Studies on Synthetic-Polymer Plates with High Surface Energy. V. Diethylene Glycol Bis(allyl Carbonate)–Acrylic Acid Copolymer Plate by Vapor-Phase Transfer Process

NORIO KANEKO, AKIRA TAKAHASHI, and YASUJI OHTSUKA,*

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan

Synopsis

Synthetic-polymer plates with carboxyl group on their surface were prepared by a two-step copolymerization process transferring M_2 monomer via vapor phase. Diethylene glycol bis(allyl carbonate) (CR-39) was used as M_1 monomer, and acrylic acid was used as M_2 monomer. The relations between the experimental conditions and the surface properties of the resulting plates were examined in the following terms: (1) composition of CR-39 prepolymer gel plate used and (2) concentration of benzoyl peroxide as the initiator. The plates had good water wettability and an excellent anti-fogging property.

INTRODUCTION

Various modification methods of polymer surfaces have been proposed so far, e.g., chemical treatments with reactive reagents in liquid phase,[1] oxidation with reactive gases,[2] photoinduced[3] and gamma-radiation-induced[4] graft copolymerization, etc. In the previous papers,[5–8] we have proposed the following two-step copolymerization process (designated as the aqueous-solution method) to prepare the synthetic-polymer plates with a functional group, such as carboxyl group and sulfonic group, on their surface and to modify water wettability of hydrophobic polymer substrates: A prepolymer gel plate (PGP) obtained by partial polymerizing a diallyl compound (M_1 monomer) in a casting cell is immersed in an aqueous solution of hydrophilic, water-soluble monomer (M_2 monomer) under heating.

In this paper, a new two-step copolymerization process transferring M_2 monomer via vapor phase (designated as the vapor-phase method) was proposed to prepare the synthetic-polymer plate with carboxyl group on its surface, and the relations between preparation conditions and surface properties of the resulting plates were examined. In addition, a comparison of the vapor-phase method with the aqueous-solution method was carried out. Diethylene glycol bis(allyl carbonate) (CR-39) was used as M_1 monomer, and acrylic acid (AA) was used as M_2 monomer.

EXPERIMENTAL

Materials

CR-39 (PPG Industries, Ltd.) and AA (Wako Pure Chemical Industries, Ltd.) were purified by distillation (bp 130–140°C/0.01–0.03 Torr for CR-39 and 43°C/14 Torr for AA).

Benzoyl peroxide (BPO, Wako Pure Chemical Industries, Ltd.) as an initiator was precipitated from chloroform with methanol and dried under reduced pressure at room temperature. Methylene blue trihydrate (reagent grade, Wako Pure Chemical Industries, Ltd.) and hydroquinone (HQ, extra pure grade, Junsei Co., Ltd.) were used without further purification.

The Vapor-Phase Method

The block diagram of the vapor-phase method is shown in Figure 1, and the apparatus used is shown schematically in Figure 2.

CR-39 containing BPO (I wt %) was used to fill up the casting cell (assembled with two glass plates and a silicone gasket) and heated at T_1°C and t_1 min to obtain a PGP with the size of 15 mm × 50 mm × 1.5 mm and the weight of W_{PGP} g.

To examine the composition of the PGP, the resulting PGP was separated into the following three parts by means of the procedure in the previous paper[6]: methanol-soluble part, residual monomer (C_m, wt %); methanol-insoluble and acetone-soluble part, linear polymer (C_1, wt %); acetone-insoluble part, network polymer (C_n, wt %).

The above PGP taken apart from the casting cell was suspended into the reaction tube. 5g M_2 monomer containing HQ (0.1 wt %) was placed in the monomer vessel and frozen with liquid nitrogen. In order to replace the atmosphere in the whole system with nitrogen, the cycle of reducing the pressure in the whole system and injecting nitrogen into the whole system was repeated three times. Then only the reaction tube was heated under nitrogen for t_p min until the temperature in the reaction tube attained to T_2°C, followed by reducing the
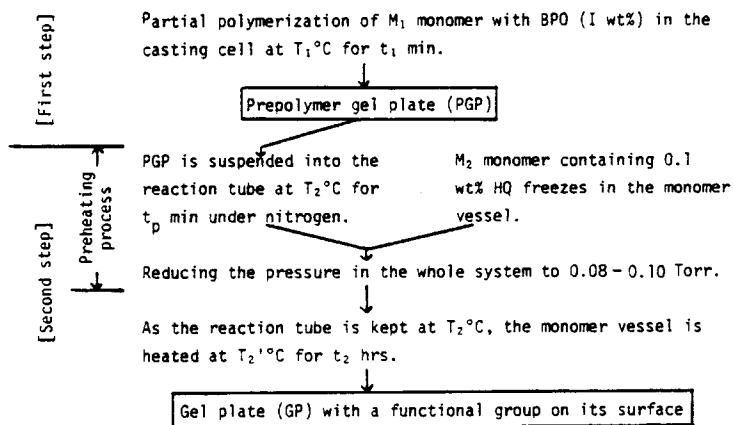

