

Solubility Parameters of Polymethacrylonitrile, Poly(Methacrylic Acid) and Methacrylonitrile/Methacrylic Acid Copolymer

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SYNOPSIS

The solubility behaviors of polymethacrylonitrile (PMAN), poly(methacrylic acid) (PMAA), and its random copolymer methacrylonitrile (MAN)/methacrylic acid (MAA) in various solvents were investigated. The results were used in a computer program to obtain a 3-dimensional representation of the polymer solubility region in the Hansen space. Thus, the values of dispersion ($\delta_{d,p}$), polar ($\delta_{p,p}$) and hydrogen bonding ($\delta_{h,p}$) components of the total solubility parameter ($\delta_{t,p}$) were obtained. Comparisons between the experimental results and the estimated values are discussed. Also, prediction for solubility parameter values for MAN/MAA copolymer via their homopolymers, PMAN, and PMAA has been evaluated.

INTRODUCTION

Homopolymers, polymethacrylonitrile (PMAN) and poly(methacrylic acid) (PMAA), and random copolymers poly(MAN-co-MAA) have been studied frequently due to their potential uses as photoresist materials. However, most efforts had been devoted to the properties of thermal degradation.¹⁻⁷ Very little information is available on their solubility behavior in solvents.

On the predication of total solubility parameter, the following equation is often used

$$\delta_t = \left(\frac{E_{\text{coh}}}{V} \right)^{1/2} \quad (1)$$

where E_{coh} is the cohesive energy and V is the molar volume. Dunkle⁸ derived group contributions for the cohesive energy of liquids at room temperature. Hayes,⁹ Di Benedetto,¹⁰ Hoftzyer and Van Krevelen¹¹ have applied Dunkel's method to polymers. Small¹³ has demonstrated that the combination $(E_{\text{coh}}V(298\text{ K}))^{1/2} = F$, the molar attraction

constant, is a useful additive quantity for low-molecular as well as for high-molecular substances. Hoy¹⁴ and Van Krevelen¹⁵ also derived a set of group contributions and atomic contributions to calculate F . Therefore, the value of E_{coh} for polymer can be calculated from F also.

For many liquids and amorphous polymers, the cohesive energy is also dependent on the interaction between polar groups and on hydrogen bonding. Therefore, the cohesive energy may be divided into three parts, corresponding to the three types of interaction forces:

$$E_{\text{coh}} = E_d + E_p + E_h$$

where E_d , E_p , and E_h are contributions of dispersion, polar, and hydrogen bonding forces, respectively. The corresponding equation for the total solubility parameter (δ_t) is

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

where δ_d , δ_p , and δ_h are the solubility parameters due to dispersion, polar, and hydrogen bonding forces. Unfortunately, values of δ_d , δ_p , and δ_h cannot be determined directly.

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Hansen¹⁶⁻¹⁸ treated the solubility parameter as a vector in a three-dimensional δ_d , δ_p , δ_h space. From the experimental measurements of the solubility parameter of a number of polymers in a series of solvents, theoretical calculations, and plenty of computer fitting, the individual components δ_d , δ_p , and δ_h of many solvents and polymers have been developed and tabulated.^{19,20}

In this paper, the solubility behavior of homopolymer, PMAN and PMAA, and MAN/MAA copolymer in 55 solvents with known solubility parameters has been examined. From these experiments the solubility regions of the homopolymers and copolymer in 3-dimensional Hansen space¹⁶⁻¹⁸ have been determined and the values of solubility parameters evaluated. The total solubility parameters as well as their components for these polymers were also calculated from the group contribution method.^{19,20} Comparisons between the experimental results and the calculated values are also discussed.

