

Studies on Synthetic Polymer Plates with High Surface Energy. III. Diethylene Glycol Bis(allyl Carbonate)–Unsaturated Sulfonic Acid System

NORIO KANEKO and YASUJI OHTSUKA,* *Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223, Japan*

Synopsis

Synthetic polymer plates (GPs) with high surface energy were prepared by the two-step copolymerization process previously reported, using diethylene glycol bis(allyl carbonate) (CR-39) as M_1 monomer and unsaturated sulfonates [sodium vinyl sulfonate (VS^-Na^+), potassium styrene sulfonate (StS^-K^+), and sodium 2-sulfoethyl methacrylate (SEM^-Na^+)] as M_2 monomer. The contact angle (θ_H) of water for the acid-treated (immersed in an aqueous 0.1 N HCl solution for 2 h) GPs decreased in the order StS^-K^+ , VS^-Na^+ , and SEM^-Na^+ . In the case of $M_2 = SEM^-Na^+$, the θ_H value was about 20°. By adding NaCl in the immersion solution and changing the pH of the immersion solution, the θ_H values for the CR-39- SEM^-Na^+ GPs were lowered to 18.9 and 13.1°, respectively. The θ_H values for the above GPs were smaller than those for the CR-39-acrylic acid or the CR-39-methacrylic acid GPs in the previous report, whereas the contact angle (θ_{Na}) of water for the former after alkali treatment (immersed in an aqueous 0.1 N NaOH solution for 2h) was larger than those for the latter. The former had durability of water wettability superior to the latter because of the difference in dissociation characteristic of the respective functional group.

INTRODUCTION

Chemical modifications of polymers such as introduction of sulfonic groups on their surfaces, have been carried out to alter their surface properties.¹⁻⁴ We previously reported preparation of synthetic polymer gel plates (GPs) with high surface energy by the following two-step copolymerization process: Diallyl compound (M_1 monomer) is partially polymerized to obtain a prepolymer gel plate (PGP) (first step), and then the PGP is immersed in an aqueous solution of unsaturated carboxylic acid (M_2 monomer), such as acrylic acid (AA) and methacrylic acid (MAA) (second step). The surface properties of the resulting GPs depend on the form of the carboxyl group on the surface (i.e., free acid or salt) due to differences in the degree of dissociation.^{5,6}

In this study, we attempted to introduce sulfonic groups on the surface of synthetic polymer plates by the above-mentioned procedure and to examine their surface properties. Diethylene glycol bis(allyl carbonate) (CR-39, product of PPG Industries, Ltd.) was used as M_1 monomer, and unsaturated sulfonates were used as M_2 monomer.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Diethylene glycol bis(allyl carbonate) (CR-39, PPG Industries, Ltd.) was purified by distillation (boiling point 130–140°C/0.01–0.03 torr). An aqueous 25 wt % solution of sodium vinyl sulfonate (VS⁻Na⁺, Tokyo Kasei Co.) was used without purification. Potassium styrene sulfonate (StS⁻K⁺, Wako Pure Chemical Industries, Ltd.) was purified by precipitation as follows: StS⁻K⁺ was dissolved in water without heating, filtered, and precipitated with ethanol.

The simultaneous addition of a dark-brown aqueous solution of 2-sulfoethyl methacrylate (SEM⁻H⁺, 95 wt %, Polysciences, Inc.) and an aqueous 5 N NaOH solution in water was carried out under stirring at a temperature below 10°C.⁷ The resulting aqueous solution of SEM⁻Na⁺ at pH 5 to 6 was treated with hydrous ZrO(OH)₂ followed by treatment with activated charcoal.⁸ The colorless, transparent solution obtained was used without further treatment.

Benzoyl peroxide (BPO, Wako Pure Chemical Industries, Ltd.) was reprecipitated from chloroform with methanol. Methylene blue trihydrate (Wako Pure Chemical Industries, Ltd.) was used without further purification. Other reagents, such as NaCl and KCl (reagent grade for all chemicals), were also used without further purification.

