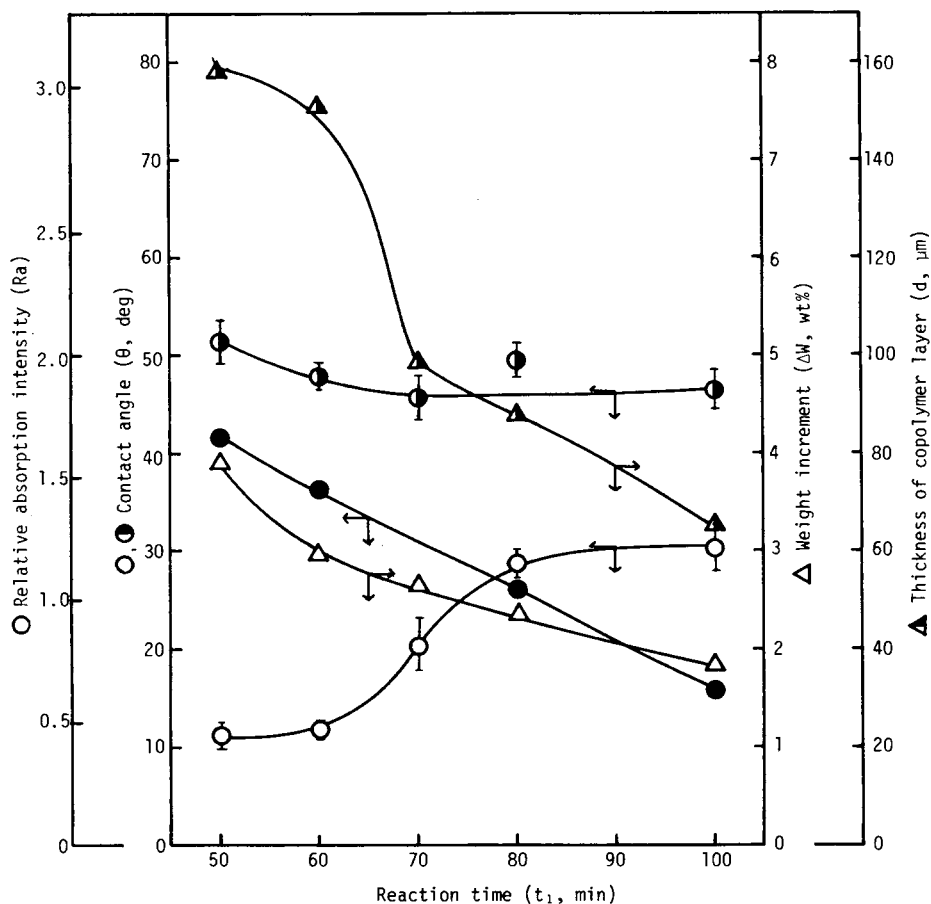
Fig. 5. Effects of reaction time $(t_1)$ on contact angle after alkali treatment ($\theta_i$, O) and after acid treatment ($\theta_f$, ◑), weight increment ($\Delta W$, △), thickness of copolymer layer ($d$, ▲), and relative absorption intensity ($Ra$, ●) for CR-39—AA GPs prepared under the condition of $T_1 = T_2 = 90°C$, $t_2 = 4$ h, and $C = 5$ wt%. Bars on the $\theta$ data point represent one SD.

amount of CR-39 monomer diffusing out of the PGP and the reduced amount decreased with an increase in $t_1$ due to the reduction in CR-39 monomer remaining. The change in composition of the PGP is shown in Figure 3. In addition, the mar resistance and the antifogging property are listed in Table I (nos. 1 and 2).

Effects of the preparation conditions ($C$ and $t_1$) of the GPs on $\theta$, $\Delta W$, and $d$ for CR-39—$M_2$ systems were found to be similar to DAP—$M_2$ systems described in the previous paper.[1]