EXPERIMENTAL

Materials

Methacrylonitrile (MAN) was washed with saturated aqueous sodium hydrogen sulfite (NaHSO_3) first, then with 1 wt % sodium hydroxide (NaOH) in saturated aqueous sodium chloride (NaCl) followed by saturated aqueous NaCl. The MAN was dried with calcium chloride (CaCl_2) and fractionally distilled under nitrogen in order to separate it from impurities. Methacrylic acid (MAA) was distilled under reduced pressure before use. α, α' -Azobisisobutyronitrile (AIBN) was recrystallized from methanol, and dried under reduced pressure at 25°C. Both homopolymers, PMAN and PMAA, were obtained from Polysciences, Inc. without further purification. All liquids used for solubility experiments were of reagent grade and used without further purification.

Copolymerization

The polymerization of MAN/MAA copolymer was performed in bulk, using AIBN as a free radical initiator. A solution prepared from 1.286 mol of MAN and 0.714 mol of MAA were placed in 1-L, three-neck, round-bottom flask equipped with a stirring mechanism, reflux condenser, and nitrogen gas inlet. The mixture of monomer was then heated to 65°C in the presence of flowing N_2 gas. A free-radical initiator consisting of 0.25 wt % to monomer of

AIBN was added to initiate the polymerization. The polymerization was carried out at 65°C for 2 h. After polymerization, the polymer was precipitated with water and reprecipitated from dimethyl formamide (DMF) solution. It was ground to a fine powder and dried in a vacuum oven at 50°C for 24 h. The composition of the MAN/MAA copolymer was determined by elemental analysis, the molar fraction of MAN was found to be $X_{\text{MAN}} = 0.525$. The intrinsic viscosity of the MAN/MAA copolymer was measured at 30°C in DMF solution using a Ubbelohde viscometer and was found to be 4.18 dL/g. The density of the MAN/MAA copolymer measured at 25°C using a volume-calibrated pycnometer was 1.16 g/cm³ while those of the homopolymers, PMAN and PMAA, were 1.04 and 1.29 g/cm³, respectively.

Film Preparation

To better evaluate the solubility behavior of the polymers in testing liquids, powder from the polymers were transformed into films by following procedure. A concentrated solution (10–20 wt % polymer in dimethyl sulfoxide) was first cast at room temperature on a cleaned glass plate, and placed in a force-ventilation oven at 75°C for 8 h to evaporate the solvent. Then to allow complete solvent evaporation, dried under vacuum at 75°C for 24 h. After cooling at room temperature, the corresponding film was leached with water (homopolymer PMAA was leached with acetone) overnight in a Soxhlet apparatus, vacuum dried, and finally cut into strips for solubility tests.

Solubility Tests

Solubility tests were carried out by the following procedures.¹⁶⁻¹⁸ Strips of 0.2000 ± 0.0005 g were immersed in 2 mL of liquid in sealed glass tubes. The tubes were placed in a water bath at 25°C and continuously shaken for 7 days. After 7 days, the samples were inspected. Since the dissolving rate of polymers in some solvents was extremely low at room temperature, in some cases samples were heated to 70°C, for the same time interval afterwards they were cooled to 25°C for visual inspection. On the basis of their ability to dissolve or swell the polymer, the liquids were classified into four categories: good solvent, good swelling agent, poor swelling agent, and nonsolvent. Table I lists the liquids used and their extents of solubilities for PMAN, PMAA, and poly(MAN-co-MAA).

Table I Extent of Solubility of PMAN, PMAA, and MAN/MAA Copolymer in Liquids: Good Solvent (1), Good Swelling Agent (2), Poor Swelling Agent (3), and Nonsolvent (4)