Preparation of GP and Measurement of Surface Properties

Synthetic polymer plates (GPs) with sulfonic groups on their surfaces were prepared by the two-step copolymerization method, whose block diagram is shown in Figure 1.^{5,6} As a measure of the amount of M₂ monomer diffusing into a PGP, the weight increment (ΔW_{OGP}) was defined as

$$\Delta W_{\text{OGP}} = \left(\frac{W_{\text{OGP}}}{W_{\text{PGP}}} - 1 \right) \times 100\% \quad (1)$$

where W_{PGP} and W_{OGP} are the weight of the PGP and the original gel plate (OGP), respectively. The ΔW_{OGP} value does not exactly represent the amount of M₂ monomer diffused into the PGP, because the diffusion of CR-39 monomer from the PGP to the aqueous phase occurs during the immersion process.

To remove the unbound functional groups from the resulting OGP completely, the cycle of alkali treatment (immersing in an aqueous 0.1 N NaOH solution for 2 h) and acid treatment (immersing in an aqueous 0.1 N HCl solution for 2 h) was repeated several times until the GP weight no longer decreased. The weight increment (ΔW_{GP}) of the GP after the above treatment was defined as

$$\Delta W_{\text{GP}} = \left(\frac{W_{\text{GP}}}{W_{\text{PGP}}} - 1 \right) \times 100\% \quad (2)$$

where W_{GP} is the weight of the GP. The value of $\Delta W_{\text{OGP}} - \Delta W_{\text{GP}}$ corresponds to the amount of the water-soluble part on the OGP surface.

Prior to the measurement of surface properties, the resulting GP was treated as follows: The GP after acid or alkali treatment was washed with water and *n*-hexane, followed by drying under reduced pressure. The surface properties of the above-treated GP were evaluated in the following terms: (1) As a measure

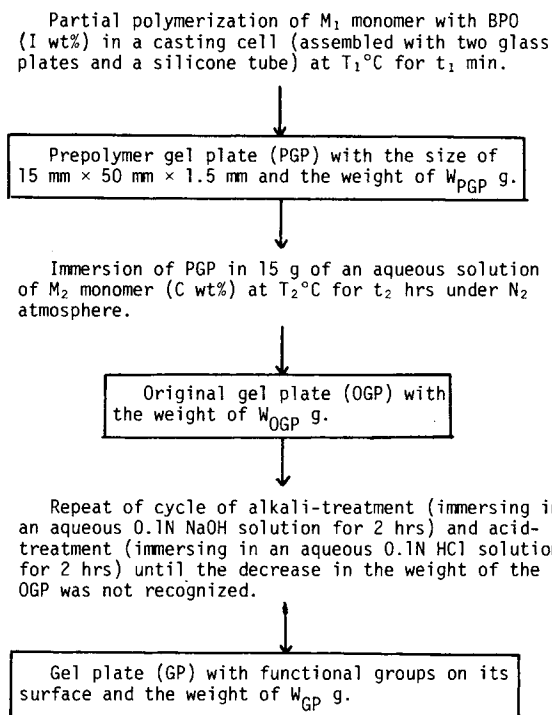


Fig. 1. Block diagram for the preparation of GPs by two-step copolymerization process.

of water wettability, an equilibrium contact angle (θ) of distilled water drops on the GP was measured with an Erma model G-I contact angle meter at 20°C . The mean of five measurements was taken with each specimen. The θ values for the acid- and alkali-treated GPs were designated as θ_{H} and θ_{Na} , respectively. (2) Antifogging property was estimated qualitatively by fogging or dewing on the GP surface.⁵ (3) A scratch hardness test of the GP surface was carried out with a TYPE-HEIDON-14 surface tester in air (70% relative humidity) at 25°C , and the value was expressed as the vertical load against a sapphire needle point. (4) Thickness (d) of the copolymer layer was measured from the micrograph of the methylene blue-stained slice (about $100\ \mu\text{m}$ thick), which was prepared by cutting and grinding perpendicularly to the GP surface and then immersing in an aqueous 0.01 mol/L methylene blue solution at 90°C for 2 h. (5) An equilibrium water content (ΔW_w) was defined as

$$\Delta W_w = \left(\frac{W_{\text{SGP}}}{W_{\text{GP}}} - 1 \right) \times 100\% \quad (3)$$

where W_{SGP} is the weight of the water-swollen GP after immersion in water for 24 h. (6) 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. The specimen was prepared by cementing the GP on a metal block, followed by coating with Au-Pt by means of an ion sputter coater (JEOL Fine Coat LFC-1100) for 4 min.

