

## On the Solubility Parameter of Polar Polymers

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### Synopsis

The binary cluster integral,  $\beta$ , was computed from intrinsic viscosity data. Subtracting from  $\beta$  the polar contribution,  $\beta_e$ , calculated from YRCR theory,<sup>9</sup> the nonpolar interaction parameter,  $\beta_n$ , was found. The calculations were performed for poly(vinyl acetate) and poly(methyl methacrylate), each in 16 solvents. The correlation between  $\beta_n$  and the solvent solubility parameter,  $\delta_1$ , was found to be similar to that reported<sup>8,17</sup> for solutions of natural rubber, *cis*-polybutadiene and for poly(vinyl chloride). This correlation can be crudely approximated by the formula

$$\beta_n = E - F|\delta_1 - \delta_m|$$

where  $E$  and  $F$  are functions of the ill-defined symmetry of the solvent molecule and  $\delta_m$  is the  $\delta_1$  value for the local maximum of the function. At  $\delta_1 = \text{constant}$ , the more spherical is the molecule, the higher is the  $\beta_n$  value. It was shown that for most cases separation of the solvent into two classes (linear and nonlinear) is sufficient. This  $\beta_n$  behavior finds support in the Funk and Prausnitz<sup>6</sup> report on aromatic-saturated hydrocarbon mixtures and in the theoretical calculations of Huggins.<sup>21,22</sup>

### INTRODUCTION

The concept of the solubility parameter:

$$\delta \equiv (\Delta E_v/V)^{1/2} \quad (1)$$

where  $\Delta E_v$  is the energy of vaporization to the gas at zero pressure and  $V$  is the molar volume of the liquid, was introduced some forty years ago by Hildebrand.<sup>1,2</sup> For polar liquids, a square of the parameter was written<sup>2</sup> as a sum of squares of the polar,  $\delta_p$ , and nonpolar,  $\delta_a$ , contributions. Recently Hansen<sup>3</sup> added to this relation a hydrogen-bonding parameter  $\delta_h$ :

$$\delta^2 = \delta_a^2 + \delta_p^2 + \delta_h^2. \quad (2)$$

Equation (2) was rewritten by Bagley et al.<sup>4</sup> in the following form:

$$\delta^2 = \delta_v^2 + \delta_r^2 \quad (3)$$

where the volume dependent contribution,

$$\delta_v^2 = \delta_a^2 + \delta_p^2, \quad (4)$$

is given by the internal pressure  $P_i$ , whereas the residual contribution is given by

$$\delta_r^2 = \delta_h^2 = (\Delta E_v/V) - P_i. \quad (5)$$

For a binary mixture, the molar excess free energy of mixing can be expressed<sup>2</sup>

$$\Delta G^E/V_M\varphi_1\varphi_2 = \sum_i(\delta_{1i} - \delta_{2i})^2 \quad (6)$$

where  $V_M$  is total volume of the mixture;  $\varphi_1$  and  $\varphi_2$  are the volume fractions of components 1 and 2, respectively; and  $i = (d,p)$  for the Hildebrand and Scott,  $i = (d,p,h)$  for the Hansen, and  $i = (v,r)$  for the Bagley et al. systems, respectively.

In spite of the fact that the  $\delta$  or  $(\delta_v, \delta_r)$  parameters can be determined quite accurately,<sup>4,5</sup> eq. (6) should be treated as an approximation<sup>6,7</sup> only. Apparently, the geometric mean rule, which is the basis for this equation, severely limits its applicability. In the case of aromatic (benzene, toluene)-saturated hydrocarbon mixtures ( $\delta = \delta_d$ ), Funk and Prausnitz<sup>6</sup> found the following relation to be valid:

$$\Delta G^E/V\varphi_1\varphi_2 = (\delta_1 - \delta_2)^2 + 2l_{1,2}\delta_1\delta_2 \quad (7)$$

where subscripts 1 and 2 refer to solvent and solute, respectively, and  $l_{1,2}$  is an empirical parameter. The term  $l_{1,2}$  was found to be a linear decreasing function of the degree of branching of the saturated hydrocarbon molecules:  $r = (\text{number of CH}_3 \text{ groups})/(\text{total number of carbon atoms})$ . For  $r \simeq 1/3$ ,  $l_{1,2} = 0$ , and eq. (7) reduces to eq. (6). It is to be expected that the geometric mean rule will represent the intermolecular potential of the polar and hydrogen-bonding types even less accurately.