No.	Liquid	$\delta_{d,s}$	$\delta_{p,s}$	$\delta_{h,s}$	$\delta_{t,s}$	Extent of Solubility		
						PMAN	Copolym.	PMAA
1	Acetic acid	7.1	3.9	6.6	10.5	4	3	3
2	Acetic anhydride	7.8	5.7	5.0	10.9	1	1	3
3	Acetone	7.6	5.1	3.4	9.8	1	2	3
4	Acetonitrile	7.5	8.8	3.0	11.9	1	4	4
5	Acrylonitrile	8.0	8.5	3.3	12.1	1	4	4
6	Aniline	9.5	2.5	4.9	11.0	1	4	4
7	Benzaldehyde	9.2	4.2	2.6	10.4	1	4	4
8	Benzene	9.0	0.5	1.0	9.0	4	4	4
9	Benzyl alcohol	9.0	3.1	6.7	11.7	2	2	4
10	1-Butanol	7.8	2.8	7.7	11.3	4	4	3
11	<i>n</i> -Butyl acetate	7.7	1.8	3.1	8.5	4	4	4
12	Chlorobenzene	9.3	2.1	1.0	9.6	4	4	4
13	1-Chlorbutane	7.5	3.4	1.7	8.4	4	4	4
14	Chloroform	8.7	1.5	2.8	9.3	3	4	4
15	<i>m</i> -Cresol	8.8	2.5	6.3	11.1	1	4	4
16	Cyclohexane	8.2	0.0	0.0	8.2	4	4	4
17	Cyclohexanone	8.7	3.1	2.5	9.6	1	4	4
18	1,2-Dichloroethane	6.9	5.5	4.5	9.6	3	4	4
19	Diethyl ether	7.1	1.4	2.5	7.7	4	4	4
20	Diethylene glycol	7.9	7.2	10.0	14.6	4	1	1
21	Diisobutyl ketone	7.8	1.8	2.0	8.3	4	4	4
22	<i>N,N</i> -dimethyl acetamide	8.2	5.6	5.0	11.1	1	1	2
23	<i>N,N</i> -dimethyl formamide	8.5	6.7	5.5	12.1	1	1	2
24	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	1	1	1
25	1,4-Dioxane	9.3	0.9	3.6	10.0	3	3	3
26	Ethanol	7.7	4.3	9.5	13.0	3	2	1
27	Ethanol amine	8.4	7.6	10.4	15.4	1	1	2
28	Ethyl acetate	7.7	2.6	3.5	8.8	4	4	4
29	2-Ethyl hexanol	7.8	1.6	5.8	9.9	4	4	4
30	Ethyl cellocolve	7.9	4.5	7.0	11.5	4	2	2
31	Formic acid	7.0	5.8	8.1	12.2	1	2	3
32	<i>n</i> -Heptane	7.2	0.0	0.0	7.2	4	4	4
33	<i>n</i> -Hexamethyl phosphoramidate	9.0	4.2	5.5	11.3	1	4	4
34	Isoamyl alcohol	6.8	4.1	6.1	10.0	4	4	4
35	Isopropyl ether	6.7	2.3	0.7	7.0	4	4	4
36	Methyl acetate	7.6	3.5	3.7	9.1	3	4	4
37	Methyl ethyl ketone	7.8	4.4	2.5	9.3	2	4	4
38	<i>N</i> -methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	1	1	3
39	Methylene chloride	8.9	3.1	3.0	9.9	2	4	4
40	Nitrobenzene	9.8	4.2	2.0	10.9	1	4	4
41	Nitroethane	7.8	7.6	2.2	11.1	1	4	4
42	Nitromethane	7.7	9.2	2.5	12.0	1	4	4
43	<i>n</i> -Octyl alcohol	6.9	3.4	5.3	9.3	4	4	4
44	1-Propanol	7.8	3.3	8.5	12.0	4	3	2
45	Propylene carbonate	9.8	8.8	2.0	13.3	1	4	4
46	Propylene glycol	8.2	4.0	11.4	14.8	4	4	4
47	Pyridine	9.3	4.3	2.9	10.7	1	1	2
48	Styrene	9.1	0.5	2.0	9.3	4	4	4
49	Tetrahydrofuran	8.2	2.8	3.9	9.5	2	2	3
50	Tetralin	9.6	1.0	1.4	9.8	4	4	4
51	Tetramethylurea	8.2	4.0	5.4	10.6	1	1	4
52	1,1,1-Trichloroethane	8.3	2.1	1.0	8.7	4	4	4
53	Triethyl phosphate	8.2	5.6	4.5	10.9	1	1	3
54	Trimethyl phosphate	8.2	7.8	5.0	12.4	1	1	3
55	Toluene	8.8	0.7	1.0	9.1	4	4	4