The CR-39 homopolymer plate (HP) was also prepared by a similar process of the OGP, except that the immersion solution was a total of 15 g distilled water

TABLE I
 Composition of PGPs of CR-39 Used

<i>I</i> , wt %	<i>T</i> ₁ , °C	<i>t</i> ₁ , min	Composition ^a		
			<i>C</i> _n , wt %	<i>C</i> _l , wt %	<i>C</i> _m , wt %
6	90	50	67	2	31
6	90	60	72	2	26
6	90	80	79	2	19

^a *C*_m, methanol-soluble part, residual monomer; *C*_l, methanol-insoluble and acetone-soluble part, oligomer and linear polymer; *C*_n, acetone-insoluble part, network polymer.

without M₂ monomer. The HPs in the case of *t*₁ = 50, 60, and 80 min are designated as HP-1, HP-2, and HP-3, respectively.

RESULTS AND DISCUSSION

The composition of the PGPs separated into the following three parts by means of fractional extraction is shown in Table I: methanol-soluble residual monomer (*C*_m, wt %); methanol-insoluble and acetone-soluble oligomer and linear polymer (*C*_l, wt %); acetone-insoluble network polymer (*C*_n, wt %).

Several properties of the resulting GP are compiled in Table II, where the results for *t*₁ < 50 min were omitted because the mechanical strength of the PGP was too weak to handle. The following relations are found:

- (1) Gelation occurs in the immersion solution in the case of *C* > 5 wt % for the

 TABLE II
 Properties of the PGPs for the CR-39-Unsaturated Sulfonate Systems^a

GP No.	M ₂ monomer	<i>t</i> ₁ , min	<i>C</i> , wt %	Δ <i>W</i> _{OGP} , wt %	Δ <i>W</i> _{GP} , wt %	<i>d</i> , μm	θ _H , deg
1	VS ⁻ Na ⁺	50	5	-1.39	-1.81	8.5	41.6
2	VS ⁻ Na ⁺	50	25	-1.10	-1.68	13.1	34.9
3	VS ⁻ Na ⁺	50	40 ^b	-0.55	-1.30	13.2	32.2
4	VS ⁻ Na ⁺	60	25	-0.20	-1.37	7.6	41.9
5	StS ⁻ K ⁺	50	1	-1.23	-2.96	10.0	43.3
6	StS ⁻ K ⁺	50	3	-1.42	-3.18	10.6	46.8
7	StS ⁻ K ⁺	50	5	-1.50	-3.26	13.1	42.2
8	StS ⁻ K ⁺	60	5	-0.94	-2.57	11.6	42.0
9	StS ⁻ K ⁺	80	5	-0.51	-2.06	8.1	45.9
10	SEM ⁻ Na ⁺	50	3	-0.72	-2.06	9.4	23.1
11	SEM ⁻ Na ⁺	50	6.5	-0.97	-2.32	10.5	27.3
12	SEM ⁻ Na ⁺	50	9.1	-0.91	-2.26	13.1	24.4
13	SEM ⁻ Na ⁺	50	15.2	-1.38	-2.90	18.8	20.4
14	SEM ⁻ Na ⁺	60	15.2	-0.88	-2.45	16.7	21.3
15	SEM ⁻ Na ⁺	80	15.2	-0.38	-1.98	13.3	20.0
16	AA	50	5	7.37	5.75	157.9	51.6
17	MAA	50	1.5	5.78	4.13	100.7	51.1
HP-1	—	50	—	-1.79	—	—	(56.9) ^c
HP-2	—	60	—	-1.39	—	—	(62.1)
HP-3	—	80	—	-0.77	—	—	(58.8)

^a *T*₁ = *T*₂ = 90°C and *t*₂ = 4 h.

