

Studies on Synthetic-Polymer Plates with High Surface Energy. IV. Determination of Critical Surface Tension with Aqueous Solutions of Salts

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Synopsis

The critical surface tension (γ_c) of synthetic-polymer plates with a functional group (amide, sulfonic, or carboxyl group) on their surface was determined by the Zisman plot using series of pure liquids (thiodiglycol, formamide, and water) and the aqueous solutions of the salts (NaCl, NaNO₃, etc.) as a hydrogen-bonding liquid. The Zisman plots gave a straight line, and the trends in the γ_c values coincide with those in the hydrophilicity anticipated from the θ values. The use of the aqueous salt solution coupled with the pure liquids as a hydrogen-bonding liquid offers a practical determination procedure of the γ_c value for the materials with high surface energy.

INTRODUCTION

Surface-free energy of polymeric materials is a very important characteristic with respect to the interfacial phenomenon (e.g., adhesion, wettability, printing, biocompatibility, etc.) from both a theoretical and a practical standpoint. However, there is no direct method of measuring surface-free energy of the polymeric solids due to their poor fluidity. Several indirect methods of estimating the energy have been proposed so far.¹ Meanwhile, Zisman² has empirically found that a plot of the surface tensions (γ_L) of a homologous series of organic liquids vs. the cosine of the contact angle (θ) gives a straight line, and has defined the critical surface tension (γ_c) as the intercept of the straight line on the horizontal line of $\cos \theta = 1$ ($\theta = 0^\circ$). In practice, either the contact angle³ or the γ_c value have often been used as a characteristic parameter of the relationship between interfacial phenomenon and surface properties of polymeric solids.

It had later been found that the γ_c value varies largely with the property of the used liquid series (nonpolar, polar, or hydrogen bonding) in most cases and that the γ_c value determined with liquid series of the same property as polymer surfaces accurately reflects the surface properties of polymeric solids.⁴ On the other hand, it was difficult to provide liquid series of hydrogen bonding compounds with a wide range of surface tension. The liquid series with the wide range of the γ_L value were proposed so far as follows: (1) mixtures of water and water-soluble organic compounds with low surface tension⁵; (2) nonaqueous mixtures of the organic compounds having high γ_L value with those having low γ_L value⁶; (3) a series of glycols, polyglycols, and alcohols.⁷

The γ_L values of both the pure liquid series and the blended liquid series are smaller than that of water. It should be noted that such liquid series are un-

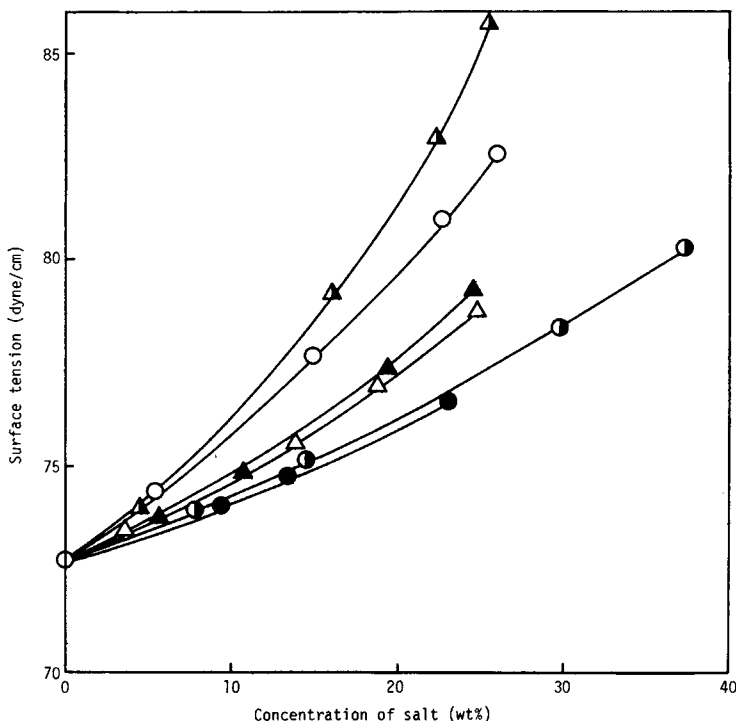


Fig. 1. Relationships between surface tension (γ_L) at 20°C and concentration of salt in aqueous solution. (○) NaCl; (◐) NaNO₃; (●) NaBr; (△) KCl; (▲) MgCl₂; (▲) MgSO₄.

suitable to determine the γ_c value of polymers with high surface energy comparable to that of water.

