

Determination of Cohesive Energy Densities of Unsaturated Polyester Resins from Swelling Measurements

SEIICHI TAKAHASHI, *Dainippon Ink and Chemicals Inc., 35-58 3-Chome Sakashita Itabashi-Ku, Tokyo, Japan*

Synopsis

The cohesive energy densities (ced) of five unsaturated polyester resins with varying degree of crosslinks were determined by swelling measurements in 17 single solvents and 11 binary solvents of the acetone–benzene system. The solubility parameters (δ_p) of these resins were calculated by six methods. It is concluded that the values of δ_p for the unsaturated polyester resins decrease with increasing degree of crosslinks. Since the unsaturated polyester resin consists of polar and nonpolar parts in molecular structure, the choice of solvents is very important in order to obtain the maximum degree of swelling when δ_p is estimated by swelling measurements.

INTRODUCTION

A crosslinked polymer absorbs the solvent and swells to some extent when it is placed in the solvent. Equilibrium swelling for the crosslinked polymer is attained when the dilution force accompanying the swelling equals the contraction force of the rubberlike elasticity. Since the molecular chain in the crosslinked structure acts not only as the solute, but also as the osmotic membrane, it is believed that the swelling behavior is similar to the osmotic pressure behavior. The swelling phenomenon which determines the interaction of the polymer with a solvent and also the solvent resistance are of great fundamental and technical importance.

In this study, the unsaturated polyester resins are used as the crosslinked polymer model. Swelling measurements have been made on five resins which had different degrees of crosslinks using 17 single solvents and 11 binary solvents of the acetone–benzene system. The swelling power of different solvents and the relation between the polymer structure and swelling properties have been examined.

Many workers¹⁻⁹ have used the solubility parameter concept to select solvents for polymers, pigments, plasticizers, etc. The solubility parameter of low molecular weight compounds is calculated by using a number of theoretical equations.¹⁰⁻¹³ Determination of the solubility parameter of crosslinked polymers by using such equations is not possible because the data on their physical constants, i.e., boiling point, surface tension, van der Waal constants, heat of evaporation, compressibility factors, etc., are usually not available. There is no direct, experimental method for determining the solubility parameter of a crosslinked polymer. In one indirect method, the solubility parameter is equated to that of the solvent in which the crosslinked polymer has a maximum swelling coefficient at a constant temperature in comparison to other probable solvents.

In this study, the cohesive energy densities (ced) and solubility parameters (δ_p) of resins were obtained by methods of Gee,² Boyer and Spencer,¹⁴ Bristow and Watson,¹⁵ Small,⁴ Hoy,¹² Krevelen¹⁶ methods. The relative merits of these methods and a critical appraisal of the previous work on swelling are discussed.

SOLUBILITY PARAMETER EQUATION

The behavior of polymer in a solvent, the selection of solvents for polymers, and swelling properties of crosslinked polymers are evaluated by a polymer solvent interaction parameter (χ). The values of χ was introduced by Flory¹⁷ and Huggins,¹⁸ and it has been extended by Flory and Rehner¹⁹

$$\chi_g = \frac{-\ln(1 - v_{2g}) - v_{2g} - (\rho_p V_1/M_c)(v_{2g}^{1/3} - v_{2g}/2)}{v_{2g}^2} \quad (1)$$

where V_{2g} is the volume fraction of polymer in the swollen gel, ρ_1 and ρ_p are densities of the solvent and polymer, respectively, V_1 is the molar volume of solvent, M_c is the molecular weight between crosslinks in the polymer, and χ_g is the polymer solvent interaction parameter for the solvent polymer pair.

The ced and δ_p are closely connected with the degree of swelling and χ_g . The values of δ_p are calculated by the following methods.

Gee's Method

Gee has pointed out² that the degree of swelling is greatest in a solvent of the same ced as the ced of polymer for vulcanized rubbers. In other words, like dissolves like.

A plot of volume swelling coefficient (Q) against the square root of the ced of solvent (δ_1) gives an approximately Gaussian curve²:

$$Q = Q_{\max} \cdot e^{-KV_1(\delta_1 - \delta_p)^2} \quad (2)$$

and

$$\delta_1 = \delta_p \pm [(1/KV_1 \cdot \ln(Q_{\max}/Q))]^{1/2} \quad (3)$$

where Q_{\max} is the maximum swelling coefficient (maximum volume of liquid imbibed per unit volume of the polymer), Q is swelling coefficient, δ_1 and δ_p are solubility parameters of solvent and polymer, respectively, and K is a constant. Hence, from a plot of $[(1/V_1 \ln(Q_{\max}/Q))]^{1/2}$ vs. δ_1 , δ_p can be determined.

Boyer and Spencer's Method

Since χ_g is a free energy term, it can be expressed as the sum of entropy term (χ_s) and enthalpy term (χ_h). From a refinement of the lattice model, Huggins¹⁸ deduced the value of χ_g with the aid of the Hildebrand-Scatchard assumptions²⁰:

$$\chi_g = \chi_s + (KV_1/RT)(\delta_1 - \delta_p)^2 \quad (4)$$

where R is the gas constant and T is the absolute temperature. The swelling ratio depends not only on the $(\delta_1 - \delta_p)^2$, but also on V_1 and χ_s . Unfortunately,

χ_s cannot be predicted accurately, and the experimental values are temperature-dependent.^{1,21} Furthermore, χ_g values are concentration dependent if the experiments are carried out over a wide range of polymer concentrations.^{1,21,22} Although the observed temperature dependence of χ_s and concentration dependence of χ_g are inconsistent with the theory, the deviations are small. The combined Flory-Huggins and Hildebrand-Scatchard picture gives an adequate approximation for the interpretation of most polymer solution data. Neglecting variations in K and V_1 from one solvent to another, a plot of χ_g against δ_1 should be a parabola whose minimum ordinate is equal to χ_s and it occurs when polymer and solvent have the same ced.

The Huggins equation can be rewritten as

$$(\chi_g - \chi_s)/V_1 = (K/RT)(\delta_1 - \delta_p)^2 \quad (5)$$

Boyer and Spencer plotted $(\chi_g - \chi_s)/V_1$ against δ_1 for different solvents and obtained a family of parabolic curves for the styrene-divinyl benzene gel.¹⁴ Since good solvents should not be seriously affected by this concentration dependence of χ_g , the choice of solvents is very important in the estimation of δ_p from eq. (5).

Bristow and Watson's Method¹⁵

Rearrangement of eq. (5) gives, if $K = 1$,

$$\frac{\delta_1}{RT} - \frac{\chi_g}{V_1} = \left(\frac{2\delta_p}{RT}\right) \cdot \delta_1 - \frac{\delta_p^2}{RT} - \frac{\chi_s}{V_1} \quad (6)$$

Assuming that χ_s is in the range of 0.1–0.4 and it is not a function of ced, χ_s/V_1 is only 3% or less of δ_p^2/RT for reasonable values of δ_p of 5–10. By plotting the left hand side of eq. (6) against δ_1 , a straight line is obtained, and δ_p can be calculated from the slope and intercept of this line:

$$\text{slope } A = 2\delta_p/RT \quad (7)$$

$$\text{intercept } B = -\delta_p^2/RT - \frac{\chi_s}{V_1} \quad (8)$$

EXPERIMENTAL

Materials²³

Five unsaturated polyester resins I-1, I-2, I-3, I-4, and I-5 were prepared by varying the molar ratios of maleic anhydride and succinic acid. Each resin contains two moles styrene for each mole of maleic anhydride.