^b Concentrated from 25 wt % to 40 wt % by evaporation.

^c Data for the original HP.

CR-39-StS-K⁺ system, with a rise in viscosity of the immersion solution. Gelation does not occur up to 40 wt % for the CR-39-VS-Na⁺ system and up to 15.2 wt % for the CR-39-SEM-Na⁺ system, respectively.

(2) The d values increase with an increase in C , and decrease with an increase in t_1 due to the reduction in the remaining CR-39 monomer in the PGP.

(3) It is clear from the ΔW_{OGP} value for the HPs (HP-1, HP-2, and HP-3, Table II) that a significant amount of CR-39 monomer diffuses from the PGP in the immersion solution. On the other hand, it is conceivable from the value of the partition coefficient ($\alpha = [M_2]_{\text{CR-39}}/[M_2]_{\text{water}}$, at ambient temperature) that a very small amount of M_2 monomer diffuses into the PGP. Consequently, the ΔW_{GP} values for the CR-39-unsaturated sulfonate systems are of negative sign.

(4) The ΔW_{GP} values for the CR-39-StS-K⁺ and the CR-39-SEM-Na⁺ systems are smaller than the ΔW_{OGP} values for the HPs. This is explained as follows: After immersion of PGP in 15 g of an aqueous 5 wt % potassium *p*-toluene sulfonate solution, the reduced amount of the ΔW_{OGP} value is 2.35 wt %, which is larger than that for the HP-1 (1.79 wt %). This indicates that the diffusion of CR-39 monomer out of the PGP is enhanced by the presence of an ionic compound such as M_2 monomer.

(5) From the above results, paragraphs (3) and (4), the ΔW_{GP} values increase with an increase in t_1 due to the reduction in the amount of the diffusion of CR-39 monomer in the immersion solution, but the dependence of C on the ΔW_{GP} values is not clear.

(6) The θ_{H} values are little affected by the change in t_1 and C due to high hydrophilicity of M_2 monomer. On the whole, the θ_{H} values slightly decrease with increase in C and with decrease in t_1 .

(7) The θ_{H} values decrease in the order StS-K⁺, VS-Na⁺, and SEM-Na⁺. For the CR-39-SEM-Na⁺ system, the θ_{H} value is about 20° and is much smaller than the θ value for the HP-1.

Table III indicates the following differences in the properties of M_2 monomer: (1) The hydrophilicity for M_2 monomer decreases in the order VS-Na⁺, SEM-Na⁺, and StS-K⁺, as shown in the HLB_{G} values. (2) The affinity of M_2 monomer for CR-39 monomer increases in the order VS-Na⁺, SEM-Na⁺, and StS-K⁺, as shown in the α values. (3) M_2 monomer unit content in CR-39- M_2 copolymer increases in the order VS-Na⁺, SEM-Na⁺, and StS-K⁺, as predicted from the $r_1 - r_2$ values.

To clarify the influence of the type of M_2 monomer, VS-Na⁺, StS-K⁺ and SEM-Na⁺, comparisons of GPs 1, 7, and 10 (or 11) in Table II were carried out, where M_2 monomer concentrations in the immersion solution were of a similar level. The variation of the properties of the GPs are explicable in terms of the above difference in M_2 properties as follows: (1) The order of the d values agrees with the order of the hydrophilicity of M_2 monomer and the affinity of M_2 monomer for CR-39 monomer. (2) The order of the $\Delta W_{\text{OGP}} - \Delta W_{\text{GP}}$ values agrees with the order of M_2 monomer unit content in CR-39- M_2 copolymer, because the copolymer with high M_2 content should be soluble in water. (3) The θ_{H} values decrease in the order StS-K⁺, VS-Na⁺, and SEM-Na⁺. In the case of $M_2 = \text{StS-K}^+$, the highest value of $\Delta W_{\text{OGP}} - \Delta W_{\text{GP}}$ suggests that a significant amount of the copolymer dissolves in an aqueous phase and that the StS-K⁺ content on the surface of the GP is lowered. Consequently, the θ_{H} value of this