RESULTS AND DISCUSSION

Homopolymer PMAN

The solubility region of homopolymer PMAN in the Hansen 3-dimensional space as well as the total solubility parameter composed of dispersion ($\delta_{d,p}$), polar ($\delta_{p,p}$), and hydrogen bonding ($\delta_{h,p}$) components has been determined as follows. Each liquid used for solubility experiments is represented as a point on a three-dimensional plot with δ_d , δ_p , and δ_h as axes. The scale of δ_d is twice as that used for δ_p and δ_h .

The boundaries of the solubility region for each of the δ_d - δ_p , δ_d - δ_h , and δ_p - δ_h planes have been drawn in such a way to include all the good solvents and exclude all the nonsolvents as well as poor swelling agents, with good swelling agents at the boundaries. The analytical representation of the solubility region in the Hansen three-dimensional space is obtained by a computer iteration based on the linear regression method. The solubility region in the Hansen space is represented by the equation

$$4(\delta_d - \delta_{d,p})^2 + (\delta_p - \delta_{p,p})^2 + (\delta_h - \delta_{h,p})^2 = 5.0^2 \quad (3)$$

where the parameters with subscript p referred to the coordinates of the center of the spheroid, which correspond to the solubility parameter components of PMAN and the solubility sphere of radius in Hansen space is 5.0. Thus, the following values have been obtained for PMAN: $\delta_{d,p} = 8.8$, $\delta_{p,p} = 7.8$, and $\delta_{h,p} = 3.9 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. According to eq. (4)

$$\delta_{t,p}^2 = \delta_{d,p}^2 + \delta_{p,p}^2 + \delta_{h,p}^2 \quad (4)$$

the total solubility parameter $\delta_{t,p}$ is $12.4 \text{ cal}^{1/2} \text{ cm}^{-3/2}$.

Alternatively theoretical and semiempirical methods could be used to evaluate the polymer solubility parameter as well. Among them, the group contribution method is widely used. Based on an examination of a vast amount of data on simple liquids, Fedors¹² found that a general system for estimating both energy of vaporization, E_v , and molar volume, V , could be set up simply by assuming equations as

$$E_v = \sum_i \Delta e_i \quad (5)$$

$$V = \sum_i \Delta V_i \quad (6)$$

where Δe_i and ΔV_i are the additive atomic and group contribution for the energy of vaporization and molar volume, respectively.

Using eqs. (5) and (6), the total solubility parameter of high molecular polymer becomes

$$\delta_t = \left(\frac{\sum_i E_i}{\sum_i V_i} \right)^{1/2} \quad (7)$$

where E_i and V_i are the additive atomic and group contribution of the repeating unit for the energy of vaporization and molar volume, respectively. The group contribution of E_i and V_i taken from the Fedors¹² for PMAN are shown in Table II. Then, the total solubility parameter is evaluated according to eq. (7)

$$\delta_t = \left(\frac{\sum_i E_i}{\sum_i V_i} \right)^{1/2} = \left(\frac{8755}{54.4} \right)^{1/2} = 12.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$$

Using the molar attraction constant in conjunction with eq. (7), the total solubility parameter can be written as

$$\delta_t = \frac{\sum_i F_i}{\sum_i V_i} \quad (8)$$

where F_i are the additive atomic and group contribution of the repeating unit for the molar attraction constant. Hoy¹⁴ and Van Krevelen¹⁵ also derived a set of atomic contribution F_i to calculate δ_t . By using the F_i values collected in Table III and using eq.