A three-neck 2-L flask was charged with raw materials. The flask was fitted with a stirrer, inert gas (CO_2) inlet and outlet, and thermometer. The flask and raw materials were heated to 220°C using a heating mantle. The reaction temperature was maintained at $220 \pm 2^\circ\text{C}$ under a CO_2 atmosphere. After the viscosity and acid value of resins reached the prescribed value, the resin solids were dissolved in the required amount of styrene monomer. At the reaction temperature of 220°C, maleic acid isomerizes to fumaric acid, which copolymerizes readily with styrene monomer.²⁴

TABLE I
Compositions and Physical Properties of Unsaturated Polyester Resins

Samples	I-1	I-2	I-3	I-4	I-5
Compositions (mol)					
Maleic anhydride	10	15	20	25	30
Succinic acid	40	35	30	25	20
Propylene glycol	50	50	50	50	50
Properties of resin solution					
Polyester resin contents (%)	81.1	73.6	68.1	64.2	58.0
Styrene monomer contents ^a (%)	8.9	26.4	31.9	35.8	42.0
Viscosity ^b	Z ₄ -Z ₅	X-Y	T-U	T-U	L
Acid value	33.0	32.3	28.8	27.9	25.2
Color number ^b	2	3	1	2	1
Density (g/cc) at 21°C	1.170	1.141	1.120	1.109	1.090
Properties of the cured film					
Molecular weight between crosslinks, M_c	1400	576	363	189	130
Density (g/cc) at 25°C	1.232	1.236	1.215	1.210	1.200

^a Maleic anhydride/styrene monomer = 1/2 (mole ratio).

^b Gardner method.³⁶

For sample films I-1 to I-5, 0.03% by weight of cobalt naphthenate and 1.2% by weight of methyl ethyl ketone peroxide were added to 50 g of unsaturated polyester resin-styrene solution with stirring. The mixed material was poured between two glass plates and held at 25°C for 24 h. The space distance of two glass plates is 1 mm. These resin films were then cured, annealed for 8 h at 50°C and 150°C each, and removed from the glass plates. The compositions and physical properties of the resins are given in Table I.

Solvents

The solvents used were reagent-grade materials which were redistilled. δ_1 and related physical properties were obtained from the literature.²⁵ These values are given in Table II.

Swelling Procedure

Polymer samples were cut into small rectangular pieces of approximately 10 mm × 13 mm × 1 mm, weighing from 0.1 to 0.2 g each. They were accurately weighed and immersed in about 15 mL of the solvent in closed sample tubes. The samples were taken out at intervals of 24 h. The surfaces were dried with filter paper, and the samples were placed in a previously weighed bottle and were quickly weighed by using a chemical balance. This was repeated for more than a week to determine the equilibrium swelling. All measurements were carried out at room temperature, 25°C.

In most cases, maximum swelling took place within 2-3 days and stayed constant over a period of 1 week. In a few cases, the weight of the swollen polymer showed a small decrease with time after reaching the maximum. In such cases, equilibrium swelling was obtained by plotting the volume swelling ratio (R_v) against time.²⁶

TABLE II
Molar Volumes (V_1), Densities (ρ_1), and Solubility Parameters (ρ_1) for Solvents at 25°C²⁵

Solvents	V_1 (cc/mol)	ρ_1 (g/cc)	δ_1 (cal/cc) ^{1/2}
Methanol	40.41	0.7929	15.00
Ethanol	58.37	0.7893	12.95
<i>n</i> -Propanol	74.70	0.8044	12.09
<i>i</i> -Propanol	76.37	0.7862	11.60
<i>n</i> -Butanol	91.73	0.8080	11.50
<i>i</i> -Butanol	92.23	0.8034	11.26
Acetone	73.33	0.7920	9.68
Methyl ethyl ketone	89.57	0.8050	9.24
Methyl <i>n</i> -propyl ketone	106.07	0.8120	8.92
Methyl <i>i</i> -butyl ketone	124.93	0.8017	8.83
Methyl acetate	79.88	0.9274	9.32
Ethyl acetate	97.79	0.9009	8.85
<i>n</i> -Propyl acetate	115.14	0.8870	8.60
<i>n</i> -Butyl acetate	131.70	0.8820	8.49
Benzene	88.86	0.8790	9.14
Toluene	106.29	0.8668	8.92
Xylene	122.26	0.8683	8.85

The value of R_v was calculated using sample weights before and after swelling, W and W' , the densities of solvent and polymer, ρ_1 and ρ_p :

$$R_v = 1 + (\rho_p/\rho_1)(W'/W - 1) \quad (9)$$

$$R_w = W'/W \quad (10)$$

$$v_{2g} = 1/R_v \quad (11)$$

where R_w is the weight swelling ratio and v_{2g} is the volume fraction of polymer in the swollen gel.

RESULTS AND DISCUSSION

Swelling Measurements by a Single Solvent

The values of R_v and χ_g for five unsaturated polyester resin films measured in several different solvents are given in Tables III and IV.

As to the effect of various kinds of solvents on swelling, and swelling power is strong and the value of R_v is high in ketone and ester solvents. The order of R_v is ketone = ester > aromatic hydrocarbon > alcohol.

The degree of swelling decreases with decrease of M_c and with the increase of packed film structure. The elastic entropy effect of crosslinks has a significant effect on R_v . When the value of R_v is low, the swelling dependence of different kinds of solvents becomes small. The esters and ketones, having strong swelling power, greatly affect R_v dependence of M_c , and the alcohols, having weak swelling power, have a weak effect.

In homologous solvents, swelling power increases with a decrease in molar

TABLE III
Equilibrium Volume Swelling Ratios (R_v) for Samples I-1, I-2, I-3, I-4, and I-5 in Various Solvents at 25°C

Solvents	I-1	I-2	I-3	I-4	I-5
Methanol	1.90	1.45	1.26	1.21	1.12
Ethanol	1.67	1.39	1.20	1.04	1.02
<i>n</i> -Propanol	1.58	1.37	1.06	1.03	1.23
<i>i</i> -Propanol	1.50	1.37	1.03	1.02	1.01
<i>n</i> -Butanol	1.49	1.38	1.03	1.02	1.01
<i>i</i> -Butanol	1.46	1.08	1.02	1.07	1.00
Acetone	2.62	1.66	1.47	1.36	1.31
Methyl ethyl ketone	2.71	1.83	1.46	1.34	1.24
Methyl <i>n</i> -propyl ketone	2.47	1.74	1.43	1.08	1.05
Methyl <i>i</i> -butyl ketone	1.95	1.64	1.34	1.03	1.02
Methyl acetate	2.71	1.89	1.48	1.37	1.32
Ethyl acetate	2.51	1.78	1.45	1.24	1.15
<i>n</i> -Propyl acetate	2.31	1.71	1.35	1.07	1.04
<i>n</i> -Butyl acetate	1.88	1.51	1.10	1.03	1.02
Benzene	1.90	1.58	1.28	1.05	1.03
Toluene	1.74	1.43	1.09	1.04	1.02
Xylene	1.51	1.25	1.04	1.03	1.02

volume. Isomeric solvents have a different swelling power. As to the effect of the chemical structure of alcohols on R_v , R_v is high in the linear structure and is low in the branching structure, i.e., R_v of *n*-propanol > R_v of isopropanol, R_v of *n*-butanol > R_v of isobutanol. The swelling tendency in aromatic hydrocar-

TABLE IV
Polymer Solvent Interaction Parameters (χ_g) for Samples I-1, I-2, I-3, I-4, and I-5 Swelled in Various Solvents at 25°C