TABLE III
Physical Properties of M_2 Monomers Used and Monomer Reactivity Ratios for the CR-39- M_2 Systems

M_2 monomer	Partition coefficient (α) ^a	HLB _G ^b	e	Q	Monomer reactivity ratio ^c	
					r_1	r_2
VS ⁻ Na ⁺	0.02	15.9	0.41	0.064	0.38	2.6
SEM ⁻ Na ⁺	0.05	13.6	(0.6)	1.4 ^d	0.019	52
StS ⁻ K ⁺	0.06	12.1	-0.40	2.0	0.008	56

^a The α values were determined as follows: (1) For VS⁻Na⁺ and SEM⁻Na⁺, 5 mL of CR-39 monomer, 5 mL of an aqueous 1 g/L solution of M_2 monomer, and a slight amount of hydroquinone were put into a test tube, followed by shaking for a few minutes. For StS⁻K⁺, 5 mL CR-39 monomer, 5 mL water, 0.1 g StS⁻K⁺, and a slight amount of hydroquinone were put into a test tube, followed by shaking for a few minutes. (2) The contents were left at ambient temperature for 24 h. (3) The concentration of M_2 monomer in the separated water layer was determined from the absorbance (at 193 nm for VS⁻Na⁺, at 204 nm for StS⁻K⁺, and at 208 nm for SEM⁻Na⁺).

^b The HLB_G values were calculated from the Griffin equation: $HLB_G = 20 \times (M_H/M)$, where M is the molecular weight of M_2 monomer and M_H is that of the hydrophilic part of M_2 monomer.⁹

^c The Q (0.025) - e (0.48) value for CR-39 monomer was calculated from the Alfrey-Price equation with the experimental values of $r_1 - r_2$ for the CR-39-unsaturated carboxylic acid systems.⁶ The $r_1 - r_2$ values for CR-39-unsaturated sulfonate systems were calculated from the respective $Q - e$ values.^{10,11}

^d The $Q - e$ value of SEM⁻H⁺ was substituted for that of SEM⁻Na⁺, considering their high dissociation constant.⁷

GP is the highest among them. The order of the θ_H value between VS⁻Na⁺ and SEM⁻Na⁺ agrees with the order of copolymerizability.

For the purpose of lowering the θ_H value for the CR-39-SEM⁻Na⁺ system, the following two attempts were carried out: (1) addition of NaCl in the immersion solution; (2) change in a pH of the immersion solution by addition of H₂SO₄ and HCl. The results for case (1) are shown in Table IV. Comparisons of GP 13 (Table II) with GPs 18 and 19 indicate that the ΔW_{GP} and d values increased with addition of NaCl, because the amount of SEM⁻Na⁺ diffusing into the PGP is enhanced due to the salting-out effect. Consequently, the θ_H value for GP 19 decreases slightly. The results for case (2) are compiled in Table V. The ΔW_{OGP} values for the HP decrease with a lowering of the pH, and the θ_H values remain almost constant in the range of the pH examined. Comparisons of GP 13 with GPs 20, 21, 22, and 23 indicate that a lowering of the pH brought about an increase in the ΔW_{GP} and d values and a decrease in the θ_H values (except for the case of pH < 1.0), because the diffusion of SEM⁻Na⁺ into the

TABLE IV
Properties of the CR-39-SEM⁻Na⁺ GPs Prepared by Addition of NaCl in the Immersion Solution^a

GP No.	Amount of NaCl added, g	t_1 min	C , wt %	ΔW_{GP} , wt %	d , μm	θ_H , deg
18	1	50	15	-1.93 (-1.34)	19.8	25.4 (59.2)
19	3	50	15	-0.98 (-1.04)	22.6	18.9 (55.7)

^a ($T_1 = T_2 = 90^\circ\text{C}$ and $t_2 = 4\text{ h}$). Data designated in parentheses are of the CR-39-HP prepared under the same condition, except for $C = 0\text{ wt \%}$.