In the previous papers, we reported the preparation of synthetic-polymer gel plates (GPs) with the functional group, such as the amide,⁸ carboxyl,^{9,10} or sulfonic group,¹¹ on their surface by the two-step copolymerization process, and measured the equilibrium contact angle for a water drop placing on the GPs as a measure of their surface properties. As mentioned above, it was impossible to determine the γ_c value of the GPs by the proposed liquid series because the GPs had high surface energy.

In this paper, we proposed the determination procedure of the γ_c value for the above GPs using the aqueous solutions of the salts, whose surface tensions are larger than that of water and increase with an increase in the concentration of the salts,¹² as a series of hydrogen-bonding liquid.

EXPERIMENTAL

Materials

NaCl, KCl, NaNO₃, NaBr, MgCl₂·6H₂O, and MgSO₄·7H₂O (reagent grade for all chemicals, Junsei Chemical Co., Ltd.) were used without further purification. The relationships between the surface tension (γ_L) and the concentration of the salts in the aqueous solution at 20°C are shown in Figure 1.¹²

Thiodiglycol (TDG, $\gamma_L = 54.0$ dyn/cm at 20°C) and formamide (FA, $\gamma_L = 58.4$

dyn/cm at 20°C) (reagent grade, Wako Pure Chemical Industries, Ltd.) were used without further purification.

The GPs used as a specimen were prepared as follows: (1) diallyl or divinyl compound (M_1 monomer) is partially polymerized to obtain a prepolymer gel plate (PGP), and then the PGP is immersed in an aqueous solution of hydrophilic, water-soluble monomers (M_2 monomer), such as acrylamide, unsaturated carboxylic acid, or unsaturated sulfonic acid. The resulting GP was designated as the original GP (OGP). (2) To remove the water-soluble part on the surface layer 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. In the case of $M_2 =$ acrylamide, the OGP was immersed in water for 300 h to remove the water-soluble part.

The abbreviations used in this paper are as follows: (1) CR-39, diethylene glycol bis(allyl carbonate); DAP, diallyl phthalate; 4ED, tetraethylene glycol dimethacrylate; AA, acrylic acid; MAA, methacrylic acid; SEM, 2-sulfoethyl methacrylate; StS, styrenesulfonic acid; AAm, acrylamide; MMA, methyl methacrylate. (2) The designation M_1 — M_2 GP represents the GP with M_2 monomer unit on the surface layer of M_1 polymer substrate. The designation M_1 —HP represents M_1 homopolymer plate.

As reported in previous papers,⁸⁻¹¹ the values of the equilibrium water content $\{= [(W_2/W_1) - 1] \times 100\%$, where W_1 is the weight of the GP and W_2 is the weight of the GP after immersing in water for 24 h} for the used GPs were 0.5–1.5 wt %. They scarcely swelled in water and organic liquids.

Measurement of Contact Angle and Determination of γ_c Value

Prior to the measurement of the contact angle, the specimens in the case of $M_2 =$ AA, MAA, SEM, and StS were immersed in an aqueous 0.1N NaOH solution for 2 h (alkali treatment) or immersed in an aqueous 0.1N HCl solution for 2 h (acid treatment), then were washed with water and *n*-hexane, followed by drying under reduced pressure. The designations M_1 — M_2 -H⁺ GP and M_1 — M_2 -Na⁺ GP represent the acid-treated GP and alkali-treated GP, respectively. The specimens in the case of $M_2 =$ AAm were also washed with water and *n*-hexane, followed by drying under reduced pressure.