Solvents	I-1	I-2	I-3	I-4	I-5
Methanol	0.727	0.914	1.130	1.145	1.434
Ethanol	0.804	0.933	1.232	2.192	2.798
<i>n</i> -Propanol	0.833	0.933	2.017	2.422	2.359
<i>i</i> -Propanol	0.889	0.918	2.558	3.048	3.046
<i>n</i> -Butanol	0.884	0.878	2.554	3.002	3.555
<i>i</i> -Butanol	0.909	1.873	3.159	1.656	1.648
Acetone	0.444	0.650	0.703	0.642	0.537
Methyl ethyl ketone	0.462	0.473	0.655	0.583	0.619
Methyl <i>n</i> -propyl ketone	0.390	0.479	0.629	1.504	1.832
Methyl <i>i</i> -butyl ketone	0.556	0.503	0.719	1.806	2.729
Methyl acetate	0.396	0.473	0.664	0.582	0.456
Ethyl acetate	0.400	0.476	0.644	0.772	0.942
<i>n</i> -Propyl acetate	0.426	0.469	0.724	1.611	1.920
<i>n</i> -Butyl acetate	0.580	0.623	1.502	2.306	2.416
Benzene	0.645	0.667	0.940	1.952	2.321
Toluene	0.694	0.777	1.625	2.194	2.411
Xylene	0.831	1.041	2.306	2.210	2.448

bons is also similar. The order of R_v value is benzene > toluene > xylene. Although the effects of the molar volume and the chemical branching structure of solvents on R_v have the same tendency in a limited range of homologous solvents, these effects may not be applied as a general rule for every solvent. The effects of various kinds of solvents on swelling phenomenon depend upon not only the molecular shape, bulkiness, and the mobility of the solvent, but also upon the affinity of solvent and polymer as well. The maximum degree of swelling appears in a solvent with a molar volume intermediate between the ketones and esters. Although the value of χ_g is apparently an inverse function of R_v , it also depends on M_c , V_1 , and χ_s .

Kawai showed that R_v has a higher correlation with the value of $(\frac{1}{2} - \chi_g)/V_1$ than χ_g for the case of rubber.²⁷ In the present study, where the value of R_v is fairly low, the value of χ_g is not always below 0.5. It can't be asserted positively which is better, χ_g or $(\frac{1}{2} - \chi_g)/V_1$, as the measure of the degree of swelling under the conditions of this experiment.

χ_g increases with the decrease of M_c for alcohols and aromatic hydrocarbons (I-1 < I-2 < I-3 < I-4 < I-5). But the relation between χ_g and M_c is not simple for esters and ketones. For instance, I-3 sample shows the maximum value of χ_g for acetone in the ketone series and the methyl acetate in the ester series.

The unsaturated polyester resin films consist of polar polyester segments in the main chain and nonpolar polystyrene segments in the crosslinks. The polar solvents such as ketones, esters, and alcohols do not act as good solvents for the nonpolar polystyrene segments in the polymer structure. Therefore, even if M_c increases, the degree of swelling does not increase. χ_g does not simply decrease with the increase of M_c .

Determination of Solubility Parameters of Polymers by the Swelling Measurement Using Single Solvents

Figure 1 shows plots of $[(1/V_1) \ln(Q_{\max}/Q)]^{1/2}$ vs. δ_1 [eq. (3)] for the polymer samples. Although linearity is not remarkable, the esters and ketones, having high swelling power, show an adequate graphical determination of δ_p for each sample.

The values of δ_p , obtained by Gee's method, and Q_{\max} are given in Tables V and VI, respectively. Equation (3) is not obeyed for the aromatic hydrocarbons and alcohols, which are poor swelling solvents. Since the values of Q or Q_{\max} in these solvents are small, the errors in δ_p become large. The values of δ_p are between 9.1 and 9.5. The δ_p value increases slightly, and the Q_{\max} value decreases with the increase of maleic acid content in polyester resins (increasing degree of crosslinks).

Figure 2 shows a plot of the function $(\chi_g - \chi_s)/V_1$ against δ_1 , which Boyer and Spencer have recommended as the procedure for computation of δ_p [see eq. (5)].

The results for esters and ketones, which have strong swelling power, fit all points with a single parabola curve. χ_s is calculated from its minimum value of χ_g using eq. (4). δ_p and χ_s are given in Tables V and VI. The values of δ_p and χ_s are from 8.9 to 9.7 and 0.36 to 0.63, respectively. δ_p values, obtained by the Boyer-Spencer method, are lower than the values obtained by Gee's method. δ_p value for the sample I-3 is minimum among the five samples using the

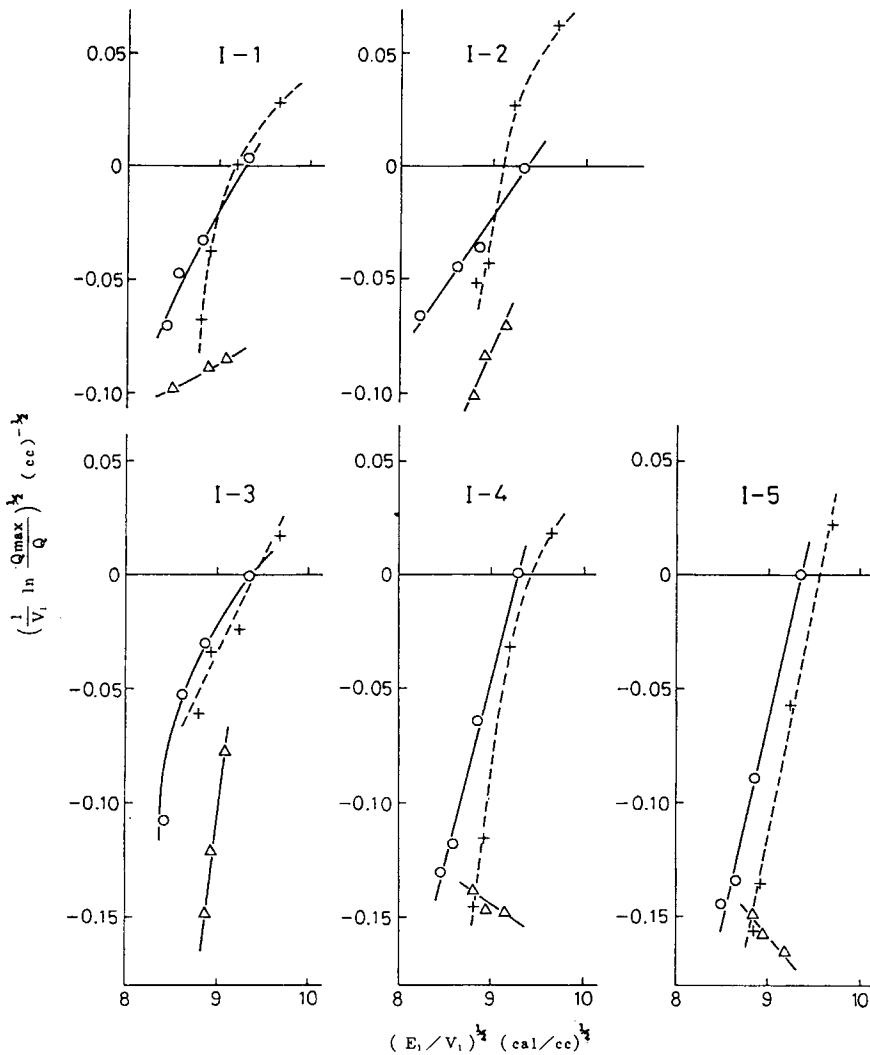


Fig. 1. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by Gee's method. Swelling of unsaturated polyester resins in a single solvent. The solvent types: (+) ketones; (O) esters; (Δ) aromatic hydrocarbons.