Table II Group Contribution to Energy of Vaporization E_i and Molar Volume V_i Taken from Fedors¹²

Group	E_i (cal/mol)	V_i (cm ³ /mol)
—CH ₃	1125	33.5
—CH ₂ —	1180	16.1
—C—	351	-19.2
—CN	6099	24.0
—COOH	6600	28.5

Table III Group Contribution to F_i ($\text{cal}^{1/2} \text{cm}^{3/2}/\text{mol}$) Taken from Literature¹³⁻¹⁵

Group	F_i		
	Small	Van Krevelen	Hoy
—CH ₃	104	100	72.5
—CH ₂ —	64.8	66.9	64.3
 —C— 	-45.4	0.0	15.6
—CN	200	234.6	173.3
—COOH	—	155.8	238.9

(8), we find $10.4 \text{ cal}^{1/2} \text{cm}^{-3/2} < \delta_{t,p} < 12.8 \text{ cal}^{1/2} \text{cm}^{-3/2}$ for PMAN.

The group contribution method is also applicable to evaluate dispersion, polar and hydrogen bonding components.^{19,20} By direct analogy to eqs. (7) and (8), it follows that:

$$\delta_{d,p} = \frac{\sum_i F_{di}}{\sum_i V_i} \quad (9a)$$

$$\delta_{p,p} = \frac{(\sum_i F_{pi}^2)^{1/2}}{\sum_i V_i} \quad (9b)$$

$$\delta_{h,p} = \left(\frac{\sum_i E_{hi}}{\sum_i V_i} \right)^{1/2} \quad (9c)$$

where F_{di} , F_{pi} , and E_{hi} are the molar attraction constants for dispersion, polar, and hydrogen bonding

Table V Comparison of Experimental and Calculated Solubility Parameters ($\text{cal}^{1/2} \text{cm}^{-3/2}$) of PMAN

Method	$\delta_{d,p}$	$\delta_{p,p}$	$\delta_{h,p}$	$\delta_{t,p}$
Experiment	8.8	7.8	3.9	12.4
Group contribution	—	—	—	12.6 ^a
	—	—	—	10.4 ^b
	—	—	—	12.8 ^c
	—	—	—	10.4 ^d
	8.0	8.4	3.0	12.0 ^e

^a Calculated from Fedors method.

^b Calculated from Small method.

^c Calculated from Van Krevelen method.

^d Calculated from Hoy method.

^e Calculated from solubility parameter component group contribution method.

forces, respectively. The group contribution of the molar attraction constants of F_{di} , F_{pi} , and E_{hi} taken from the literature^{19,20} are shown in Table IV. According to eqs. (4) and (9), the values of the solubility parameter and its components are: $\delta_{d,p} = 8.0$, $\delta_{p,p} = 8.4$, $\delta_{h,p} = 3.1$, and $\delta_{t,p} = 12.0 \text{ cal}^{1/2} \text{cm}^{-3/2}$.

All the experimental and calculated solubility parameters for PMAN are collected in Table V. It appears that they are in good agreement.

Homopolymer PMAA

Homopolymer PMAA does not dissolve in any liquid but only swells in some of them at 25°C. After raising the temperature to 70°C, three good solvents were found for PMAA, namely: diethylene glycol, dimethyl sulfoxide, and ethanol.

Table IV Solubility Parameter Component Group Contribution from Literature^{19,20}

Group	F_{di} ($\text{cal}^{1/2} \text{cm}^{3/2}/\text{mol}$)	F_{pi} ($\text{cal}^{1/2} \text{cm}^{3/2}/\text{mol}$)	E_{hi} (cal/mol)
—CH ₃	205	0.0	0.0
—CH ₂ —	132	0.0	0.0
 —C— 	-34.2	0.0	0.0
—CN	210	537.6	597
—COOH	259	205	2389

Following the same procedures described in the previous section, the solubility envelope of the PMAA in the Hansen space as well as the values of the solubility parameters have been determined. The solubility of PMAA in terms of Hansen parameters is represented by a spheroid, best fitted by equation

$$4(\delta_d - \delta_{d,p})^2 + (\delta_p - \delta_{p,p})^2 + (\delta_h - \delta_{h,p})^2 = 3.0^2. \quad (10)$$

The individual parameters of PMAA thus obtained are: $\delta_{d,p} = 8.5$, $\delta_{p,p} = 6.1$, $\delta_{h,p} = 7.8$, and $\delta_{t,p} = 13.1$ $\text{cal}^{1/2} \text{cm}^{-3/2}$.