An equilibrium contact angle of liquid drops was measured with an Erma Model G-I Contact Angle Meter at 20°C and 55 ± 10% RH. All measurements were made after the equilibrium was reached. It took about 10 s for water and the aqueous salt solutions, and about 10 min for TDG and FA. Unnecessary elongation of the time should be avoided, because the dropped liquid vaporizes.

The γ_c value for each specimen was determined from the Zisman plot by the least squares method, using three pure, hydrogen-bonding liquids and the aqueous solutions of the salts.

RESULTS AND DISCUSSION

The Zisman plots for four HPs prepared in a casting cell (assembled two glass plates and a silicone tube) are shown in Figure 2. Regardless of pure liquids or aqueous salt solutions, the plots of the respective specimen fell in the respective

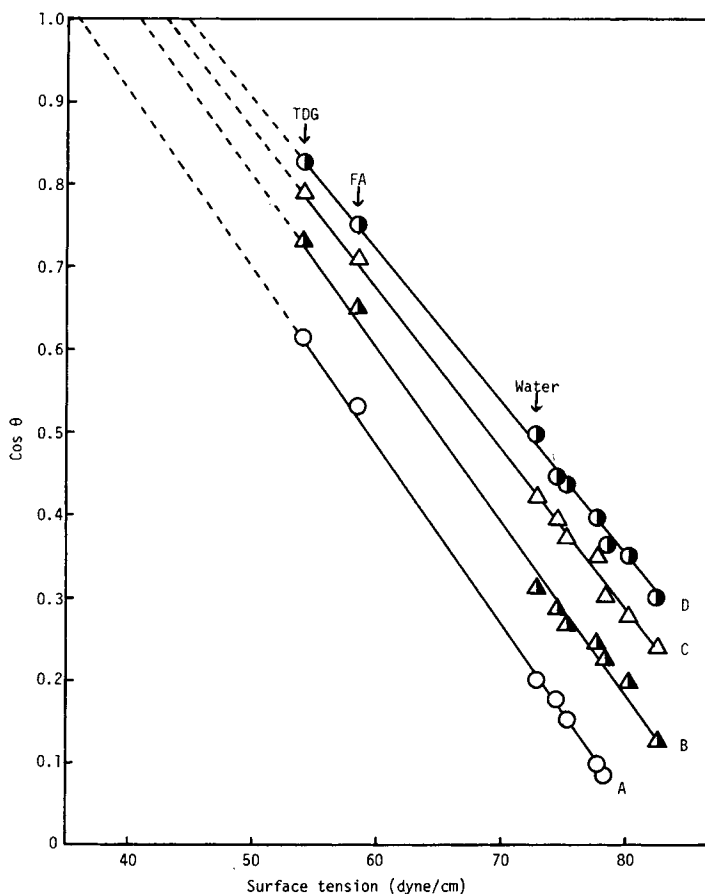


Fig. 2. Relationships between surface tension (γ_L) of pure liquids and aqueous salt solutions and cosine of contact angles (θ) for four HPs prepared in the casting cell: (A) MMA—HP; (B) DAP—HP; (C) CR-39—HP; (D) 4ED—HP.

straight line, which implicitly provides the validity for use of the aqueous salt solution coupled with the pure liquids. From line A in Figure 2, the γ_c value for the MMA—HP is 36 dyn/cm, whereas the γ_c value measured using a series of polar liquids is reported to be 39~41 dyn/cm and is larger than the former.¹³ This discrepancy is explained from the fact that the γ_c value using liquids series of the same property as the polymer surface is the highest among them.⁴

For other three HPs, the γ_c values and the hydrophile-lipophile balance (HLB_D) estimated by the Davies' equation¹⁴ are compiled in Table I, where the abbreviation I represents the HP completely polymerized in the casting cell and the abbreviation II represents the HP prepared by a similar preparation method of the GP except that the immersion solution was distilled water without M_2 monomer. Table I indicates the following terms: (1) The order (4ED—HP > CR-39—HP > DAP—HP) of the γ_c value in the case of both I and II agrees with the order of the hydrophilicity anticipated from the HLB_D values. (2) The γ_c values for the HPs (I) are smaller than those for the HPs (II) due to the difference in the prepared condition. (3) The result of (1) or (2) coincides with that anticipated from the θ values with water.