TABLE V
Properties of the CR-39-SEM⁻Na⁺ GPs Prepared by Changing the pH of the Immersion Solution^a

GP No.	Reagent	pH	t_1 , min	C, wt %	ΔW_{GP} , wt %	d , μm	θ_H , deg
20	H ₂ SO ₄	4.9	50	15	-2.87 (-2.29)	18.1	17.6 (57.2)
21	H ₂ SO ₄	1.9	50	15	-1.56 (-2.32)	24.6	14.5 (59.3)
22	H ₂ SO ₄	1.0	50	15	-0.69 (-2.43)	28.0	13.1 (56.0)
23	H ₂ SO ₄	0.6	50	15	0.07 (-2.17)	38.5	18.0 (55.2)
24	HCl	3.0	50	15	-2.53 (-1.65)	19.6	25.2 (60.4)
25	HCl	1.8	50	15	-1.42 (-1.91)	27.5	16.4 (60.2)
26	HCl	1.0	50	15	-0.75 (-2.05)	30.0	16.9 (63.3)
27	HCl	0.7	50	15	0.20 (-2.17)	35.3	22.9 (62.4)

^a ($T_1 = T_2 = 90^\circ\text{C}$ and $t_2 = 4$ h). Data designated in parentheses are of the CR-39-HP prepared under the same condition, except for $C = 0$ wt %.

PGP is enhanced by a lowering of the pH due to an increase in the ionic strength of the immersion solution. The alkali treatment of GP 23 (pH 0.6) decreases the θ value from 18.0° to 10.4° . This result is explained as follows: Because the rate of hydrolysis for SEM⁻Na⁺ is fast under the condition of strong acidity,^{10,11} some of the sulfonate groups on the GP surface are converted to carboxyl groups. The θ value lowered by alkali treatment is due to the carboxyl group.

Comparing GP 13 with GPs 24, 25, 26, and 27, the trends for the GPs prepared by adding HCl as a pH-adjusting reagent are similar to those for the GPs prepared by adding H₂SO₄.

Other properties for GPs 2, 7, 13, 19, 22 and 26 in the CR-39-unsaturated sulfonate systems are compiled in Table VI. The θ values for the GPs are little affected by the sulfonic groups on the surface due to the high degree of dissociation of this functional group. Hence, the θ values are unchanged by immersing the alkali-treated GPs in water, i.e., the θ value (θ_w) after immersing the alkali-treated GPs in water for 100 h is nearly equal to the θ_H and θ_{Na} values. The water

TABLE VI
Other Properties of CR-39-Unsaturated Sulfonate GPs

GP No.	M ₂ monomer	Contact angle, deg			Antifogging ^b	ΔW_w wt %	Scratch hardness, g	
		θ_H	θ_{Na}	θ_w^a			Dry	Wet
2	VS-Na ⁺	34.9	32.2	35.7	Poor	0.36	30	20
7	StS-K ⁺	42.2	42.7	38.7	Poor	0.34	30	15
13	SEM ⁻ Na ⁺	20.4	22.4	20.1	Poor	0.53	30	20
19	SEM ⁻ Na ⁺	18.9	21.2	16.3	Small	0.73	25	15
22	SEM ⁻ Na ⁺	13.1	17.5	13.8	Large	0.60	25	15
26	SEM ⁻ Na ⁺	16.9	14.4	17.0	Large	0.50	25	15
16	AA	51.6	11.5	51.0	Transparent dewling	1.34	45	35
17	MAA	51.1	9.2	54.7	Transparent dewling	1.07	50	40
HP-1	—	(56.9) ^c	—	—	Poor	0.51	40	30

^a The value of θ_w was of GP surface immersed in water for 100 h after alkali-treatment.

^b Antifogging test: water 50°C , inner room 47.5°C , outer room 25°C .

^c Data for the original HP.