The solubility parameters of PMAA have been calculated on the basis of the group contribution method. By using the E_i , F_i , F_{di} , F_{pi} , and E_{hi} values collected in Tables II to IV, and using the eqs. (4) and (7) to (9), we obtain $9.1 \text{ cal}^{1/2} \text{cm}^{-3/2} < \delta_{t,p} < 12.5 \text{ cal}^{1/2} \text{cm}^{-3/2}$, $\delta_{d,p} = 8.5$, $\delta_{p,p} = 3.1$, and $\delta_{h,p} = 6.0 \text{ cal}^{1/2} \text{cm}^{-3/2}$. Table VI lists the experimental and calculated values for PMAA. It appeared that our experimental results were higher than the calculated values, except the value of the dispersion solubility parameter $\delta_{d,p}$.

MAN/MAA Copolymer

The solubility region of MAN/MAA copolymer in the Hansen space is represented by equation

$$4(\delta_d - \delta_{d,p})^2 + (\delta_p - \delta_{p,p})^2 + (\delta_h - \delta_{h,p})^2 = 3.9^2. \quad (11)$$

The individual parameters of MAN/MAA copoly-

Table VI Comparison of Experimental and Calculated Solubility Parameters ($\text{cal}^{1/2} \text{cm}^{-3/2}$) of PMAA

Method	$\delta_{d,p}$	$\delta_{p,p}$	$\delta_{h,p}$	$\delta_{t,p}$
Experiment	8.5	6.1	7.8	13.1
Group contribution	—	—	—	12.5 ^a
	—	—	—	10.4 ^b
	—	—	—	12.2 ^c
	8.5	3.1	6.0	9.1 ^d

^a Calculated from Fedors method.

^b Calculated from Van Krevelen method.

^c Calculated from Hoy method.

^d Calculated from solubility parameter component group contribution method.

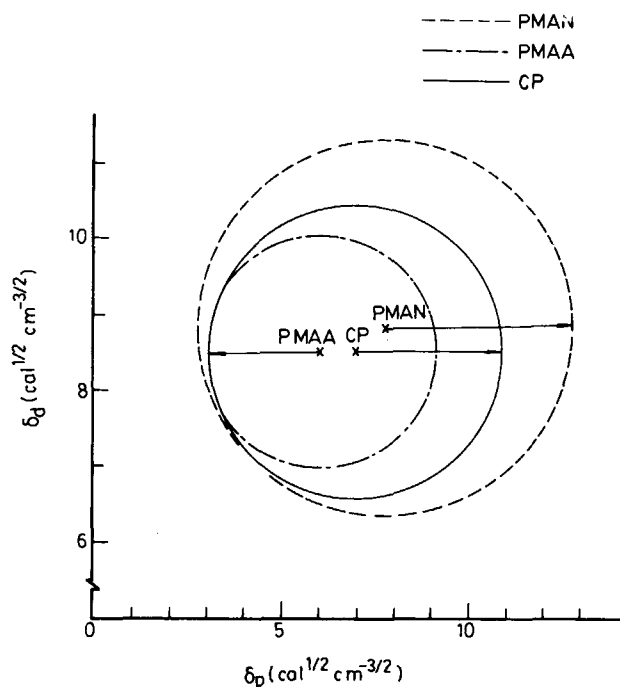


Figure 1 The solubility regions of PMAN, PMAA, and their copolymer in the δ_d - δ_p plane.