Fig. 1. Block diagram for preparation of GP's by the two-step copolymerization transferring M_2 monomer via vapor phase.
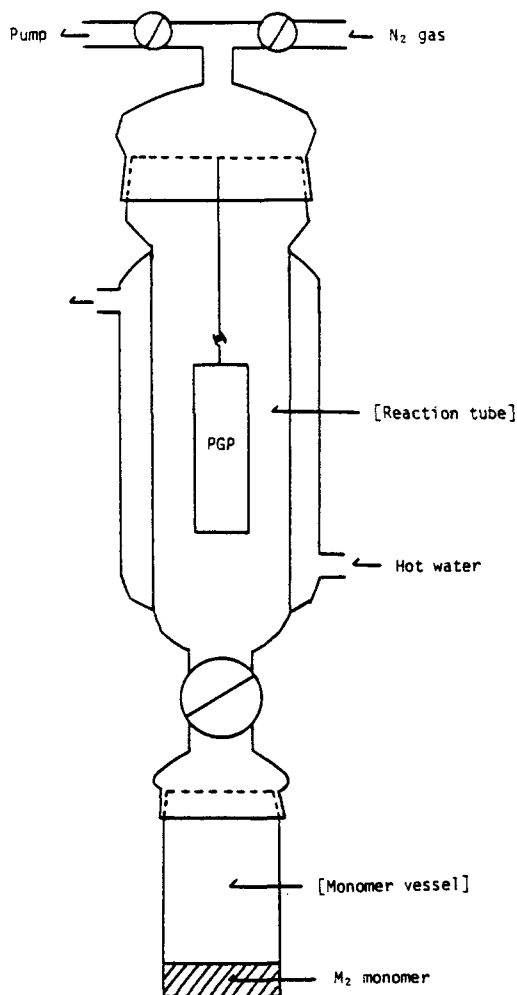
Fig. 2. Schematic representation of the apparatus used.

pressure in the whole system to 0.08–0.1 Torr. The procedure by this point was designated as the preheating process. The weight of the PGP after the above process was W'_{PGP} g, and ΔW_p was defined as follows:

$$\Delta W_p = (W'_{\text{PGP}}/W_{\text{PGP}} - 1) \times 100\%$$

As the reaction tube was kept at a specified temperature T_2, the monomer vessel was heated to vaporize M_2 monomer and kept at a specified temperature T'_2 to maintain a constant vapor pressure.[9] The temperature T_2 should be higher than the temperature T'_2 to prevent the condensation of M_2 monomer on the surface of the PGP. The respective temperatures were maintained for t_2 to copolymerize completely. The resulting plate was designated as the original gel plate (OGP).

In order to completely remove the water-soluble component from the surface of the OGP, 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 OGP

was not recognized. The above-treated OGP was designated as the gel plate (GP).

Measurement of Surface Properties

Measurements of an equilibrium contact angle (θ) for a distilled water drop on the GP at 20°C, a thickness (d, with an error of ± 1 μm) of the copolymer layer of the GP, a surface density (A) of carboxyl groups on the GP and an equilibrium water content (ΔW_w) were carried out by the procedure in the previous paper.[6] Here θ values for the alkali-treated and acid-treated GP's are designated as θ_{Na} (with an error of $\pm 1°$) and θ_H (with an error of $\pm 3°$), respectively. Antifogging test and the observation of the GP surface by means of a scanning electron microscope were also carried out by the procedure in the previous paper.[5]

As a measure of M_2 monomer diffusing into the PGP and copolymerizing with residual allylic group in the PGP, a weight increment (ΔW_{GP}) was defined as

$$\Delta W_{GP} = (W_{GP}/W'_{PGP} - 1) \times 100\%$$

where W_{GP} and W'_{PGP} are the weight of the GP and the PGP after preheating process, respectively.