For CR-39—AA system, effects of $C$ on $\theta$, $\Delta W$, $d$, and $Ra$ under the condition of $t_1 = 50$ min are shown in Figure 4, where the results for $C > 5$ wt % were omitted because there occurred a gelation in the immersion solution. Further, effects of $t_1$ on $\theta$, $\Delta W$, $d$, and $Ra$ under the condition of $C = 5$ wt % are shown in Figure 5, where the results for $t_1 < 50$ min were omitted because the mechanical strength of the PGP was too much weak to handle. The following relations were found: (1) The values of $\Delta W$ and $d$ increased with an increase in $C$, and decreased with an increase in $t_1$ due to reduction in the remaining CR-39 monomer
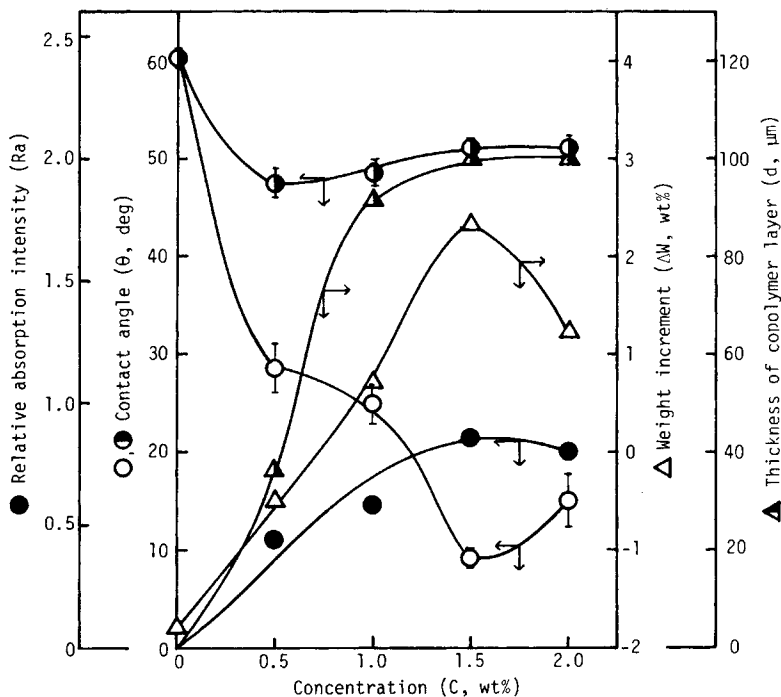
Fig. 6. Effects of concentration ($C$) of immersion solution on contact angle after alkali treatment ($\theta_i$, O) and after acid treatment ($\theta_f$, ◐), weight increment ($\Delta W$, △) thickness of copolymer layer ($d$, ▲), and relative absorption intensity ($RA$, ●) for CR-39—MAA GPs prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, and $t_2 = 4$ hr. Bars on the $\theta$ data point represent one SD.

in the GP. (2) The water wettability for the GP surface depends upon the surface density and the orientation of carboxyl group of the GP. The values of $\theta_i$ were lower than those of $\theta_f$ due to the high degree of dissociation of carboxylic salt. As can be seen from the change in the values of $Ra$, the proportions of $M_2$ monomer unit to $M_1$ monomer unit existing in the surface layer of the GPs increased with an increase in $C$ and a decrease in $t_1$. Such an increase leads to a reduction in the values of $\theta_i$. The change in $\theta_f$ with $C$ and $t_1$ is similar to that for the DAP—$M_2$ systems, and is presumably due to the burial of carboxyl groups in the grain on the surface mentioned above.

As shown in Figures 6 and 7, the trends for CR-39—MAA system, except the case of $C > 1.5$ wt %, were found to be similar to CR-39—AA system. In the case of $C = 2$ wt %, a white powdered polymer was observed to be deposited on the PGP surface. The above results at $C = 2$ wt % are presumably attributed to reduction in diffusion rate of MAA monomer into the PGP brought by the deposited polymer.

Various properties of the GPs prepared under the optimum conditions are listed in Table I (nos. 3, 4, 5, and 6). The surface of the alkali-treated GPs had good water wettability and antifogging property, whereas that of the acid-treated GPs had poor water wettability and antifogging property. The mar resistance of the GPs in a dry state was much the same as that of the CR-39 HPs, and the GPs in a wet state had slightly poorer mar resistance than those in a dry state due to a large amount of water in the surface layer due to $M_2$ monomer units.