Boyer-Spencer method, but this tendency does not appear in the case of Gee's method. This suggests that the behavior of the maximum value of χ_s and the minimum value of δ_p for sample I-3 depends on the nonlinear characteristic of the polymer structure. As the effect of δ_p contribution for polyester parts (increasing of δ_p) competes with δ_p contribution for polystyrene parts (decreasing of δ_p), the δ_p value for the polyester resin film is reflected as the total effect. The structural characteristics of the polymer will slightly affect the Q and χ_g values. Such a tendency can also be detected from the following data; the values of δ_p are obtained by the Bristow-Watson method.

Figure 3 shows a plot of the function $(\delta_1^2/RT - \chi_g/V_1)$ against δ_1 [eq. (6)]. The linear plots of eq. (6) were obtained from the data of Table IV, with the exception

TABLE V
 Collected Values of the Solubility Parameter (δ_p) for Unsaturated Polyester Resins Swelled in a Single Solvent and Acetone-Benzene Binary Solvent Mixtures

Solvent Types	Determination Method							
	δ_p obtained by Gee's method		δ_p obtained by Boyer-Spencer method		δ_p obtained by Bristow-Watson method			
	Single ^a	Binary ^b	Single ^a	Binary ^b	Slope intercept Single ^a	Slope intercept Binary ^b		
I-1	9.15-9.25	9.50	8.90-9.32	9.40-9.60	9.47	9.45	9.62	9.82
I-2	9.10-9.32	9.44	8.85-9.32	9.36-9.46	9.32	9.34	9.47	9.50
I-3	9.32	9.46	8.85-9.32	9.30-9.41	9.17	9.23	9.32	9.37
I-4	9.32-9.40	9.52	9.24-9.32	9.46-9.57	10.95	10.87	—	—
I-5	9.32-9.50	9.65	9.32-9.68	9.57-9.67	11.84	11.65	—	—

^a Ketones and esters.

^b Acetone-benzene binary solvent mixtures.

TABLE VI
Entropy Terms of Polymer-Solvent Interaction Parameter (χ_s) and Maximum Values of Equilibrium Volume Swelling Coefficient (Q_{\max}) for Samples I-1, I-2, I-3, I-4, and I-5 Swelled in a Single Solvent and Acetone-Benzene Binary Solvent Mixtures

Sample	Values of Q_{\max} calculated using eq. (2)		Values of χ_s calculated using eq. (4)	
	Single ^a	Binary ^b	Single ^a	Binary ^b
I-1	1.714	1.896	0.362	0.352
I-2	0.886	0.902	0.469	0.457
I-3	0.485	0.558	0.629	0.568
I-4	0.365	0.401	0.582	0.529
I-5	0.324	0.321	0.456	0.506

^a Ketones and esters.

^b Acetone-benzene binary solvent mixtures.

of alcohols. However, the plots of samples I-3, I-4, and I-5 are often scattered. The values of δ_p are given in Table V. The values of δ_p obtained from the slope and the intercept of eq. (6) are very similar, and the δ_p value of sample I-3 shows the minimum value among the five samples. This trend is in agreement with

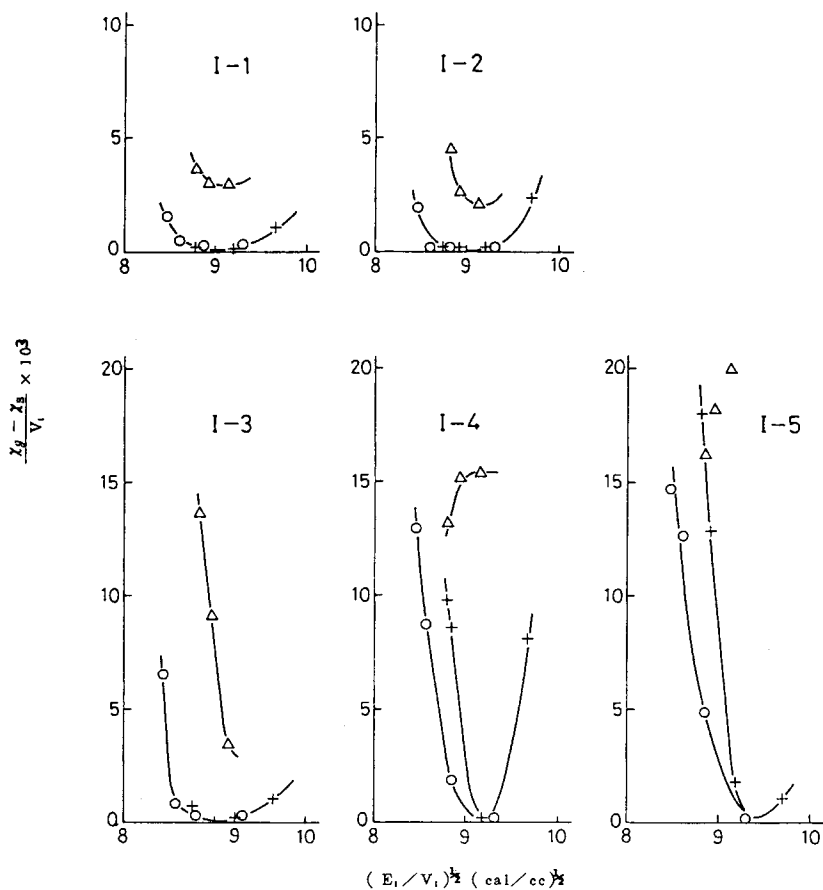


Fig. 2. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by the Boyer-Spencer method. Swelling of unsaturated polyester resins in a single solvent. The solvent types: (+) ketones; (O) esters; (Δ) aromatic hydrocarbons.

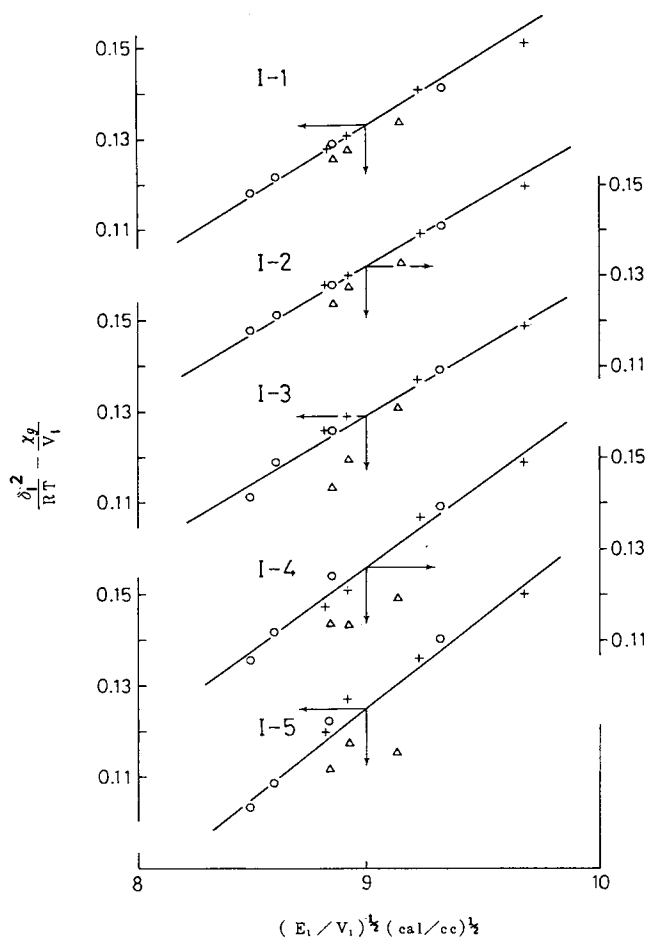


Fig. 3. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by the Bristow-Watson method. Swelling of unsaturated polyester resins in a single solvent. The solvent types: (+) ketones; (O) esters; (Δ) aromatic hydrocarbons.