The distribution of carboxyl group in the surface layer of the GP was determined by the following method: (1) A slice of the GP about 200 μm thick, which was prepared by cutting and grinding perpendicular to the surface, was alkalitreated. (2) The above-treated slice was cemented on an aluminum block with silver paste, followed by evaporating gold on its surface. (3) The distribution of the sodium atom adsorbed in the surface layer of the slice, i.e., that of the carboxyl group was determined with an X-ray microanalyzer (an Electron Microprobe X-Ray Analyzer, Shimazu Seisakusho Ltd.). In order to examine the chemical composition of the copolymer in the surface layer of the GP's, infrared spectra were measured by means of a Hitachi Model 225 Infrared Spectrophotometer using the fine powder obtained by filing the GP surface.

RESULTS AND DISCUSSION

The compositions of the CR-39 PGP's used are compiled in Table I. It is clear from ΔW_p that a small amount of CR-39 monomer diffused out of the PGP into the vapor phase during the preheating process.

In the case of $I = 6$ wt %, the effects of T'_2 and t_1 on the characteristic values of the GP are shown in Figure 3. The results of $t_1 < 40$ min were omitted, because the mechanical strength of the PGP was too weak to handle. Here the existence of carboxyl group in the surface layer of the GPs was confirmed from the fact that the infrared spectra of the alkali-treated GPs contained a peak at 1580 cm^{-1} due to carboxylic ion.

Elevating T'_2 brought a slight increase in ΔW_{GP}, little change in d, and decreases in both θ_{Na} and θ_H. These results indicate that the surface density of the AA monomer unit slightly increases with an elevation of T'_2 due to an increase in the vapor pressure of the AA monomer (19 mm Hg at 50°C and 47 mm Hg at 70°C). Increasing t_1 brought decreases in both ΔW_{GP} and d and increases in both θ_{Na} and θ_H. These results are attributed to a reduction in the remaining CR-39 monomer in the PGP.

TABLE I
Composition of CR-39 PGP's Used ($T_1 = T_p = 90°C$)

Code	I (wt %)	t_1 (min)	Composition before preheating[a]			t_p (min)	ΔW_p (wt %)	Composition after preheating[a]		
			$\overline{C_n}$ (wt %)	C_1 (wt %)	C_m (wt %)			$\overline{C_n'}$ (wt %)	C_1' (wt %)	C_m' (wt %)
A	6	40	63	2	35	20	-0.71	71	3	26
B	6	50	67	2	31	20	-0.52	74	2	24
C	6	60	72	2	26	20	-0.44	76	1	23
D	3	50	50	2	48	20	-0.83	57	3	40
E	3	70	62	1	37	20	-0.69	65	1	34
F	1	130	48	1	51	30	-1.12	55	3	42
G	1	150	52	1	47	30	-0.83	61	2	37
H	1	240	62	1	37	30	-0.65	70	1	29

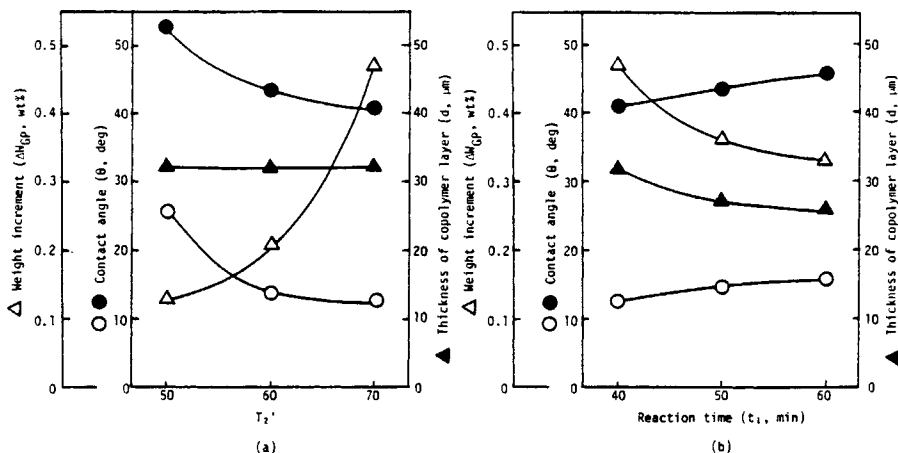[a] All of data of the range of experimental errors of ±0.5 wt %.