TABLE I
Values of Contact Angle (θ) with Water, Critical Surface Tension (γ_c), and HLB_D for the HPs

	DAP		CR-39		4ED	
	I	II	I	II	I	II
θ with water ($^\circ$)	71.7	66.1	65.0	60.4	60.2	50.4
γ_c (dyn/cm)	41	42	43	44	45	47
HLB _D ^a	6.1		9.7		10.3	

^a HLB_D = 7 + ΣL + ΣH , where L and H are the HLB group numbers for hydrophobic and hydrophilic groups, respectively.

The GPs used are classified into two groups, i.e., with nonionic surface (M_2 = AAm) and with ionic surface (M_2 = SEM, StS, AA, and MAA). The latter are further divided into two groups, i.e., a strongly acidic group (sulfonic acid, M_2 = SEM and StS) and a weakly acidic group (carboxyl group, M_2 = AA and MAA).

First the γ_c values for the CR-39—AAm OGP and GP (the case of amide group) were determined with the pure liquids and the aqueous solutions of NaCl. As shown in Figure 3, the Zisman plots yield the respective straight line. Hence, the aqueous solutions of the salt will be able to use for the determination of the γ_c value of nonionic polymer surfaces as a hydrogen-bonding liquid. We have already reported that the θ value for the OGP was increased by immersing it in water for a long time due to lowering in AAm monomer unit content on the surface of the GP.⁸ Corresponding to the above change in the θ value with water (from 12.0–29.5 $^\circ$), the γ_c value for the OGP (71 dyn/cm) reduced to that for the GP (55 dyn/cm). Comparing the γ_c value for the GP with that for the CR-39—HP (II, 44 dyne/cm), however, it is sure that the AAm monomer unit was still existing on the surface of the GP.

The Zisman plots for both the CR-39—SEM—H⁺ and —SEM—Na⁺ GP are shown in Figures 4(a) and 4(b), respectively. Regardless of the type of the salts (NaCl, NaNO₃, NaBr, KCl, MgCl₂, and MgSO₄), the plots fell in a straight line, respectively. In addition, the Zisman plots for both the CR-39—StS—H⁺ and

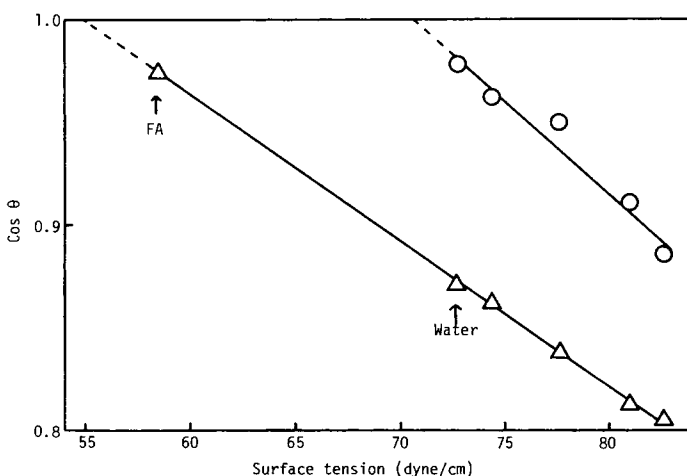


Fig. 3. Relationships between surface tension (γ_L) of pure liquids and aqueous salt solutions and cosine of contact angles (θ) for CR-39—AAm OGP (\circ) and CR-39—AAm GP (Δ).