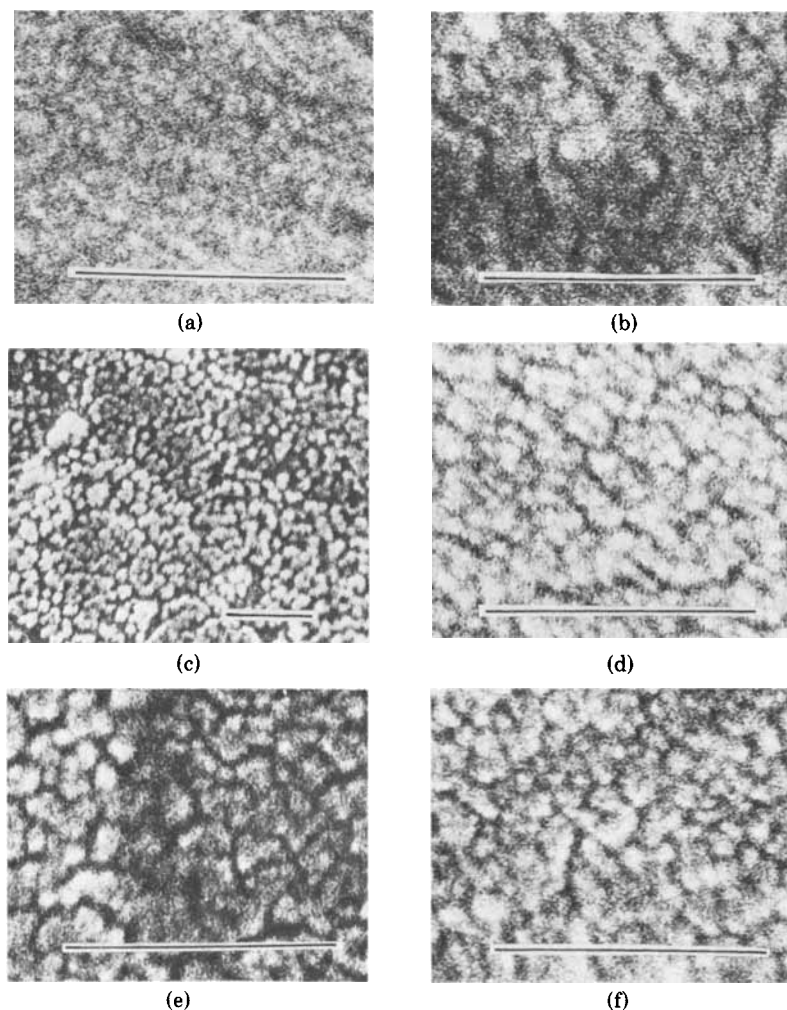


Fig. 2. Scanning electron micrographs of the surfaces of HPs and CR-39 – SEM⁻Na⁺ GPs. The bars represent 0.1 μm . (a) HP-1; (b) HP prepared under the condition of $t_1 = 50$ min and $\text{pH} = 1.0$ using H_2SO_4 as a pH-adjusting reagent; (c) GP 13; (d) GP 25; (e) GP 29; (f) GP 22.

contents for the GPs are the same as that for HP-1. The scratch hardness for the GPs in both dry and wet states are slightly smaller than those for HP-1.

The surface structures of the GPs were observed by scanning electron microscopy. The surface structure of the HPs (HP-1 and HP prepared under the condition of $t_1 = 50$ min and $\text{pH} = 1.0$ using H_2SO_4 as a pH-adjusting reagent) is almost flat (Fig. 2), but that of the GPs (GPs 13, 22, 26, and 19) in the CR-39-SEM⁻Na⁺ system exhibits an orange-peel surface covered with grains of about 0.005–0.01 μm in size.

To clarify the difference between the GPs for the CR-39-unsaturated sulfonate systems and the GPs for the CR-39-unsaturated carboxylic acid systems, comparisons of GPs 13, 19, 22, and 26 with 16 and 17 were carried out. The ΔW_{GP} , d , and ΔW_w values for the sulfonate systems are much smaller than those for the carboxylate systems. The θ_{H} values for the sulfonate systems are smaller

than those for the carboxylate systems, whereas the θ_{Na} values for the sulfonates are larger than those for the carboxylates. The scratch hardness values for the sulfonates are slightly lower than those for the carboxylates in dry and wet states. These results are explained as follows: (1) The partition coefficient values (α) between CR-39 monomer and water for AA (0.95) and MAA (3.42) at 90°C indicate that the affinity of SEM^-Na^+ for CR-39 is much smaller than that of AA and MAA. Hence, the surface density of the sulfonic group for the CR-39- SEM^-Na^+ GPs is smaller than that of carboxyl group for the CR-39-AA and -MAA GPs, and the d values for the former are one-tenth of those for the latter. (2) The θ values for the former are little affected by the form of the sulfonic group on their surface due to the high degree of dissociation of this functional group, whereas the θ values for the latter change with the form of carboxyl group due to the difference in the degree of dissociation.