general results computed by the Boyer-Spencer method. One of the merits of the Bristow-Watson method is that the dependence of the kinds of solvents on χ_s is not greatly altered in computing δ_p . However, the variations of K value have a large effect on χ_g in eqs. (5) and (6). This behavior, showing the minimum point of δ_p for sample I-3 and scattering in the plots of samples I-4 and I-5, suggests the following: (1) the deviation from unity of K value and (2) the heterogeneous morphology and disorder of the polymer structure. These problems indicate the limitation of the theory for the former and irregularities in the curing process for the latter. These polymer-solvent systems have specific interactions and the value of χ_s/V_1 cannot be neglected when the value of χ_s/V_1 is large in eq. (6). As the curing reaction progresses, the crosslinking reaction of the maleic acid parts in the unsaturated polyester chain with the styrene monomer is generally restrained by the steric hindrance. 1-mol maleic acid and 2-mol styrene monomers are difficult to copolymerize stoichiometrically. There are polystyrene oligomers plus crosslinked polyester networks in the cured films. If the polystyrene oligomers are dissolved during the swelling process, the swollen

polymer contains much more polyester parts than the initial composition. The value of M_c , calculated by the viscoelastic experiments, becomes lower due to the entanglement effect for the highly crosslinked polymer.²³ The irregular relation between δ_p and polymer composition is attributable to these factors.

The view of the swelling behavior, based on the concept of the heat of mixing needed to compensate the potential energy change, is premised on the fact that the mixing is random and the interaction between a given pair of molecules is not influenced by the presence of others. In crosslinked polymers, considering the combination of eqs. (1) and (4), the degree of swelling is not only a function of $(\delta_p - \delta_1)$, but also of V_1 and χ_s . Furthermore, the concentration dependence of χ_g and the temperature dependence of χ_s are inconsistent with the theory. The intermolecular interactions are mainly due to dispersion forces. Hydrogen bonding especially has a potent influence on the swelling results. And the strong steric hindrance of bulky polystyrene parts of unsaturated polyester resin is one of the causes of the swelling disorder.

Swelling Measurements in Binary Solvent Systems

Selection of Binary Solvent Systems

Swelling measurements have been made on the sample I-2 in *n*-hexane, benzene, acetone, and carbon disulfide as typical solvent, having different polarities and δ_1 . The physical properties¹³ of each solvent are given in Table VII.

Figure 4 shows the plot of χ_g vs. solvent composition for sample I-2 in binary solvent systems. The effective solubility parameter of the mixture of component A and B can be estimated by Small's formula, based on the principle of additivity of δ_1 for each component⁴:

$$\delta_{(a+b)} = \phi_a \times \delta_a + \phi_b \times \delta_b \quad (12)$$

where $\delta_{(a+b)}$ is the solubility parameter of A-B mixed solvent, δ_a and δ_b are the solubility parameters of solvents A and B, and ϕ_a and ϕ_b are the volume fractions of solvents A and B, respectively.

For the *n*-hexane/carbon disulfide (CS₂) binary system, both solvents are nonpolar; the solvent composition for the minimum value of χ_g seems to be at the CS₂-rich composition, the range being 100/0–90/10 = CS₂/*n*-hexane. For the *n*-hexane/acetone binary solvent (nonpolar–polar system), *n*-hexane acts as a poor solvent and acetone acts as a good solvent for sample I-2. On the other hand, for the benzene/acetone binary solvent (polar–polar system), the benzene

TABLE VII
Solubility Parameters (δ_1), Molar Volumes (V_1), and Dipole Moments (μ) of Solvents¹³

Physical properties	<i>n</i> -Hexane	Benzene	Carbon disulfide	Acetone
δ_d (dispersion force)	7.27	8.95	9.97	7.58
δ_p (dipole force)	0	0.5	0	5.1
δ_h (hydrogen bonding)	0	1.0	0	3.4
ced $\delta_a^2 + \delta_p^2 + \delta_h^2$	52.4	84.1	99.4	95.0
V_1 (cc/mol)	131.6	89.4	60.6	73.9
μ (D)	0.085	0	0.06	2.69

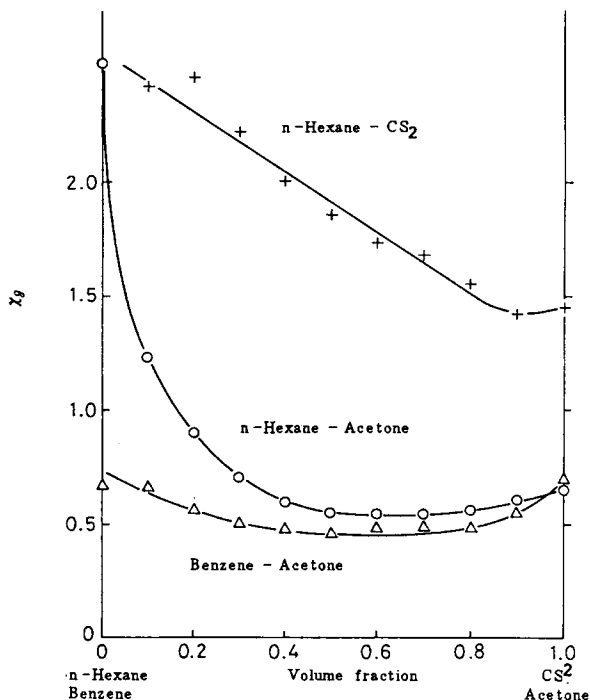


Fig. 4. Plots of polymer solvent interaction parameter vs. composition of binary solvent mixtures for sample I-2. Binary solvent systems: (+) *n*-hexane-carbon disulfide; (O) *n*-hexane-acetone; (Δ) benzene-acetone.

attacks the polystyrene parts and acetone preferentially attacks the polyester parts for sample I-2.

Figures 5 and 6 show the plots of $[(1/V_1) \ln(Q_{\max}/Q)]^{1/2}$ against δ_1 and of $(\delta_1^2/RT - \chi_g/V_1)$ against δ_1 , respectively. The values of δ_p have been computed from the analysis of these results. The values of δ_p are given in Table VIII. The values of δ_p , calculated by Gee's method, decrease in order of *n*-hexane/CS₂ system, acetone/benzene, and acetone/*n*-hexane system. From the Bristow-Watson estimate, δ_p values for the acetone/benzene and acetone/*n*-hexane systems are equal. The χ_s value of sample I-2 is minimum and the Q_{\max} value of sample I-2 is maximum in the acetone/benzene system among three binary solvent systems. Thus, the solvent diffuses into the polymer and the swelling advances sufficiently. The dependence of δ_p on the kinds of solvent system occurs because the composition of mixed solvent is different at the inside and outside of the gel phase and the concentration dependence of χ_g is high in a poor solvent.