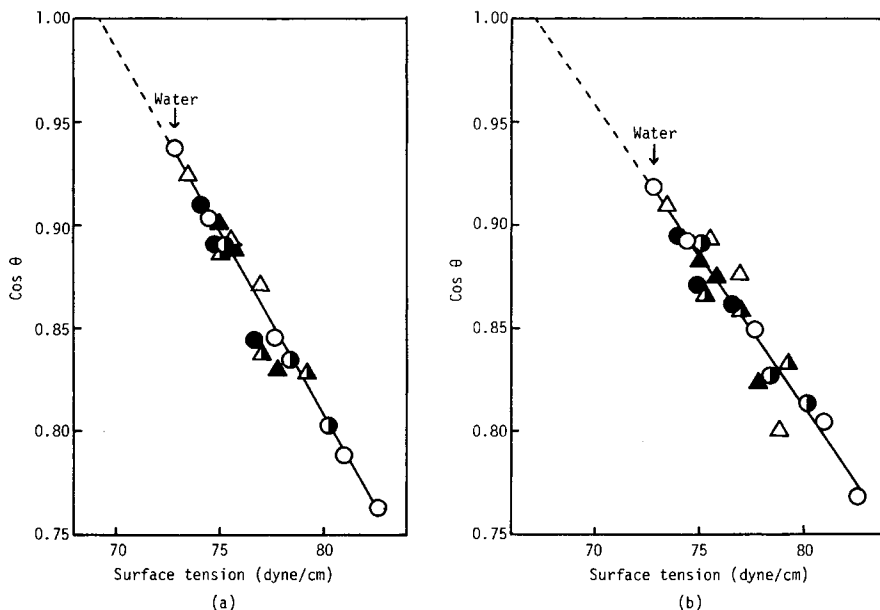


Fig. 4. Relationships between surface tension (γ_L) of pure liquid and aqueous salt solutions and cosine of contact angles (θ): (a) CR-39—SEM—H⁺ GP; (b) CR-39—SEM—Na⁺ GP; (○) NaCl; (●) NaNO₃; (●) NaBr; (△) KCl; (▲) MgCl₂; (▲) MgSO₄.

—StS—Na⁺ GP also gave a straight line, respectively, where the details were omitted. The γ_c values with a series of the pure liquid and the aqueous salt solutions (NaCl and NaNO₃) are shown in Table II.

As shown in Figure 5, the Zisman plot for the CR-39—MAA—H⁺ GP was linear regardless of the type of the salts. On the other hand, the Zisman plot for the CR-39—MAA—Na⁺ GP did not fall in a single straight line, where Mg²⁺-containing solutions gave a quite different line from that yielding from monovalent-cation-containing solutions. This trends in the Zisman plots for the other GPs with the carboxyl group on their surface were also similar, and the γ_c values obtained with series of the pure liquids and the salt solutions (NaCl and NaNO₃) are compiled in Table II. To confirm the influence of cation valency on the γ_c values, the γ_c values for the following pretreated specimen were measured with

TABLE II
Values of Contact Angle (θ) with Water and Critical Surface Tension (γ_c) for the GPs Used

	Acid-treated GP		Alkali-treated GP	
	θ with water (°)	γ_c (dyn/cm)	θ with water (°)	γ_c (dyn/cm)
CR-39—SEM	20.5	69	23.5	67
CR-39—StS	39.6	62	40.2	62
CR-39—AA	53.0	51	11.5	72
CR-39—MAA	51.7	51	9.2	72
DAP—AA	56.4	53	10.5	72
DAP—MAA	50.4	57	13.1	72
4ED—AA	46.7	54	8.9	72
4ED—MAA	50.2	54	11.6	72