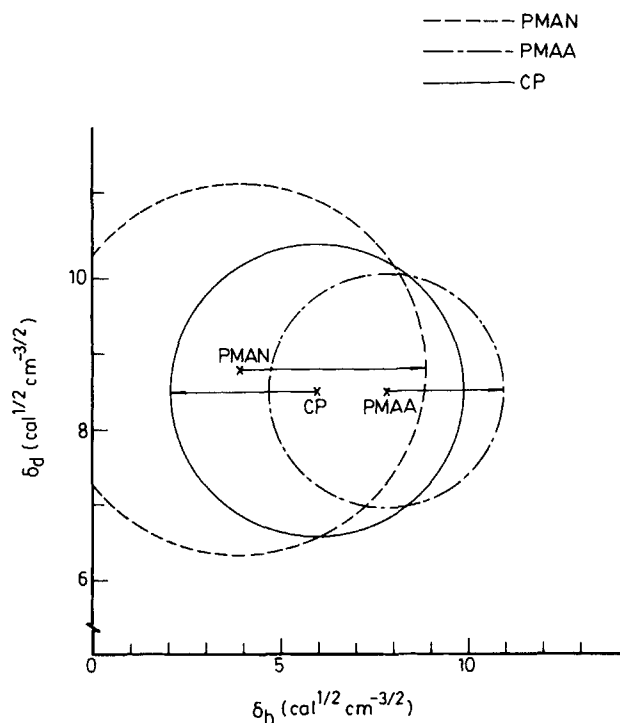


Figure 2 The solubility regions of PMAN, PMAA, and their copolymer in the δ_d - δ_h plane.

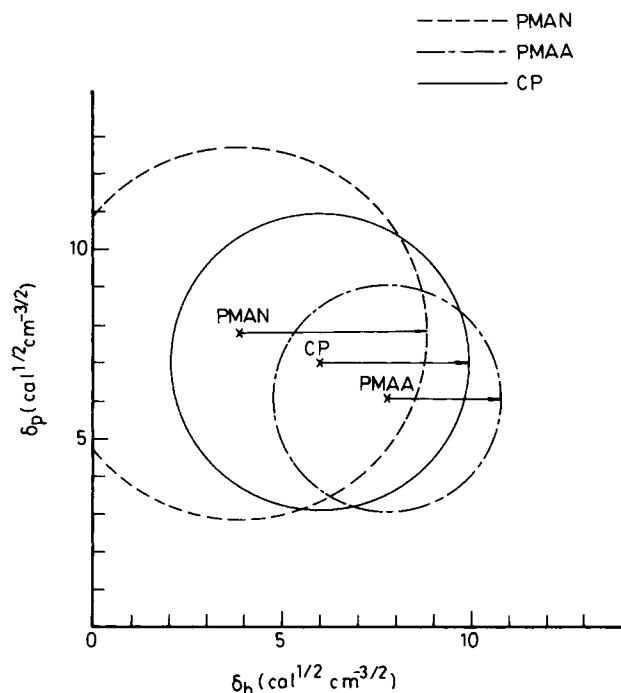


Figure 3 The solubility regions of PMAN, PMAA, and their copolymer in the δ_p - δ_h plane.

mer are: $\delta_{d,p} = 8.5$, $\delta_{p,p} = 7.0$, and $\delta_{h,p} = 6.0$ $\text{cal}^{1/2} \text{cm}^{-3/2}$. According to eq. (4), the total solubility parameter $\delta_{t,p}$ is $12.6 \text{ cal}^{1/2} \text{cm}^{-3/2}$. From our experimental results, the solubility parameter of random copolymer MAN/MAA is between those of the homopolymer constituents as shown in Figures 1-3.