In order to estimate durability of water wettability, the values of $\theta$ for the al-
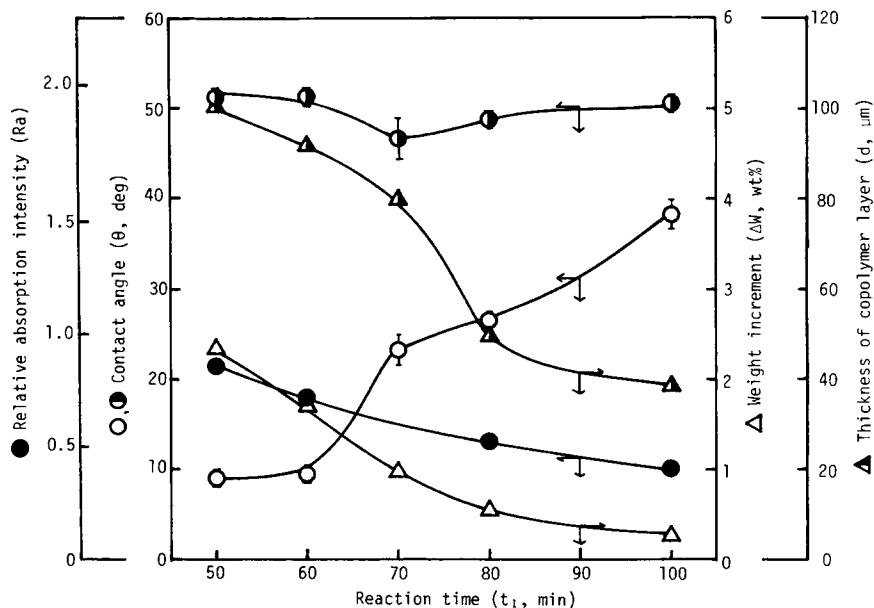
Fig. 7. Effects of reaction time ($t_1$) on contact angle after alkali treatment ($\theta_i$, O) and after acid treatment ($\theta_f$, ◑), weight increment ($\Delta W$, △), thickness of copolymer layer ($d$, ▲), and relative absorption intensity ($Ra$, ●) for CR-39—MAA GPs prepared under the condition of $T_1 = T_2 = 90°C$, $t_2 = 4$ h, and $C = 1.5$ wt %. Bars on the $\theta$ data point represent one SD.

kali-treated GPs after immersion in a large amount of water for a long time were examined. As shown in Figure 8, those increased with an increase in water-immersion time due to a conversion of carboxylic salt existing in the GP surface into free form, and consequently the GPs became poor in water wettability. By the alkali treatment, however, the values of $\theta$ and $Ra$ for the above GPs were regained, and the GPs exhibited good water wettability again. This mode could be repeated again and again.

## Estimation of the Surface-Density of Carboxyl Groups on the GP Surface

As shown in Figure 9, plots of $\sqrt{t}$ vs. $A_t$ in the short duration of HCl immersion give a straight line, which implies that eq. (3) is applicable in this case. As listed in Table I, the values of $A_0$ are in the range of 0.18–0.46. On the other hand, the amount of carboxyl group on the lateral face of the specimen was estimated to be of the order of a few per cent compared to that on the surface. In addition, the amount of sodium ion in the GP surface layer was estimated as less than 0.01 molecule/Å² from a blank run, in which the CR-39 HP was examined by the same procedure as that for the GP. It is clear that the adsorbed amount of sodium ion is negligibly small compared to the above $A_0$ values. Therefore, the $A_0$ values can be stated to correspond to the amount of carboxyl group on the GP surface without any correction. Assuming that $M_2$ monomer units exist on the GP surface in a monolayer mode, the above $A_0$ values seem to be too large. However, such high $A_0$ values can be conceivable due to the irregular surface structure of the GPs, as shown in Figure 1. It appears that the slope of $\sqrt{t}$ vs. $A_t$ plots became steep with an increase in $M_2$ content in the GP surface layer.