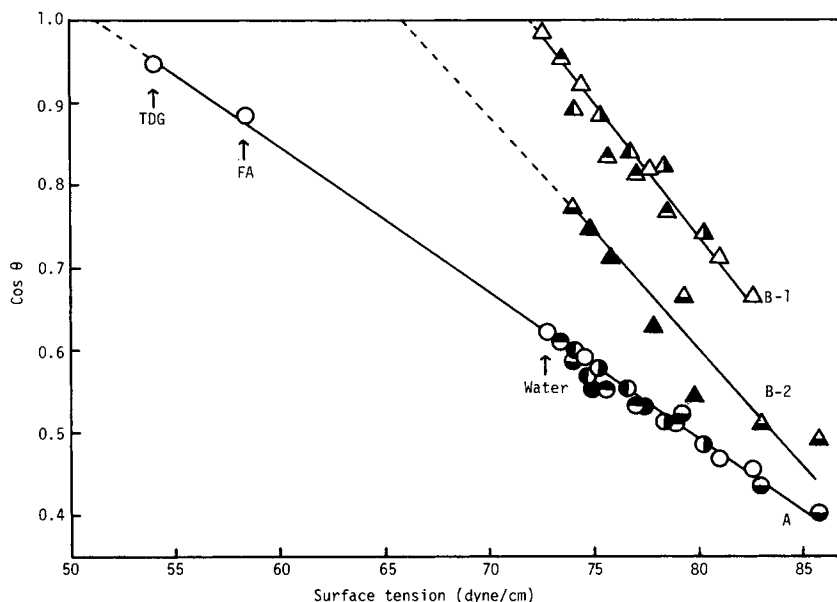


Fig. 5. Relationships between surface tension (γ_L) of pure liquids and aqueous salt solutions and cosine of contact angles (θ): (A) Circular plot, CR-39—MAA $^-$ H $^+$ GP; (B-1, B-2) triangular plot, CR-39—MAA $^-$ Na $^+$ GP. (O, Δ) NaCl; (\bullet , \blacktriangle) NaNO $_3$; (\circ , \blacktriangle) NaBr; (\odot , \blacktriangle) KCl; (\ominus , \blacktriangle) MgCl $_2$; (\bullet , \blacktriangle) MgSO $_4$.

series of the pure liquids and the salt solutions (NaCl): The CR-39—MAA GP was immersed in an aqueous solution (20 wt %) of NaCl, MgCl $_2$, or NaOH for 1 min. The γ_c values of the CR-39—MAA $^-$ H $^+$ GP for NaCl, MgCl $_2$, and NaOH pretreatment were 52, 51, and 71 dyn/cm, respectively. The γ_c values of the CR-39—MAA $^-$ Na $^+$ GP for NaCl and MgCl $_2$ pretreatment were 71 and 67 dyn/cm, respectively. The value for the latter agreed with the value (67 dyn/cm) estimated from the plot B-2 in Figure 5. The above results indicate that the salts, having the same ionic species as that generated from the substrate polymer and unreacting with the carboxyl group, should be available for the determination of the γ_c value.

The γ_c values in Table II indicate the following terms: (1) the surface energy of the GPs with the sulfonic or sulfonate group on their surface is little affected by the type of cationic and anionic species of the salts due to the strong acidity of this group; (2) the surface energy of the GPs with the carboxyl group is little affected by the type of cationic and anionic species of the salts due to the low degree of the dissociation and the mutual aggregation of this group. On the other hand, the surface energy of the GPs with the carboxylic salt group is influenced by the type of cationic species (Na $^+$, K $^+$, or Mg $^{2+}$) of the salts due to the differences in the ionization tendency of cationic species and the ionization characteristic of the carboxyl group, but the anionic species (Cl $^-$, Br $^-$, or NO $_3^-$) had no influence on the surface energy of the GPs.

The values in Table II are explained as follows: (1) the γ_c values for the CR-39—SEM and the CR-39—StS GPs are little affected by the form (free acid or salt) of the sulfonic group due to the high degree of the dissociation of this group. (2) The larger γ_c value for the CR-39—SEM GP than that for the

CR-39—StS GP is attributed to the difference in the surface density of the sulfonic group on the respective surface. (3) The γ_c values for the GPs with carboxylic salt group are much larger than those for the GPs with carboxyl group due to the difference in the degree of the dissociation between carboxylic salt and the carboxyl group. (4) The γ_c values for the GPs with the sulfonic group were larger than those for the GPs with carboxyl group due to the difference in the degree of the dissociation of the respective group. On the other hand, the γ_c values for the GPs with sulfonate group were smaller than those for the GPs with carboxylic salt group due to the difference in the surface density of the respective group. (5) The trends in the γ_c values were the same as those in the hydrophilicity anticipated from the θ values.