The solubility parameters for random copolymer can be predicted from data available for the homopolymers. It would appear that this could be done with the assumption that total solubility parameter of the copolymer is related with the components in terms of their volume fractions. It has the following relation^{19,20}:

$${}^i\delta_{t,p} = {}^i\phi {}^i\delta_{t,p} + {}^j\phi {}^j\delta_{t,p} \quad (12)$$

where ϕ is the homopolymer volume fractions, superscript i and j referring to the components and ij referring to the copolymer. Equation (12) can be also applicable to evaluate $\delta_{d,p}$, $\delta_{p,p}$, and $\delta_{h,p}$. By direct analogy with eq. (12) it follows that^{19,20}:

$${}^i\delta_{x,p} = {}^i\phi {}^i\delta_{x,p} + {}^j\phi {}^j\delta_{x,p} \quad (13)$$

$$x = d, p, h$$

Bernard Schneler²¹ used an alternate method to calculate the $\delta_{t,p}$ of random copolymer. He proposed that:

$${}^i\delta_{t,p} = \frac{({}^i n {}^i M^2 / {}^i \rho) {}^i \delta_{t,p} + ({}^j n {}^j M^2 / {}^j \rho) {}^j \delta_{t,p}}{\{({}^i n {}^i M + {}^j n {}^j M)\} \{[({}^i n {}^i M^2 / {}^i \rho) + ({}^j n {}^j M^2 / {}^j \rho)] [1 / {}^i \rho]\}^{1/2}} \quad (14)$$

where n , M , and ρ refer to number of moles, monomer molecular weight, and density, respectively. The same relationship can also be used to evaluate $\delta_{d,p}$, $\delta_{p,p}$, and $\delta_{h,p}$ as follows:

$${}^i\delta_{x,p} = \frac{({}^i n {}^i M^2 / {}^i \rho) {}^i \delta_{x,p} + ({}^j n {}^j M^2 / {}^j \rho) {}^j \delta_{x,p}}{\{({}^i n {}^i M + {}^j n {}^j M)\} \{[({}^i n {}^i M^2 / {}^i \rho) + ({}^j n {}^j M^2 / {}^j \rho)] [1 / {}^i \rho]\}^{1/2}} \quad (15)$$

$$x = d, p, h$$

Experimental results and calculated values are summarized in Table VII. It appears that they are in good agreement. However, calculated solubility parameters of MAN/MAA copolymer based on the calculated values of the homopolymers are lower than the experimental results.

CONCLUSIONS

Solubility tests have been carried out to evaluate the solubility parameters of PMAN and PMAA ho-

mopolymers and MAN/MAA copolymer. The solubility behavior of PMAN, PMAA, and MAN/MAA copolymer have been examined in about 55 liquids. The theoretical values of the solubility parameters calculated from the group contribution method are in good agreement with the experimental results for PMAN, but appear to be low for PMAA and MAN/MAA copolymer. The solubility parameters of MAN/MAA copolymer obtained either by experiment or by calculation were intermediate between those of the homopolymer constituents PMAN and PMAA. Methods to predict solubility parameters of

Table VII Comparison of Experimental and Calculated Solubility Parameters ($\text{cal}^{1/2} \text{cm}^{-3/2}$) of MAN/MAA Copolymer

Method	$\delta_{d,p}$	$\delta_{p,p}$	$\delta_{h,p}$	$\delta_{t,p}$
Experiment (I) ^a	8.5	7.0	6.0	12.6
	8.66	6.98	5.78	12.74 ^c
	—	—	—	12.55 ^d
	—	—	—	11.64 ^e
	—	—	—	11.27 ^f
(II) ^b	8.24	5.85	4.45	10.6 ^g
	8.64	6.87	6.03	12.78 ^c
	—	—	—	12.54 ^d
	—	—	—	11.48 ^e
	—	—	—	11.38 ^f
	8.27	5.5	4.64	10.42 ^g

^a Calculated from eqs. (12) and (13).

^b Calculated from eqs. (14) and (15).

^c Data of PMAN and PMAA calculated from our experimental results.

^d Data of PMAN and PMAA calculated from Fedors method.

^e Data of PMAN and PMAA calculated from Van Krevelen method.

^f Data of PMAN and PMAA calculated from Hoy method.

^g Data of PMAN and PMAA calculated from solubility parameter component group contribution method.

copolymer via known value of homopolymer constituents were justified by comparing with experimental results.

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