## INTERACTIONS IN POLYMER SOLUTIONS

### Calculation of Polar Interactions

In the following discussion, two assumptions will be made: (a) that the unperturbed dimension of a polymer coil does not depend on the nature of the solvent and (b) that the long-range interactions originate in dispersion and polar forces only. The first assumption can be responsible for only a minor error<sup>8</sup>; the second limits the field of the discussion to systems in which the hydrogen-bonding forces do not constitute the major contribution.

The binary cluster integral  $\beta$  can be written as a sum of nonpolar,  $\beta_n$ , and polar,  $\beta_e \leq 0$ , contributions:

$$\beta = \beta_n + \beta_e \quad (8)$$

where, according to Yamakawa, Rice, Corneliusen, and Kotin<sup>9</sup> (YRCK),

$$\beta_e^* = -\beta_e V_0 = \frac{4\pi^2}{3\epsilon^2} \left( \frac{3\epsilon}{2\epsilon + 1} \right)^4 \frac{\mu^{*2}}{3kT} \left( \frac{\mu^{*2}}{3kT} + \alpha^* \right) \quad (9)$$

$$\mu^* = \frac{2\epsilon + 1}{2\epsilon + n_R^2} \frac{n_R^2 + 2}{3} \mu \quad (10)$$

$$\alpha^* = \frac{2\epsilon + 1}{2\epsilon + n_R^2} \frac{n_R^2 + 2}{3} \alpha. \quad (11)$$

TABLE I  
Characteristic Parameters of Four Polar Polymers<sup>a</sup>

Polymer	Code	$V_0, \text{\AA}^3$	$\mu (D)$	$n_D$	$\alpha \times 10^{24}, \text{\AA}^3$	Ref.
1. Polystyrene	PS	180.60	0.60	1.60	13.3	10
2. Poly(vinyl chloride)	PVC	74.93	1.64	1.550	5.606	8
3. Poly(methyl methacrylate)	PMMA	137.38	1.73	1.4864	5.675	this work
4. Poly(vinyl acetate)	PVAc	120.12	1.80	1.4675	4.795	this work

<sup>a</sup>  $V_0$  is calculated from mer molecular weight and polymer density at 25°C,  $\mu$  is taken from ref. 11,  $n_D$  values were determined from  $dn_D/dc$ -vs- $n_D$  plot,<sup>8</sup> and  $\alpha$  values were computed from Clausius-Mossotti equation.<sup>10</sup>

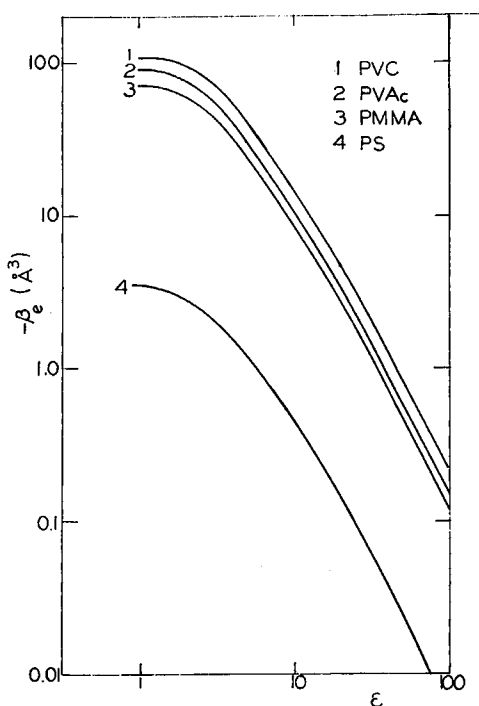


Fig. 1. Dipolar interaction parameter  $-\beta_e$  as a function of solvent dielectric constant. Values were computed from YRCK theory<sup>9</sup> for polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), and poly(vinyl chloride) (PVC).