As mentioned above, the Zisman plots for the pure liquids and the aqueous solutions of salts fell in a single straight line, which indicates a minor effect of the adsorption of the salt on the specimen surface. Considering that the high surface tension of salt solutions is due to negative adsorption and that the used salts ionize and hydrate completely in water, less adsorption of the salt would be expected. Now, the aqueous solutions of the salts can be used for the determination of the γ_c value of polymeric solids with hydrogen-bonding and/or ionic surface.

CONCLUSION

The critical surface tension (γ_c) of polymer surfaces with high surface energy was determined with a series of the pure liquids (TDG, FA, and water) and the aqueous solutions of the salts (NaCl, NaNO₃, etc.) as a hydrogen-bonding liquid.

(1) The Zisman plots for the GPs with the amide, sulfonic, or carboxyl group on their surface gave a straight line.

(2) The trends in the γ_c values estimated from the above plots coincided with those in the hydrophilicity anticipated from the θ values.

(3) As a result of (1) and (2), the aqueous solutions of the salts will be able to use for the determination of the γ_c value as a hydrogen-bonding liquid.

References

1. For example, see: (a) Y. Ikada, and T. Matsunaga, *J. Adhesion Soc., Jpn.*, **14**(11), 427 (1978); **15**(1), 18 (1979); **15**(3), 91 (1979); (b) Y. Lipatov, and A. Feinerman, *Adv. Colloid Interface Sci.*, **11**, 195 (1975); (c) H. F. Mark, N. G. Gaylord, and N. H. Bakaies, *Encyclopedia of Polymer Science and Technology*, Interscience, New York, 1964, Vol. 1, pp. 445–477.
2. W. A. Zisman, *Adv. Chem. Ser.*, **43**, 1 (1964).
3. A. W. Newmann, *Adv. Colloid Interface Sci.*, **4**, 105 (1974).
4. (a) J. R. Dann, *J. Colloid Sci.*, **32**(2), 302 (1970); (b) Y. Kitazaki and T. Hata, *J. Adhesion Soc., Jpn.*, **8**(3), 123 (1972).
5. (a) M. K. Bennett, and W. A. Zisman, *J. Phys. Chem.*, **63**, 1241 (1959); (b) A. J. Allan, *J. Polym. Sci.*, **38**, 297 (1959).
6. W. H. Smarook, and S. Bonotto, *Polym. Eng. Sci.*, **8**, 41 (1968).
7. L. Lee, *J. Polym. Sci., Part A-2*, **5**, 1103 (1967).
8. Y. Ohtsuka, Y. Terao, F. Takami, and N. Kaneko, *Polym. Prepr., Jpn.*, **28**(6), 1194 (1979).
9. Y. Ohtsuka, N. Kaneko, and F. Takami, *J. Appl. Polym. Sci.*, **26**(7), 2423 (1981).
10. Y. Ohtsuka, and N. Kaneko, *J. Appl. Polym. Sci.*, **27**, 545 (1982).
11. N. Kaneko, and Y. Ohtsuka, *J. Appl. Polym. Sci.*, to appear.
12. R. C. Weast, *Handbook of Chemistry and Physics*, 52nd ed., Chemical Rubber Co., 1971–1972, p. F-28.

13. W. J. Murphy, M. W. Roberts, and J. R. H. Ross, *J. Chem. Soc., Faraday Trans. 1*, **68**(7), 1190 (1972).

14. I. J. Lin, J. P. Friend, and Y. Zimmels, *J. Colloid Interface Sci.*, **45**(2), 378 (1973).

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