In the case of the swelling measurements of polymer in binary solvent systems, when $\chi_{ap} - \chi_{bp} < \chi_{ab}$, the χ_g value is minimum in the intermediate composition of A/B binary solvent,²⁸ where χ_{ap} , χ_{bp} , and χ_{ab} are the interaction parameters of the solvent A/polymer pair, the solvent B/polymer pair, and the solvent A/solvent B pair, respectively. This behavior is evident in the case of the polymerized oil-acetone-isooctane system,²⁹ the poly(vinyl chloride)-acetone-CS₂ system,³⁰ the poly(vinyl acetate)-methanol-water system,³¹ the polystyrene-

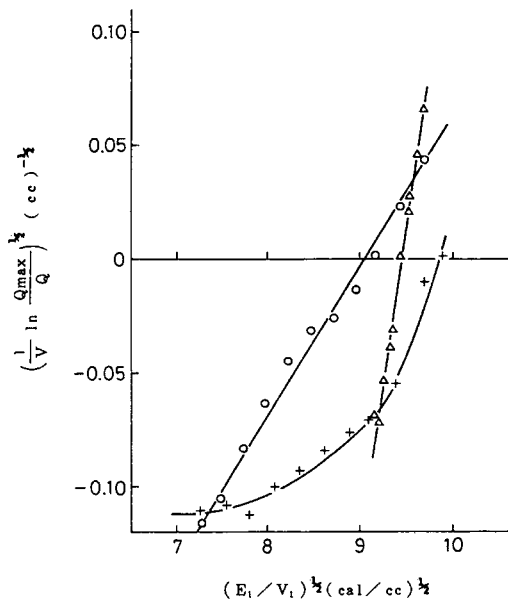


Fig. 5. Computation of solubility parameter of sample I-2 obtained by Gee's method. Swelling of unsaturated polyester resin in various binary solvent mixtures. Binary solvent systems: (+) *n*-hexane-carbon disulfide; (O) *n*-hexane-acetone; (Δ) benzene-acetone.

methyl cyclohexane-acetone system,³² the alkyd resin-benzene-acetone system,³³ etc.

This phenomenon occurs because the intermolecular repulsion between the two solvents accelerates the mixing of polymer and solvent; an example of this is the benzene-acetone-unsaturated polyester resin system.

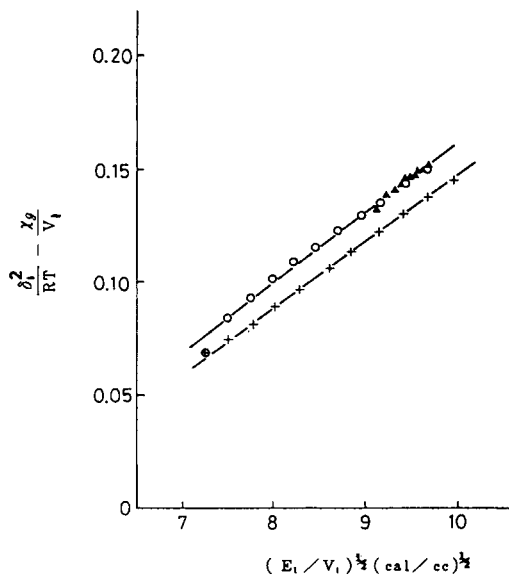


Fig. 6. Computation of solubility parameter of sample I-2 obtained by the Bristow-Watson method. Swelling of sample I-2 in various binary solvent mixtures. Binary solvent systems: (+) *n*-hexane-carbon disulfide; (O) *n*-hexane-acetone; (Δ) benzene-acetone.

TABLE VIII

Solubility Parameters (δ_p), Entropy Terms of Polymer-Solvent Interaction Parameter (χ_s), and Maximum Values of Equilibrium Swelling Coefficient (Q_{\max}), for Sample I-2 Swelled in Various Binary Solvents

	Binary solvent type		
	CS ₂ - <i>n</i> -hexane	Acetone- <i>n</i> -hexane	Acetone-benzene
δ_p obtain by			
Gee's method	9.97	9.10	9.44
Boyer-Spencer method	9.70	8.47-9.19	9.36-9.46
Bristow-Watson method			
from slope	8.72	9.47	9.47
from intercept	8.68	9.51	9.50
$\chi_s = \chi_g$ min	1.43	0.53	0.46
Q_{\max}	0.155	0.754	0.902

The swelling power is strong in the acetone/benzene binary solvent system. This mixed solvent system is an optimum solvent for the unsaturated polyester resin film. And this is supported by the excellent agreement between δ_p values obtained by Gee's, Boyer and Spencer, and Bristow and Watson methods, respectively.

Swelling Measurements in a Benzene/Acetone Binary Solvent

Swelling measurements for the unsaturated polyester resin films were made using benzene/acetone binary solvents.

Figures 7, 8, and 9 show the plots of $[(1/V_1) \ln(Q_{\max}/Q)]^{1/2}$ against δ_1 , $(\chi_g - \chi_s)/V_1$ against δ_1 , and $(\delta_1^2/RT - \chi_g/V_1)$ against δ_1 , respectively. δ_p values computed using each method are given in Table V. χ_s and Q_{\max} values are given in Table VI. δ_p values for each polymer obtained by Gee's and Boyer and Spencer's methods agree well. However, these values are higher than the values obtained using a single solvent. δ_p values from the intercept are in good agreement to δ_p values from the slope by the Bristow-Watson method. As all points are not exactly on a straight line [eq. (6)] for samples I-4 and I-5, it is difficult to compute a single δ_p using these curves. The deviation from the straight line of Figure 9 for the binary solvent and the scattering of swelling measurements for a single solvent suggest a mosaic structure (heterogeneous) of polymer film. χ_s values for a single solvent are larger than the values for the binary solvent by about 0.01 to 0.061, and Q_{\max} values for a single solvent are smaller than the values for the binary solvent by about 0.016 to 0.182. These results indicate that the benzene/acetone binary solvent is better than a single solvent for the unsaturated polyester resin films. Q_{\max} decreases with the decrease of M_c . Sample I-3 has a maximum χ_s value. Samples I-1 and I-2 are different from samples I-4 and I-5 in the swelling unit (segment) of polymer and configuration of segment to solvent.

If the χ_s value of a high molecular weight linear polymer is 0.5 or less, this polymer will dissolve in a given solvent.⁴ The χ_s value for I-1 sample with an easily swellaible structure is 0.352, and for the other sample ranges between 0.457 and 0.568. Therefore, these values of χ_s are reasonable for crosslinked polymers.