In these equations,  $V_0$  is a spherical volume of polymer statistical segment characterized by a dipole moment in vacuum  $\mu$ , polarizability  $\alpha$ , and refractive index  $n_R$ ;  $k$  is the Boltzmann constant; and  $T$  is the absolute temperature.

In eq. (9), only the solvent dielectric constant  $\epsilon$  is used to characterize the medium; i.e., for a given polymer at  $T = \text{const.}$ ,  $\beta_e^* = \beta_e^*(\epsilon)$ . However conversion of this quantity into  $\beta_e$  requires a working definition of the statistical segment. In the case of polar polymers discussed in terms of the YRCK theory, the most logical choice seems to be the monomeric unit. Consequently, the dipole moment of the statistical segment  $\mu$  in eq. (10) can be taken<sup>8-10</sup> as the dipole moment of a small molecule similar in structure to the monomeric unit.<sup>11</sup> In Table I, the magnitudes of  $V_0$ ,  $\mu$ ,  $n_R$ , and  $\alpha$  are quoted for the four polymers. Substituting these into eqs. (9)–(11), the  $\beta_e$  dependence on the solvent dielectric constant  $\epsilon$  was calculated. The result is shown in Figure 1. It should be noted that the relative importance of dipolar segment–segment interaction decreases in the order

$$\text{PVC} > \text{PVAc} > \text{PMMA} > \text{PS}.$$

(For the explanation of the polymer code, see Table I.)

### Nonpolar Interactions

Equation (8) implies that the nonpolar long-range interactions,  $\beta_n$ , can be computed for any amorphous polymer from the experimental  $\beta$  parameters and the theoretical quantities  $\beta_e$ . The nonpolar contribution,  $\beta_n$ , of the polar polymers should behave analogously to the  $\beta$ 's of the nonpolar polymers, and the correlations observed for both of them should be similar.

For a nonpolar, nonhydrogen-bonding system, the Hildebrand solubility parameter theory should be particularly applicable. From eq. (7), the Flory-Huggins interaction parameter  $\chi$  can be expressed as

$$\chi = \frac{V_1}{RT} [(\delta_1 - \delta_2)^2 + 2l_{1,2}\delta_1\delta_2] \quad (12)$$

where  $V_1$  is the molar volume of the solvent. But<sup>12</sup>

$$\beta = (1/2 - \chi)2V_0^2/V_1 \quad (13)$$

where from

$$\beta = (V_0^2/V_1) - (2V_0^2/RT)[(\delta_1 - \delta_2)^2 + 2l_{1,2}\delta_1\delta_2] \quad (14)$$

is found. Alternatively, to the right-hand side of eq. (12), a constant value  $C$  is added,<sup>13</sup> which leads to