TABLE I
Properties of the GPs for CR-39—AA and CR-39—MAA Systems

| GP no. Systems | 1 CR-39—HP | 2 CR-39—HP | 3 CR-39—AA | 4 CR-39—AA | 5 CR-39—MAA | 6 CR-39—MAA |
|---|---|---|---|---|---|---|
| Preparation condition | | | | | | |
| $t_1$ (min) | 50 | 60 | 50 | 60 | 50 | 60 |
| conversion of PGP (wt %) | 69 | 74 | 69 | 74 | 69 | 74 |
| C (wt %) | 0 | 0 | 5 | 5 | 1.5 | 1.5 |
| Physical properties | | | | | | |
| $\theta_i$ (°) | — | — | 11.5 | 12.0 | 9.2 | 9.4 |
| $\theta_f$ (°) | $(60.1)^a$ | — | 51.6 | 48.0 | 51.1 | 51.3 |
| $\Delta W_{in}$ (wt %)[b] | 0 | 0 | 5.75 | 4.38 | 4.13 | 3.08 |
| $\Delta W_{out}$ (wt %)[c] | — | — | 1.62 | 1.60 | 1.65 | 0.97 |
| $d$ (μm) | — | — | 157.9 | 151.4 | 100.7 | 92.2 |
| Water content (wt %)[d] | 0.51 | — | 1.34 | 1.05 | 1.07 | 0.90 |
| $Ra$ | — | — | 1.66 | 1.45 | 0.86 | 0.70 |
| Antifogging property | | | | | | |
| II[e] | — | — | TD[f] | TD | TD | TD |
| II[g] | poor | poor | poor | poor | poor | poor |
| Scratching hardness (g) | | | | | | |
| I | — | — | 45 | 45 | 50 | 45 |
| II | 40 | 45 | 45 | 45 | 50 | 50 |
| III[h] | 30 | 40 | 35 | 40 | 40 | 40 |
| Surface density of carboxyl group | | | | | | |
| $A_0$ (molecules/Å$^2$) | 0.01 | — | 0.41 | 0.27 | 0.46 | 0.18 |
| Slope (molecules/Å$^2 \cdot$ s$^{1/2}$) | 0.05 | — | 1.47 | 0.74 | 0.88 | 0.59 |

[a] The mean value for several CR-39 HPs.

[b] $\Delta W_{in} = \Delta W - \Delta W_0$, and is an apparent amount of $M_2$ diffusing into the PGP.

[c] $\Delta W_{out}$ is the amount of the water-soluble part in the GP surface, that is, $\Delta W_{out} = [(W_2 - W_1)/W_0] \times 100\%$, where $W_2$ is the weight of the nontreated GP.

[d] Water content $= [(W_3/W_1) - 1] \times 100\%$, where $W_3$ is the weight of the GP in a wet state.

[e] The alkali-treated GP.

[f] A transparent dewing state.
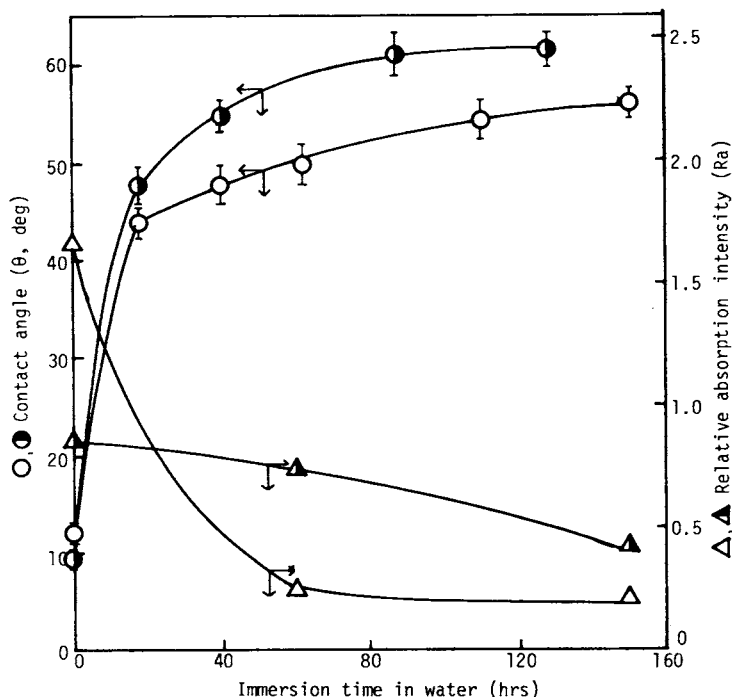
[g] The acid-treated GP.

[h] The GP in a wet state.

Fig. 8. Change of contact angle ($\theta$) and relative absorption intensity ($Ra$) of the alkali-treated GPs with immersion time in water: (O, $\triangle$), CR-39—AA GP prepared under the condition of $T_1$ = $T_2$ = 90°C, $t_1$ = 50 min, $t_2$ = 4 h, and $C$ = 5 wt %; (⦷, ▲), CR-39—MAA GP prepared under the condition of $T_1$ = $T_2$ = 90°C, $t_1$ = 50 min, $t_2$ = 4 h, and $C$ = 1.5 wt %. Bars on the $\theta$ data point represent one SD.