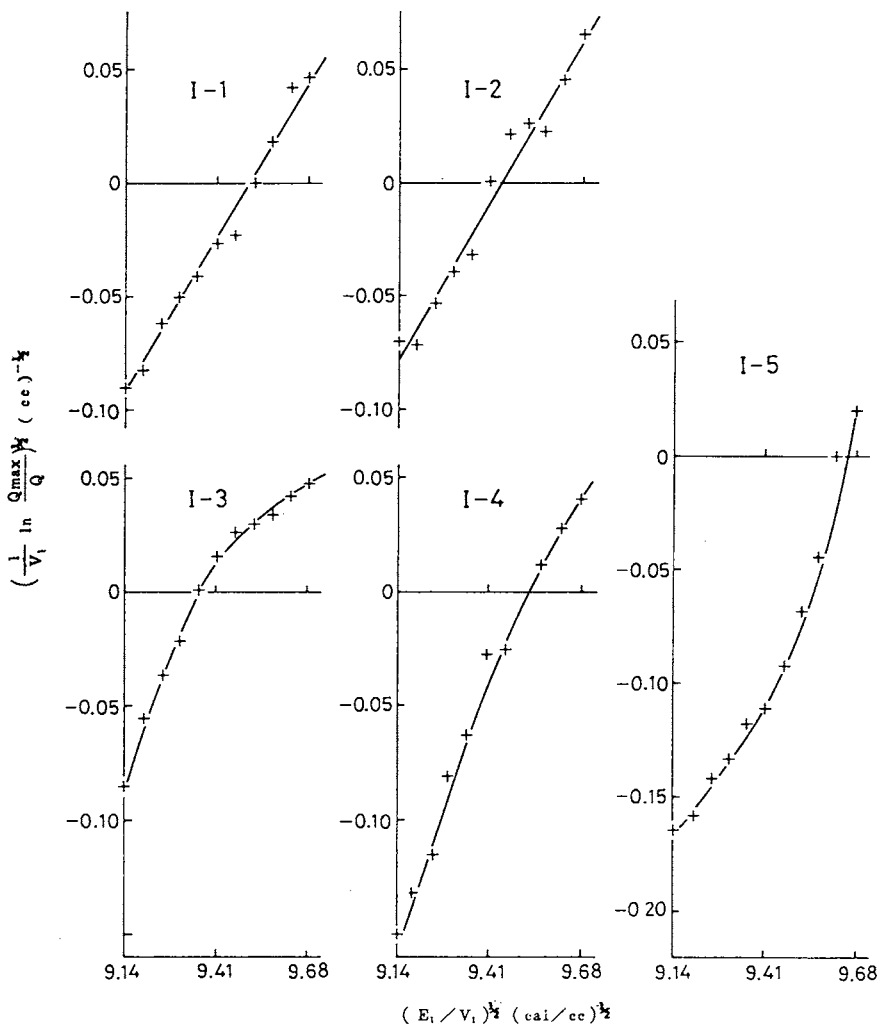


Fig. 7. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by Gee's method. Swelling of unsaturated polyester resins in benzene-acetone binary solvent mixtures.

Solubility Parameter Values Calculated by the Application of the Chemical Group Contribution Technique

The molar attraction constant (F) is the square root of the product of cohesive energy (E) and molar volume (V). F has the additivity of the contributions of chemical groups, atoms, and bonds present in the molecule. The relationship between F and δ_p is as follows:

$$\delta_p = (E/V)^{1/2} = F/V = (\rho \cdot F)/M \quad (13)$$

where ρ is the density of polymer and M is the molecular weight of polymer.

The values of F , E , and V for a given polymer can be calculated by summing up the contributions of individual groups present in a molecule:

$$F = \sum F_i \quad (14)$$

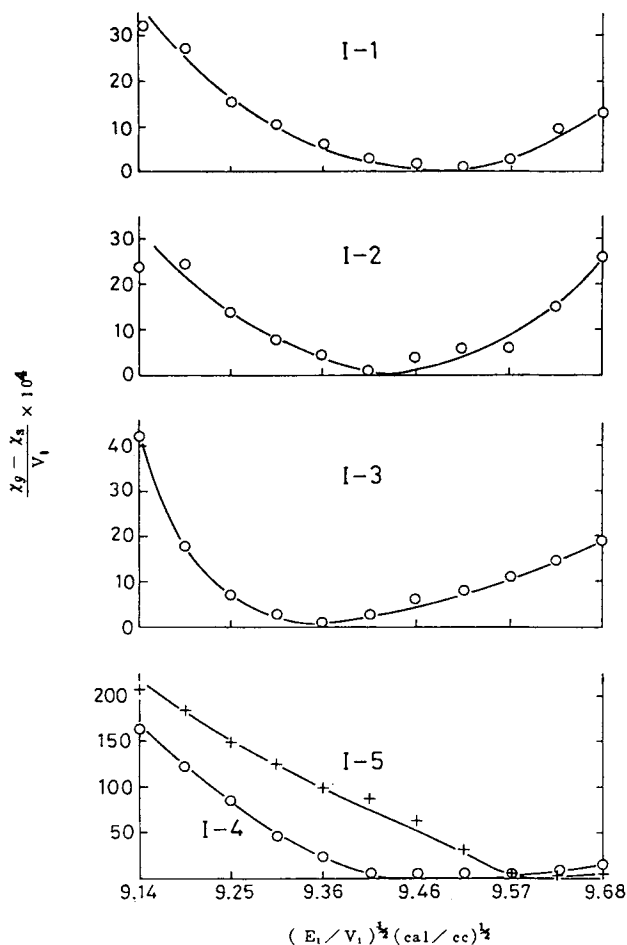


Fig. 8. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by the Boyer-Spencer method. Swelling of unsaturated polyester resin in benzene-acetone binary solvent mixture.

$$E = \sum E_i \quad (15)$$

$$V = \sum V_i \quad (16)$$

Table IX shows δ_p values calculated using the values of individual contributions, F_i , reported by Small and others.^{4,12,13,16,34}

The molar volume of the repeating unit of the amorphous polymer has been calculated by adding up the parachor contributions of atoms and bonds using the following equation³⁵:

$$V_{\text{cal}} = P/2.596 + 2.966 \quad (17)$$

where P is parachor and V_{cal} is the calculated molar volume. The δ_p values are calculated by the following relationship:

$$\delta_{p \text{ cal}} = (\sum F_i) / V_{\text{cal}} \quad (18)$$

$\delta_{p \text{ cal}}$ values are listed in Table IX. δ_p values calculated by Small's and Hoy's

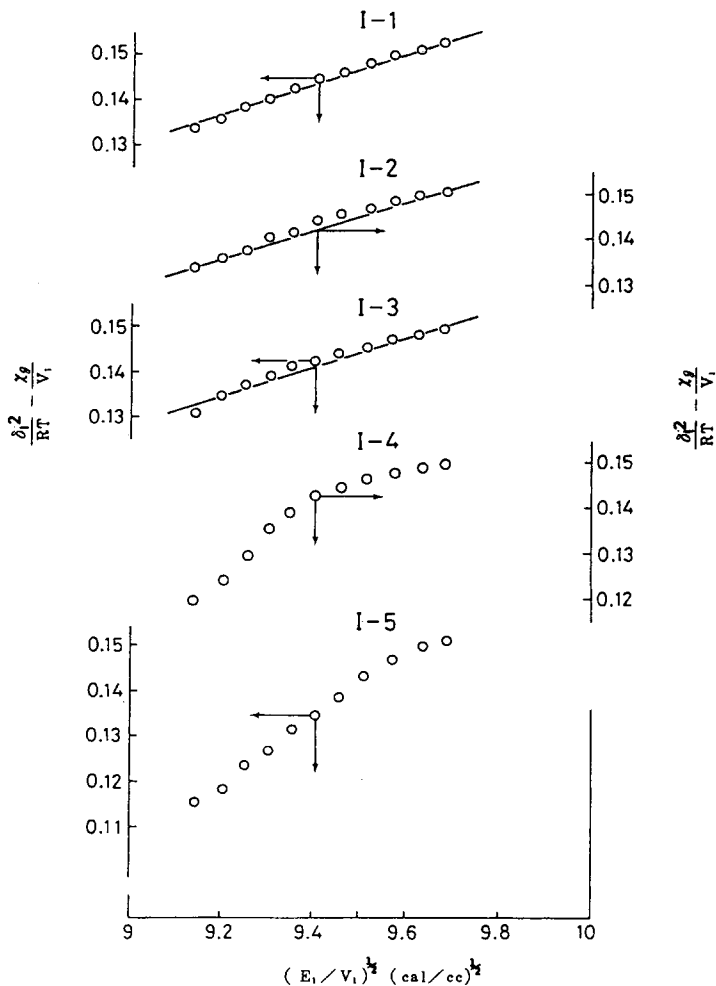


Fig. 9. Computation of solubility parameters of samples I-1, I-2, I-3, I-4, and I-5 by Bristow-Watson method. Swelling of unsaturated polyester resins in benzene-acetone binary solvent mixtures.

methods decreased in order of I-1 > I-2 > I-3 > I-4 > I-5. The values of δ_p cal are a little higher than δ_p values from the swelling data except those obtained by Krellen calculation, but the sample order of δ_p cal agrees well with the experimental results. The δ_p values calculated by Small's method closely approximate δ_p values obtained from the swelling data.