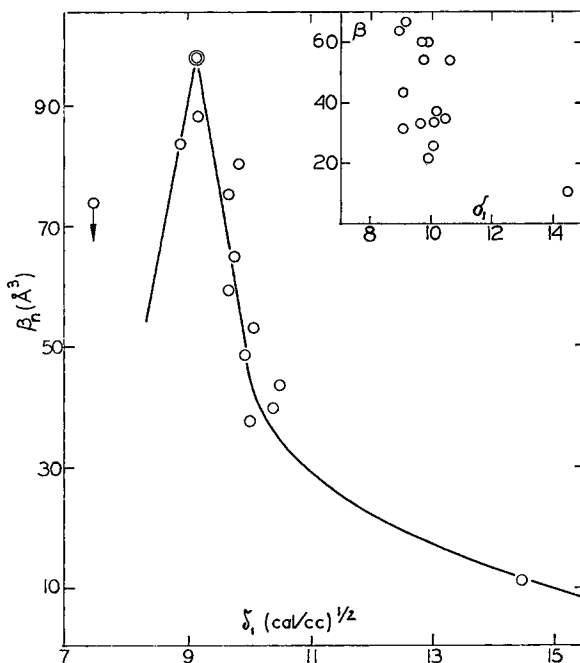


Fig. 2. Relationship between nonpolar interaction parameter  $\beta_n$  and solubility parameter of the solvent  $\delta_1$  for poly(vinyl acetate) solutions at 25.00°C. In the insert, the binary cluster integral  $\beta$  vs.  $\delta_1$  is shown.

TABLE II  
 Computation of Long-Range Interactions for Poly(vinyl Acetate) and Poly(methyl Methacrylate) Solutions at 25°C

Solvent	$\beta$		$\epsilon^a$	$\beta_n$		$\delta_1^b$
	PVAc	PMMA		PVAc	PMMA	
1. Chloroform	67.03	51.40	4.806	97.50	76.15	9.16
2. <i>s</i> -Tetrachloroethane	60.41	54.75	8.2	75.23	66.40	9.70
3. 1,1,2-Trichloroethane	60.41	37.43	6.73 <sup>c</sup>	88.01	66.03	9.88
4. Ethylene Chloride	54.63	34.64	10.36	64.54	42.57	9.8
5. Trichloroethylene	43.06	22.91	3.42	80.06	53.01	9.16
6. Acetophenone	38.93	30.17	17.39	43.05	33.45	10.58
7. <i>p</i> -Dioxane	37.27	39.11	2.209 (8.0 <sup>d</sup> )	104.70 (52.59)	85.55 (51.12)	10.13
8. Cyclohexanone	35.62	19.56	18.3	39.37	22.62	10.42
9. Chlorobenzene	33.97	25.70	5.621	58.94	45.72	9.67
10. Benzene	30.66	37.43	2.284	97.26	89.84	9.16
11. <i>o</i> -Dichlorobenzene	26.53	29.61	9.93	37.19	38.13	10.04
12. Bromobenzene	21.58	29.61	5.4	48.30	50.72	9.87
13. 1,2,4-Trichlorobenzene	20.75	—	4.38	55.30	<28.03	10.1 <sup>e</sup>
14. Toluene	19.10	19.00	2.379	83.20	69.95	8.93
15. Methanol	10.01	—	32.63	11.34	<1.09	14.5
16. <i>n</i> -Heptane	—	—	1.924	<74.09	<58.23	7.5

<sup>a</sup> From ref. 16.

<sup>b</sup> From ref. 5.

<sup>c</sup> Calculated from Onsager equation.

<sup>d</sup> Value for tetrahydrofuran.

<sup>e</sup> From ref. 14.

$$\beta_n = (1 - 2C) \frac{V_0^2}{V_1} - \frac{2V_0^2}{RT} [(\delta_1 - \delta_2)^2 + 2l_{1,2}\delta_1\delta_2]. \quad (15)$$

### Computations

The  $\beta$  parameter for PVAc and PMMA was computed from intrinsic viscosity ( $[\eta]$ ) data<sup>14</sup> by means of the equation<sup>15</sup>

$$[\eta]/M^{1/2} = 1.05 K_\theta + 0.287\phi(\beta/M_0^2)M^{1/2}. \quad (16)$$

Here,  $M_0$  and  $M$  are the molecular weights of the statistical segment and polymer, respectively; and  $\phi = 2.5 \times 10^{21}$  and  $K_\theta$  have their usual meanings. In the computation,  $K_\theta = 9.3 \times 10^{-4}$  and  $K_\theta = 7.0 \times 10^{-4}$  were assumed<sup>11</sup> for PVAc and PMMA, respectively. The results are presented in Table II and in the inserts of Figures 2 and 3.