TABLE II
Partition Coefficients between $M_1$ Monomer and Water for $M_2$ Monomer[a] and Reactivity Ratios for $M_1$ and $M_2$ Monomers[b]

| $M_2$ monomer | CR-3.9 | | | DAP | | |
|---|---|---|---|---|---|---|
| | $\alpha$ | $r_1$ | $r_2$ | $\alpha$ | $r_1$ | $r_2$ |
| AA | 0.95 | 0.03 | 33 | 0.47 | 0.044 | 19.1 |
| MAA | 3.42 | 0.009 | 100 | 1.99 | 0.021 | 44.1 |

[a] $\alpha = [M_2]_{M_1}/[M_2]_{water}$ at 90°C.

[b] The experimental values for CR-39—$M_2$ systems were estimated from the Fineman–Ross–Plots using compositions of the copolymer determined by infrared analysis, and the values for DAP—$M_2$ systems were calculated from $Q$-$e$ values.

## Comparison between AA and MAA Used as $M_2$ Monomer

Comparisons of no. 3 with no. 5 and of no. 4 with no. 6 indicate that, in spite of the considerable difference in $C$, the GPs for CR-39—MAA system had similar properties to those for CR-39—AA system. The partition coefficients ($\alpha$) between CR-39 monomer and water for $M_2$ monomer at 90°C and the monomer reactivity ratios ($r_1 - r_2$) for CR-39—$M_2$ systems are listed in Table II. It is noted from the $\alpha$ values that MAA is more hydrophobic than AA due to the existence of methyl group in $\alpha$-position, and from the monomer reactivity ratios that a composition of CR-39—$M_2$ copolymer at any specified feed ratio has always a higher content of MAA than of AA. The above results are clearly ex-
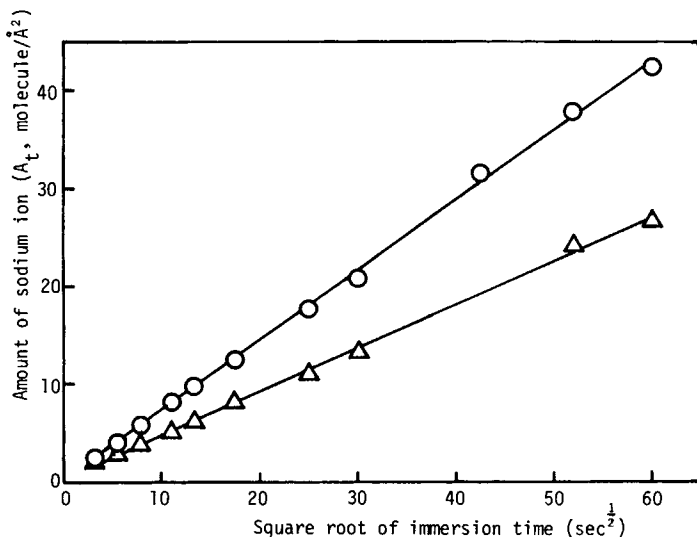
Fig. 9. Relationship between the square root of immersion time ($t$) in an aqueous $0.1N$ HCl solution and the amount ($A_t$) of sodium ion desorbed. (O) CR-39—AA GP prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, $t_2 = 4$ h, and $C = 5$ wt %. (△) CR-39—MAA GP prepared under the condition of $T_1 = T_2 = 90°C$, $t_1 = 50$ min, $t_2 = 4$ h, and $C = 1.5$ wt %.

plained from these factors in a similar manner to DAP—$M_2$ systems described in the previous paper.[1]

### Comparisons of CR-39—$M_2$ Systems with DAP—$M_2$ Systems

In order to clarify the influence of the type of $M_1$ monomer, CR-39 or DAP, comparisons of no. 3 with no. 9 and of no. 5 with no. 11 (the data for DAP—$M_2$ systems are listed in Table III) were carried out, where monomer conversions of both CR-39 and DAP PGPs were on the same level. The values of $d$ and $A_0$ for CR-39—$M_2$ systems were larger than those for DAP—$M_2$ systems, respectively. These results are explained as follows: (1) The affinity of CR-39 for $M_2$ is much higher than that of DAP, as indicated in the $\alpha$ values of Table II. (2) $M_2$ content in CR-39—$M_2$ copolymer is always higher than that in DAP—$M_2$ copolymer at any specified feed ratio ($M_1/M_2$), as calculated from $r_1 - r_2$ values in Table II.

As shown in nos. 8 and 10, GPs with high $A_0$ value could be prepared from DAP—$M_2$ systems using PGP with a low level in monomer conversion, whereas the CR-39 PGP with such a low level is too weak to handle. Poly(AA) and poly(MAA) are known to be hard and brittle solids. The difference in $M_2$ content between these monomer systems led to the following results. The DAP—$M_2$ GPs with high $A_0$ value in a dry state had better mar resistance than the CR-39—$M_2$ GPs, whereas the former in a wet state had poorer mar resistance than the latter. Further, because the surface of the GPs was covered with chains predominantly composed of $M_2$ monomer units, in spite of the difference in the $A_0$ values, the $\theta_i$ values remained almost unchanged.