Fig. 3. Dependences of properties of the GP's on T'_2 and t_1. (O) θ for alkali-treated GP; (●) θ for acid-treated GP. (a) I = 6 wt %, $T_1 = T_2 = 90°C$, t_1 = 40 min, t_p = 20 min, and t_2 = 6 h; (b) I = 6 wt %, $T_1 = T_2 = 90°C$, t_p = 20 min, $T'_2 = 70°C$, and t_2 = 6 h.

The effect of BPO concentration on the characteristic values of the GP is shown in Table II. We attempt a comparison between nos. 1, 3, and 6, because the compositions of their PGP are similar with one another (C_m = 35–37 wt %). Decreasing BPO concentrations brought the increases in ΔW_{GP}, in t_p to some extent, and in d remarkably, but the change in θ_{Na} slightly. Considering variation in the composition of the PGP used during the preheating process (C'_m = 26–34 wt %) and the slight difference in the copolyemrization condition, it seems questionable that the above trend is entirely attributed to BPO concentration. However, the effect of PGP composition (effect of t_1) is not so striking, as shown in Figure 3(b). It is understandable that the above trend is mostly due to BPO concentration. We can also find out the same trend from surveying the data in Table I.

A mechanism is proposed as follows: A decrease in the copolymerization rate brought about by a decrease in BPO concentration reduces both growing of CR-39 network structure and fixation of the AA monomer by copolymerization, and promotes diffusion of the AA monomer up to the deeper zone. On the other hand, the value of θ_{Na} is slightly affected by BPO concentration, because the surface density of the fixed AA monomer unit is affected by AA monomer concentration in the vapor phase rather than the copolymerization rate.

Several properties of the GP's prepared by the aqueous-solution method are compiled in Table III. As described in the previous paper,[6] the affinity of M_2 monomer between the CR-39 PGP and water and copolymerizability between M_1 monomer and M_2 monomer were dominant factors in the aqueous-solution method. We attempted a comparison of the vapor-phase method with the aqueous-solution method. Comparing no. 1 in Table II with no. 8 in Table III, where both preparations were carried out under the same BPO concentration and using the PGP with quite similar composition (C'_m = 26 wt % for the former and C_m = 26 wt % for the latter), the following differences in the properties of the GP's were found: (1) ΔW_{GP} for no. 1 was much smaller than that for no. 8 due to the significant difference in the amount of the AA monomer coming in contact with the PGP. It is estimated that the concentration of AA monomer

TABLE II
Properties of GP's Prepared by the Vapor-Phase Method

No.	PGP code	I (wt %)	T_1 (°C)	t_1 (min)	T_2 (°C)	t_p (min)	T'_2 (°C)	t_2 (h)	ΔW_{GP} (wt %)	θ_{Na} (deg)	θ_H (deg)	A (molecule/Å²)	d (μm)	ΔW_w (wt %)	Antifogging[a]
1	A	6	90	40	90	20	70	6	0.47	12.7	40.8	0.10	31.9	0.44	transparent dewing
2	D	3	90	50	90	20	70	6	2.48	8.1	41.2	0.51	69.5	1.17	transparent dewing
3	E	3	90	70	90	20	70	6	2.29	11.6	39.6	0.28	62.5	1.33	transparent dewing
4	F	1	90	130	90	30	70	20	5.41	11.9	49.6	—	261.2	2.16	transparent dewing
5	G	1	90	150	90	30	70	20	4.49	12.1	44.8	0.56	247.5	2.55	transparent dewing
6	H	1	90	240	90	30	70	20	3.39	13.9	48.9	—	221.9	1.76	large[b]

[a] Data for the alkali-treated GP.
[b] A state that large drops of water adhere to the GP surface.

TABLE III
Properties of GP's Prepared by the Aqueous-Solution Method

No.	PGP code	I (wt %)	T_1 (°C)	t_1 (min)	T_2 (°C)	t_2 (h)	C^a (wt %)	$\Delta W'_{GP}{}^b$ (wt %)	$\Delta W_{out}{}^c$ (wt %)	θ_{Na} (deg)	θ_H (deg)	A (molecule/Å²)	d (μm)	ΔW_w (wt %)	Antifogging^d
7	B	6	90	50	90	4	5	3.96	1.62	11.5	51.6	0.41	157.9	1.34	Transparent dewing
8	C	6	90	60	90	4	5	2.98	1.60	12.0	48.0	0.27	151.4	1.05	Transparent

^{a} Concentration of M_2 monomer in an immersion solution.