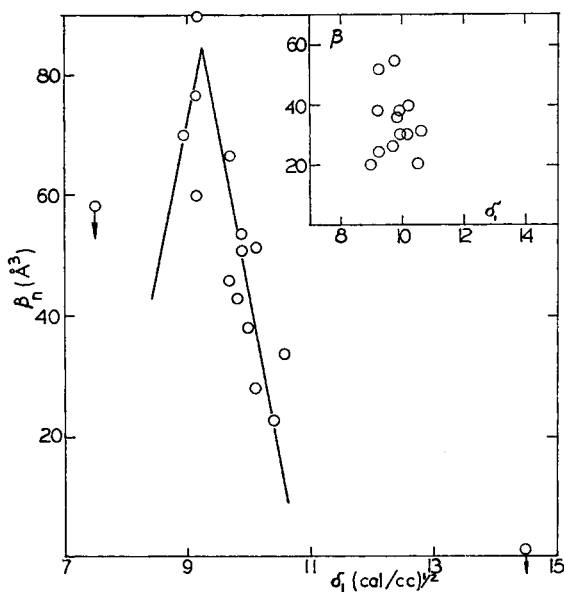


Fig. 3. Relationship between nonpolar interaction parameter  $\beta_n$  and solvent solubility parameter  $\delta_1$  for poly(methyl methacrylate) solutions at 25.00°C. In the insert, the binary cluster integral  $\beta$  vs.  $\delta_1$  is shown.

From the values of  $\epsilon$  and the appropriate curves of Figure 1, the  $\beta_e$  values were found, and then, in turn, the  $\beta_n$  values quoted in Table II and Figures 2 and 3 were calculated.

### DISCUSSION

The experimental  $\beta \propto [\eta]$  of PVAc and PMMA solutions is plotted versus  $\delta_1$  in the inserts of Figures 2 and 3, respectively; no correlation between these two quantities is observed. However, the nonpolar param-

eter,  $\beta_n = \beta - \beta_e$ , plotted versus  $\delta_1$  in Figures 2 and 3, shows a distinct dependence. A very similar behavior was reported<sup>17</sup> for solutions of natural rubber and *cis*-polybutadiene (here  $\beta_n = \beta \propto [\eta]$ ), as well as for PVC in 35 solvents.

The  $\beta_n$ -versus- $\delta_1$  dependencies show a few common features:

1. The data points for solutions of both polar and nonpolar polymers follow the same type of correlation, which can be approximated by

$$\beta = E - F|\delta_1 - \delta_m| \quad (17)$$

where  $E$  and  $F$  are constant for a given polymer in a given class of solvents, and  $\delta_m$  is the  $\delta_1$  value at which the function reaches a local maximum  $\beta_n(\delta_m) = \beta_{n(\max)} = E$ . As before,<sup>17</sup> and also in this paper, the solvents are crudely divided into two classes: a linear-molecule solvent and nonlinear ones.

2. The value of  $E$  was found to be independent of the molar volume of the solvent. For PVC,  $\beta_n$  values in cyclohexanone and in di(ethylhexyl) phthalate, both classified as nonlinear solvents, followed eq. (17) with the same values of  $E$  and  $F$ , in spite of the fact that the ratio of their molar volumes is 1:6.4.

The largest empirical values of  $\beta_n^* \lesssim E$  for PVC, PVAc, and PMMA in "nonlinear" solvents are, respectively,  $75 \text{ \AA}^3$ ,  $90 \text{ \AA}^3$ , and  $100 \text{ \AA}^3$ , i.e., comparable with the volumes of the appropriate monomeric units. The value of  $\beta_n^* \simeq 40$  was found for PVC in linear solvents.

3. The reduced slope defined as

$$F^* = FRT/2V_0^2 \quad (18)$$

depends also on "symmetry" of the solvent molecules;  $F^*$  for "linear" solvents is consistently lower than that for "nonlinear" solvents (see Table III).