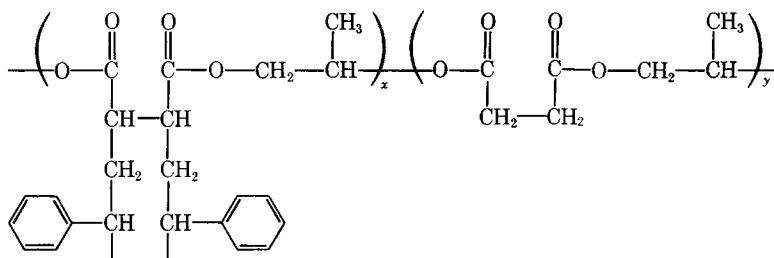
CONCLUSION

Swelling measurements have been made on five unsaturated polyester resins with varying degrees of crosslinks, using 17 single solvents and 11 binary solvents of the acetone/benzene system. The χ_g values have been estimated by the application of the Flory-Rehner theory. χ_g increases with the decrease in Q or Q_{\max} and with the increase in the degree of crosslinks. δ_p values were computed, using the methods suggested by Gee, Boyer and Spencer, and Bristow and Watson. Since the unsaturated polyester resin consists of the polar and

TABLE IX
 Values of δ_p Calculated Using Chemical Group Contribution^a

Samples			I-1	I-2	I-3	I-4	I-5
Model structure	Number of repeating unit	x	1	15	20	25	30
		y	4	35	30	25	20
Molecular weight M of model structure			996	10,990	12,020	13,050	14,080
Molar volume V of model structure (cc)			719	8,063	8,963	9,864	10,765
Density ρ (g/cc)			1.232	1.226	1.215	1.210	1.200
Total molar at traction constant ΣF	Small		7,887	86,780	94,690	102,600	110,510
	Hoy		8,121	89,769	98,326	106,883	114,395
	Krevelen		7,079	79,810	88,830	97,850	106,870
Solubility parameter (cal/mL) ^{1/2} $\rho(\Sigma F)/M$	Small		9.76	9.67	9.57	9.51	9.42
	Hoy		10.05	10.01	9.94	9.91	9.84
	Krevelen		8.76	8.90	8.98	9.07	9.11
$(\Sigma F)/V$	Small		10.97	10.76	10.56	10.40	10.27
	Hoy		11.30	11.13	10.97	10.84	10.72
	Krevelen		9.85	9.90	9.91	9.92	9.93

^a Model structure.



nonpolar parts in the molecular structure, the choice of solvents is very important in order to obtain the maximum degree of swelling when δ_p is estimated by swelling measurements. In the case of swelling measurements for unsaturated polyester resins, ketones and esters (in a single solvent) and the acetone/benzene system (in the binary solvent) are optimum solvents. This is because the chemical structure and polarity of resin and solvent are similar.

δ_p decreases with the increase in the degree of crosslinks (contents of the unsaturated group), but, when the degree of crosslinks becomes too high (M_c about 500), δ_p increases. The phenomenon suggests that the copolymerization reaction between styrene and maleic acid in resin was not perfect and the chemical structure of the cured film was heterogeneous and in a mozaic state.

Since the plot of $(\delta_1^2/RT - \chi_g/V_1)$ vs. δ_1 , a relation suggested by Bristow and Watson, is not simply linear, quantitative treatment of the relation between the structure and cohesive energy of the polymer cannot be strictly applied for samples I-4 and I-5. This is because these polymer/solvent systems have specific interactions.

δ_p values were compared with the calculated values estimated by chemical

group contribution technique suggested by Small and others. The values of δ_p calculated by Small's method closely approximate δ_p values obtained by swelling measurements.

The author wishes to thank Prof. Dr. J. Kumanotani of Tokyo University for helpful discussion and H. Katsuragi for his earnest swelling measurements.

References

1. J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Reinhold, New York, 1949.
2. G. Gee, *Trans. Faraday Soc.*, **38**, 418 (1942); **40**, 468 (1944); *Trans. Inst. Rubber Ind.*, **18**, 226 (1943).
3. G. Scatchard, *Chem. Rev.*, **44**, 7 (1949).
4. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
5. H. Burrell, *Off. Dig., J. Paint Technol. Eng.*, **27**, 726 (1955).
6. C. M. Hansen, *J. Paint Technol.*, **39**, 104 (1967); **39**, 505 (1967); **39**, 511 (1967).
7. C. M. Hansen and A. Beerbower, *Encyclopedia of Chemical Technology, Suppl. Vol. (1971)*, Wiley, New York, 1971.
8. K. A. Karim and D. C. Bonner, *Polym. Eng. Sci.*, **19**, 1174 (1979).
9. R. F. Blanks and J. M. Prausnitz, *Ind. Eng. Chem., Fund.*, **3**(1), 1 (1964).
10. H. Ahmad and M. Yaseen, *J. Color Soc.*, **13**, 7 (1974).
11. J. L. Gardon, *J. Paint Technol.*, **38**, 43 (1966).
12. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
13. D. M. Koenhen and C. A. Smolder, *J. Appl. Polym. Sci.*, **19**, 1163 (1975).
14. R. F. Boyer and R. S. Spencer, *J. Polym. Sci.*, **3**, 97 (1948).
15. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **51**, 1731 (1958).
16. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1972.
17. P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).
18. M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941), *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).
19. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 523 (1943).
20. G. Scatchard, *Chem. Rev.*, **8**, 312 (1931); S. E. Wood and J. H. Hildebrand, *J. Chem. Phys.*, **1**, 817 (1933).
21. P. J. Flory, *The Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.
22. G. Allen, W. B. Brown, C. Booth, G. Gee, G. Holden, M. N. Jones, W. D. Taylor, and G. R. Williamson, *Polymer*, **5**, 343 (1964).
23. S. Takahashi, *Shikizai Jpn.*, **37**, 115 (1964).
24. T. Akita and S. Oishi, *Ind. Chem. Jpn.*, **58**, 315 (1955).
25. A. Jayasri and M. Yaseen, *J. Oil Color Chem. Assoc.*, **63**, 61 (1980).
26. S. Takahashi and T. Omura, *Shikizai Jpn.*, **40**, 211 (1967).
27. T. Kawai, *Bull. Chem. Soc. Jpn.*, **26**, 409 (1953).
28. *Solvent Pocket Book*, Org. Synth. Soc. Japan, Tokyo (1974), p. 38.
29. N. Stolow, *J. Oil Color Chem. Assoc.*, **40**, 377 (1957).
30. K. Ishikawa and T. Kawai, *Ind. Chem. Jpn.*, **55**, 173 (1952).
31. T. Kawai, *Bull. Chem. Soc. Jpn.*, **28**, 386 (1955).
32. S. R. Palit, G. Colombo, and H. Mark, *J. Polym. Sci.*, **6**, 295 (1951).
33. S. Takahashi and T. Omura, *Shikizai Jpn.*, **39**, 448 (1966).
34. H. Ahmad and M. Yaseen, *Polym. Eng. Sci.*, **19**, 858 (1979).
35. J. H. Sewell, *J. Appl. Polym. Sci.*, **17**, 1741 (1973).
36. H. A. Gardner and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, 12th ed., Gardner Laboratory, Bethesda, Md., 1962, pp. 23, 171.

Received July 12, 1982

Accepted March 21, 1983