^{b} $\Delta W'_{GP} = [(W_{GP}/W_{PGP}) - 1] \times 100\%$, where W_{PGP} is the weight of the PGP.

^{c} $\Delta W_{out} = [W_{out}/W_{PGP}] \times 100\%$, where W_{out} is the weight of the water-soluble component.
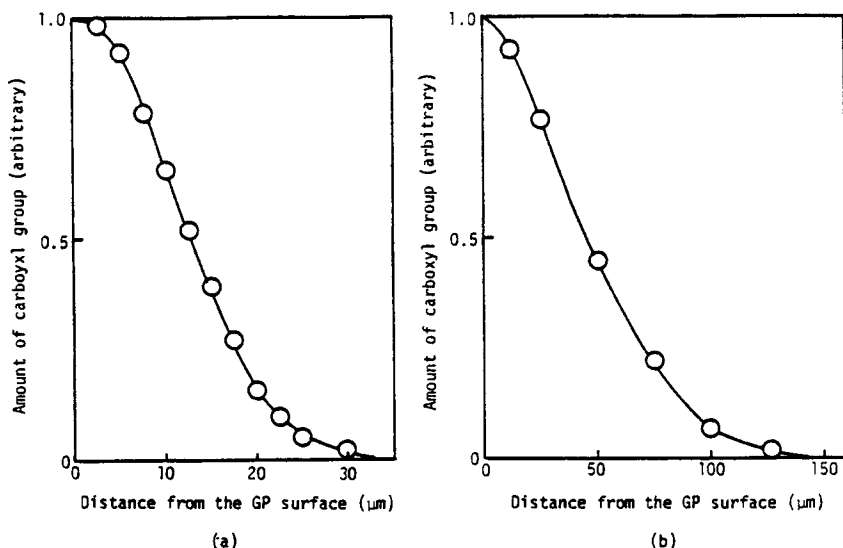
^{d} Data for the alkali-treated GP.

Fig. 4. Distribution of carboxyl group in the surface layer of the CR-39–AA GP determined by use of X-ray microanalyzer. (a) GP (no. 1) prepared by the vapor-phase method; (b) GP (no. 8) prepared by the aqueous solution method.

for the latter was about 300 times that for the former.   (2) As shown in Figure 4, the distribution of carboxyl group for the latter is similar to that for the former; i.e., the density of carboxyl group is the highest on the surface of the GP and gradually decreased from the surface to the inner zone.   It is noted that the thickness of the layer having the functional group is quite different each other. (3) The d and ΔW_w values for the former were smaller than those for the latter due to the difference in ΔW_{GP}.   (4) It is anticipated from the values of A that the surfaces of the respective GP's are covered with the AA monomer unit to the same extent, and, consequently, θ_{Na} and θ_H for the former are the same as those for the latter.   As shown in Figure 5, the surface structures of the respective GP's are almost similar and exhibits orange-peel surfaces.

The advantages of the vapor-phase method over the aqueous-solution method are as follows: (1) In the vapor-phase method, the solvent is not used.   (2) As described in the previous paper,[6] a significant amount of the water-soluble component (i.e., M_1—M_2 copolymer with high M_2 content) was produced on the surface of the OGP's by the aqueous-solution method.   On the other hand, the vapor-phase method produces a little amount of the water-soluble component on the surface.   (3) In the aqueous-solution method, the GP's prepared under the condition of $I < 6$ wt % yielded the cracked plate.   On the other hand, in the vapor-phase method BPO concentration could be reduced to 1 wt % without a loss of the water wettability for the resulting GP's.
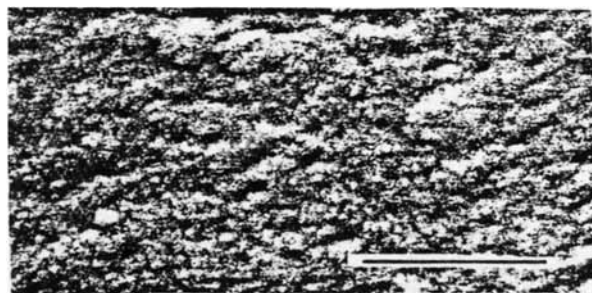
CONCLUSIONS

The GP's with carboxyl group on their surface were prepared by the vapor-phase method, using CR-39 as M_1 monomer and AA as M_2 monomer.