Matsuda and Litt² reported the chemical modification of the polystyrene surface by sulfonation with 5% fuming sulfuric acid, where the resulting polystyrene surface has an advancing contact angle of 31° and surface density of 5.6×10^{-4} units/Å². According to Gibson and Bailey,¹ polystyrene film sulfonated with 100% sulfuric acid has a surface density of 3.9×10^{-2} units/Å² and a layer thickness of 3.5 μm. In comparing our results with the above, differences in the monomer, preparation procedure, and determination method of the contact angle should be noted. A comparison between the species containing a similar functional group such as the phenylsulfonic group, the CR-39-StS-K⁺ system shows higher θ_w values than polystyrene sulfonated with sulfuric acid. On the other hand, such chemical modification with fuming or 100% sulfuric acid is inadequate for CR-39 polymer due to its poor resistance to concentrated sulfuric acid.¹²

CONCLUSIONS

(1) The θ values for acid-treated GPs decrease in the order StS-K⁺, VS-Na⁺, and SEM^-Na^+ , which is explicable in terms of the hydrophilicity of M₂ monomer and reactivity of M₂ monomer with CR-39. In the case of M₂ = SEM^-Na^+ , the θ_H value is about 20°.

(2) By adding NaCl to the immersion solution and changing the pH of the immersion solution, the θ_H values for the resulting GPs are lowered to 18.9 and 13.1°, respectively, which is explicable in terms of an increase in the amount of diffusion of SEM^-Na^+ into the PGP.

(3) The θ_H values for the CR-39- SEM^-Na^+ GPs are smaller than those for the CR-39-AA and -MAA GPs, whereas the θ_{Na} values for the former are larger than those for the latter. The d values for the former are one-tenth of those for the latter, and the scratch hardness values for the former are slightly lower than those for the latter in dry and wet states.

References

1. H. W. Gibson and F. C. Bailey, *Macromolecules*, **13**, 34 (1980).
2. T. Matsuda and M. H. Litt, *J. Polym. Sci. Polym. Ed.*, **12**, 489 (1974).
3. K. Senda and E. Nakajima, *Jpn. Pat.* 73-16,709 (1973).
4. F. Hartmann and H. G. Hirschberg, *German Offen., Chem. Abstr.*, **83**, 28864x (1975).
5. Y. Ohtsuka, N. Kaneko, and F. Takami, *J. Appl. Polym. Sci.*, **26**, 2423 (1981).
6. Y. Ohtsuka and N. Kaneko, *J. Appl. Polym. Sci.*, **27**, 545 (1982).

7. D. A. Kangas and R. R. Pelletier, *J. Polym. Sci. Part A-1*, **8**, 3543 (1970).
8. D. A. Kangas and D. P. Sheetz, U.S. Pat. 3,415,870 (1968).
9. W. C. Griffin, *J. Soc. Cosmet. Chemists*, **5**, 249 (1954).
10. H. F. Mark, N. G. Gaylord, and N. H. Bikales, *Encyclopedia of Polymer Science and Technology*, Vol. 1, Interscience, New York, 1964, pp. 454-465.
11. R. H. Yocum and E. B. Nyquist, *Functional Monomers*, Vol. 1, Marcel Dekker, New York, 1974, pp. 489-641.
12. H. F. Mark, N. G. Gaylord, and N. H. Bikales, *Encyclopedia of Polymer Science and Technology*, Vol. 1, Interscience, New York, 1964, p. 801.

Received September 10, 1981

Accepted July 6, 1982