TABLE III  
Parameter  $F^*$  for Solute-Solvent Mixtures

Solute	Solvents		Equation	Data source ref.
	Linear	Nonlinear		
1. Benzene	$2.1 \pm 0.2$	$3.6 \pm 0.4$	(21)	6
2. Toluene	$1.4 \pm 0.1$	$2.8 \pm 0.7$	(21)	6
3. <i>cis</i> -Polybutadiene	$1.2 \pm 0.5$	$2.3 \pm 0.5$	(18)	18
4. Poly(vinyl chloride)	$2.7 \pm 0.5$	$2.9 \pm 0.5$	(18)	17
5. Poly(vinyl acetate)	—	$2.9 \pm 0.5$	(18)	14
6. Poly(methyl methacrylate)	—	$2.0 \pm 0.5$	(18)	14

4. If  $T$  and  $\delta_1$  are constant, then  $\beta_n$  for solutions of a given polymer decreases with decrease in the "symmetry" of the solvent molecules; e.g., in benzene, chloroform, and 1,1,2-trichloroethane ( $\delta_1 = 9.16$ ),  $\beta_n$  values for



PVAc and PMMA are, respectively: 97.26, 97.50, and 88.01 for the first polymer and 89.84, 76.15, and 60.03 for the second. Intuitively, the ill-defined molecular "symmetry" of those three solvents decreases in the same order.

5. In the case of PVC-dioxane solution, two values of  $\beta_e$  were computed<sup>17</sup> from YRCR theory; one using the tabulated<sup>16</sup> value  $\epsilon = 2.209$  for this solvent, and the second assuming  $\epsilon = 8.0$ , the value quoted for tetrahydrofuran. In the first case, the resulting  $\beta_n = 102 \text{ \AA}^3$  was out of the range of  $\beta_n$  values computed for all the other 34 solvents, whereas  $\beta_n = 37 \text{ \AA}^3$  computed for the second assumption was well in the range of values found for the other nonlinear solvent systems. The  $\beta_n$  values for PVAc and PMMA dioxane solutions computed in the same manner are shown in Table II. As before,  $\epsilon = 2.209$  leads to very high  $\beta_n$  value, whereas the computation assuming  $\epsilon = 8.0$  is consistent with those of the other solvents. Apparently the dioxane molecule (dipole moment  $\mu_1 = 0$ ) interacts with the polymeric dipoles as a more-or-less independent single dipole, similar in magnitude to that of tetrahydrofuran ( $\mu_1 = 1.75D$ ).

It is interesting to compare the resulting  $\beta_n$ -versus- $\delta_1$  dependencies of this paper with the semitheoretical or theoretical predictions; that of eq. (15) and the formula derived from the new Huggins theory<sup>21,22</sup>:

$$\beta = (V_0^2/V_1) + 2V_1(\sigma_0/\sigma_1)[k_S - \epsilon_\Delta\sigma_0/\sigma_1RT] \quad (19)$$

where  $\sigma_0$  and  $\sigma_1$  are contacting-segment surface areas of a polymer and solvent, respectively. Their ratio,  $r^*$ , along with the entropic,  $k_S$ , and enthalpic,  $\epsilon_\Delta$ , parameters, should be determined empirically. In the investigated systems,<sup>21</sup>  $k_S < 0$ , and there seems to be a dependence of this parameter on  $\epsilon_\Delta$ . Assuming the equivalence of the  $\beta$  values computed from eqs. (15) and (19), this dependence can be expressed in terms of eq. (15), or, conversely,  $l_{1,2}$  can be given as a function of  $\epsilon_\Delta$  and  $r^*$ . If the constant  $C$  in eq. (15) is assumed to be independent of  $\delta_1$ , then the local maximum of the function (15) occurs at

$$\delta_{1(\max)} = \delta_m = \delta_2(1 - l_{1,2}). \quad (20)$$

Numerically,  $|l_{1,2}| < 0.05$  for nonpolymeric, nonpolar mixtures<sup>6</sup> and  $l_{1,2} = -0.123$  can be calculated from Huggins's  $k_S$  and  $r^*$  parameters<sup>22</sup> for natural rubber in benzene. In other words, if these theories<sup>6,21</sup> are correct, only an approximate value of  $\delta_2$  can be found from the  $\beta_n$ -versus- $\delta_1$  plot.