The resulting GP's have good water wettability and an excellent antifogging property.   In addition, a few of advantages of the vapor-phase method over the aqueous-solution method were found out.
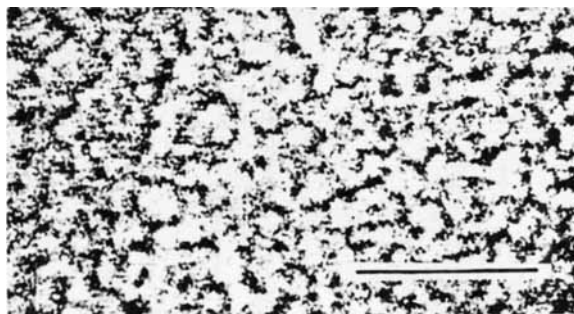
(a)

(b)

Fig. 5. Scanning electron micrographs of the surface of the GP's: (a) GP (no. 1) prepared by the vapor-phase method; (b) GP (no. 8) prepared by the aqueous solution method. The bars represent 0.05 μm.

NOMENCLATURE

CR-39   diethylene glycol bis(allyl carbonate)
AA   acrylic acid
BPO   benzoyl peroxide
HQ   hydroquinone
GP   gel plate
HP   homopolymer plate
M_1 hydrophobic monomer such as diallyl or divinyl compound
M_2 hydrophilic monomer such as AA
OGP   original gel plate
PGP   prepolymer gel plate
A surface density of carboxyl groups (molecule/Å^2)
C concentration of M_2 monomer in an immersion solution in the aqueous-solution method (wt %)
C_1 linear polymer part in the PGP before preheating (wt %)
C_m residual monomer in the PGP before preheating (wt %)
C_n network polymer part in the PGP before preheating (wt %)
C_1' linear polymer part in the PGP after preheating (wt %)
C_m' residual monomer in the PGP after preheating (wt %)
C_n' network polymer part in the PGP after preheating (wt %)
d thickness of copolymer layer (μm)
I concentration of initiator (wt %)
T_1 preparation temperature of PGP (°C)
t_1 preparation time of PGP (min)
T_p preheating temperature (°C)
t_p preheating time (min)

T_2	temperature of reaction tube (°C)
T_2'	temperature of monomer vessel (°C)
t_2	heat-treatment time (h)
W_{GP}	weight of gel plate
W_{PGP}	weight of PGP before preheating (g)
W_{PGP}'	weight of PGP after preheating (g)
ΔW_{GP}	weight increment in the vapor-phase method (wt %)
ΔW_{GP}	weight increment in the aqueous-solution method (wt %)
ΔW_{out}	weight fraction of water-soluble component on the surface of OGP in the aqueous-solution method (wt %)
ΔW_p	weight fraction of M_1 monomer lost during preheating (wt %)
ΔW_w	equilibrium water content (wt %)
θ	equilibrium contact angle (°)
θ_{Na}	θ after alkali-treatment (°)
θ_H	θ after acid-treatment (°)

References

1. E.g., (a) H. W. Rauhut, *Adhesive Age*, 12(12), 28 (1969); (b) H. W. Gibson and F. C. Bailey, *Macromolecules*, 13, 34 (1980).

2. E.g., M. Imoto, *J. Adhesion Soc., Jpn.*, 14, 581 (1979).

3. E.g., S. Tazuke and H. Kimura, *Macromol. Chem. Sci.*, 23, 2425 (1979).

4. E.g., B. D. Ratner, P. K. Weathersby, A. S. Hoffman, M. A. Kelly, and L. H. Scharpen, *J. Appl. Polym. Sci.*, 22, 643 (1978).

5. Y. Ohtsuka, N. Kaneko, and F. Takami, *J. Appl. Polym. Sci.*, 26(7), 2423 (1981).

6. Y. Ohtsuka and N. Kaneko, *J. Appl. Polym. Sci.*, 27(2), 545 (1982).

7. N. Kaneko and Y. Ohtsuka, *J. Appl. Polm. Sci.*, to appear.

8. N. Kaneko and Y. Ohtsuka, *J. Appl. Polm. Sci.*, to appear.

9. R. C. Weast, *Handbook of Chemistry and Physics*, 52nd ed., Chemical Rubber Co., Cleveland, OH, 1971–1972, p. D-151.