The advantages of the CR-39—$M_2$ system over the DAP—$M_2$ system were as follows: (1) The CR-39—$M_2$ GPs with high surface energy were obtained

TABLE III
Properties of the GPs for DAP—AA and DAP—MAA Systems

| GP no. | 7 | 8 | 9 | 10 | 11 |
| Systems | DAP HP | DAP—AA | DAP—AA | DAP—MAA | DAP—MAA |
|---|---|---|---|---|---|
| Preparation condition | | | | | |
| $T_1 = T_2$ (°C) | 90 | 90 | 90 | 90 | 90 |
| $t_1$ (min) | 100 | 100 | 160 | 100 | 160 |
| $t_2$ (h) | 6 | 6 | 6 | 6 | 6 |
| $C$ (wt %) | 0 | 5 | 5 | 2 | 1.5 |
| Conversion of PGP (wt %) | 53 | 53 | 69 | 53 | 69 |
| Physical properties | | | | | |
| $\theta_i$ (°) | — | 10.5 | 13.2 | 13.1 | 22.1 |
| $\theta_f$ (°) | (66.5)[a] | 43.0 | 52.9 | 58.2 | 57.1 |
| $\Delta W_{in}$ (wt %) | 0 | 9.88 | 4.59 | 11.11 | 4.40 |
| $\Delta W_{out}$ (wt %) | — | 0.35 | 0.44 | 0.58 | 0.57 |
| $d$ (μm) | — | 119.1 | 26.4 | 137.5 | 45.6 |
| Water content (wt %) | 0.25 | 1.08 | 0.72 | 1.33 | 0.73 |
| Scratching hardness (g) | | | | | |
| I | — | 70 | — | 65 | — |
| II | 20 | 65 | — | 55 | — |
| III | 25 | 15 | — | 15 | — |
| Surface-density of carboxyl group | | | | | |
| $A_0$ (molecules/Å²) | — | 1.29 | 0.30 | 4.17 | 0.16 |
| Slope (molecules/Å²·s$^{1/2}$) | — | 0.72 | 0.16 | 8.62 | 0.30 |

[a] The mean value for several DAP—HPs.

under the condition of higher $M_1$ monomer conversion of the PGP than the DAP—$M_2$ GPs. (2) The clarities for the CR-39—$M_2$ GPs were higher than those for the DAP—$M_2$ GPs. For example, the transmittances for the DAP—$M_2$ GPs were 84–92% at 420 nm using the CR-39—$M_2$ GPs as a reference.

## CONCLUSION

The GPs with high surface energy were prepared by the procedure described in the previous paper,[1] using CR-39 as a substrate polymer, and AA or MMA as a functional monomer.

(1)    The alkali-treated GPs for CR-39—$M_2$ systems had good water wettability and sufficient mar resistance in a dry state, and their clarities were higher than those for DAP—$M_2$ systems.

(2)    The surface-density of carboxyl groups on the GP could be estimated by an application of the McBain's equation.

(3)    In the case of $M_1$ = CR-39, the GP prepared under lower concentration of an aqueous MAA solution had almost similar properties to that under higher concentration of an aqueous AA solution. The values of $d$ and $A_0$ for CR-39—$M_2$ systems were larger than those for DAP—$M_2$ systems under the same level of monomer conversion of both CR-39 and DAP PGPs. These results are clearly explained from the $\alpha$ values and the $r_1$-$r_2$ values for the respective systems.

## References

1. Y. Ohtsuka, N. Kaneko, and F. Takami, *J. Appl. Polym. Sci.*, **26**, 2423 (1981).

2. H. F. Mark, N. G. Gaylord, and N. M. Bikaies, *Encyclopedia of Polymer Science and Technology*, Interscience, New York, 1964, Vol. 1, p. 799–802.

3. J. W. McBain, *Z. Phys. Chem.*, **68**, 471 (1909).

4. T. Shibusawa, *Preprints of the Annual Meeting of Soc. Fiber Sci. and Tech., Japan*, p. 168 (1980).

5. M. Tanaka, *Infrared and Raman Spectroscopic Analyses*, Kyoritsu, Tokyo, 1978, p. 114.