Under the  $\delta_1 = \delta_2$  condition, eq. (19) predicts that  $\beta_n(\max) = E$  decreases with the increase of  $r^*$ . According to Huggins,<sup>21</sup> "for each segment type the average intermolecular contacting segment surface area is constant at a given temperature, regardless of variations in the types and numbers of the other segments." In other words,  $\sigma_i$  values are treated as potentially accessible interacting surfaces of the interacting segments; and for mixtures of a given polymer ( $\sigma_0 = \text{const.}$ ),  $r^*$  is inversely propor-

tional to  $\sigma_1$ . Furthermore, for polymer solutions, each solvent molecule was considered<sup>22</sup> as a single segment of one type, and each mer of the polymer, as a single segment of the second type. Intuitively, in the case of a simple polymer-solvent system, the potential surface area  $\sigma_1$  can vary with the orientation of the solvent molecule, but it should be constant for a given type of molecular geometry interacting by the same mechanism. As reported, both  $E$  and  $F$  are smaller for linear-molecule solvents than for nonlinear ones. At the same time, both parameters are proportional to  $\sigma_1$ , which means that  $\sigma_1$  is nearly constant within one class of solvents: lower in value for the linear molecules, higher for nonlinear ones.

A similar explanation of the  $\beta_n$ -versus- $\delta_1$  dependence shown in Figures 2 and 3 can be deduced using the experimental approach of Funk and Prausnitz.<sup>6</sup> From eqs. (15), (17), and (18),

$$F^* = [(\delta_1 - \delta_2)^2 + 2l_{1,2}\delta_1\delta_2]/|\delta_1 - \delta_2|. \quad (21)$$

Knowing  $\delta_1$ ,  $\delta_2$ , and  $l_{1,2}$ , one can calculate the tangent  $F^*$ . This has been done for benzene (and toluene)-saturated hydrocarbon systems.<sup>6</sup> The results are presented in Table III. It can be seen that the numerical values of  $F^*$  calculated by this method are quite comparable with their counterparts computed from eq. (18) for the  $\beta_n$ -versus- $\delta_1$  dependence in polymer solutions. According to eq. (15), for a given  $\delta_1$  and  $C = \text{const.}$ , the solvent which has a more linear molecule (higher value of  $l_{1,2}$ ) should yield a lower  $\beta$  value. This, in fact, is observed.

## CONCLUSIONS

The YRCK theory<sup>9</sup> permits calculation of the nonpolar contribution of the binary cluster integral  $\beta_n$ . This parameter shows a very similar behavior to that of the binary cluster integral itself of the nonpolar polymers. This similarity can be taken as an indication that, at least for the vinyl polymers investigated, the assumption that the statistical segment of the two parameter theories is equivalent to the monomeric unit of the polymer is permissible.

The  $\beta_n$ -versus- $\delta_1$  plot can be crudely approximated by a linear equation where both constants depend on the ill-defined symmetry of the solvent molecules. This dependence can be expected on the basis of the semi-empirical<sup>6</sup> and theoretical<sup>21,22</sup> calculations.

Attempts to correlate  $\beta$  or  $\beta_n$  with the solubility parameters  $\delta_i$  ( $i = (d,p)^2$ ,  $i = (d,p,h)^3$ , or  $i = (v,r)^4$ ) by means of the relation  $\beta \propto \sum_i (\delta_1 - \delta_2)_i^2$  were unsuccessful. The failure most probably was caused by the deficiency of the geometric mean rule.

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