Cohesive Energy Density of Polytetrahydrofuran

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Synopsis

Measurements have been conducted on radiation-crosslinked polytetrahydrofuran (PTHF) of stress–strain and of swelling coefficients in simple esters. For the linear polymer, measurements have been made of density and intrinsic viscosities in the esters. $[\eta]$ was also determined under the Θ conditions of 33.5°C. in diethyl malonate. The results have been incorporated into several (sometimes interdependent) approaches towards the evaluation of the solubility parameter δ_p of PTHF. The mean of the nine values obtained is 8.55 $(\text{cal./cc.})^{1/2}$, whence the cohesive energy density is 5.17 kcal./mole. Seventeen experimental values of the Flory interaction parameter χ are also reported.

INTRODUCTION

The thermodynamic properties of polymer solutions are commonly described in terms of the Flory-Huggins equation [eq. (1)], which gives the free energy ΔG_m of mixing the liquid-like polymer with solvent.

$$\Delta G_m/RT = n_s \ln \phi_s + n_p \ln \phi_p + \chi\phi_s\phi_p (n_s + mn_p) \qquad (1)$$

The subscripts s and p refer to solvent and polymer, respectively. In eq. (1), n is the number of moles; ϕ denotes volume fraction; m represents the ratio of the molar volume of polymer to that of the solvent, and the dimensionless Flory interaction parameter χ is a function of the interaction energy of a given polymer–solvent system. Spontaneous dissolution is characterized by a negative ΔG_m. The first two terms on the right-hand side of eq. (1), representing the configurational entropy of mixing, are always negative. Hence the criterion of solubility is that the third term be a negative or small positive quantity. The same consideration applies to χ, as ϕ, n, and m are positive numbers.

Included within χ itself are enthalpy and entropy contributions. The former of these, i.e., the heat of mixing, is expressible as follows for nonpolar substances:

$$\chi \text{ (enthalpy)} = (V_s/RT)(\delta_s - \delta_p)^2 \qquad (2)$$

In eq. (2), V is the molar volume and δ, which is called the solubility

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parameter, is defined as

$$\delta = (\Delta U/V)^{1/2} \qquad\qquad (3)$$

$\Delta U/V$ is termed the internal pressure or cohesive energy density and represents the molar energy of complete vaporization per cubic centimeter. It may be shown that the maximum critical value of χ, below which there is solubility throughout the entire range of composition, is 0.5. Under these conditions χ (enthalpy) must be small, remembering that there is also an entropy contribution and hence[1] from eq. (2), $\delta_s = \delta_p$. Among the factors which render χ unsuitable as a sole practical criterion of solubility may be mentioned: (1) it is concentration-dependent, (2) it is not especially convenient to determine experimentally, and (3) it is a composite term influenced by such factors as hydrogen-bonding in polar systems to which eq. (2) is inapplicable. Lieberman[2] has advanced some techniques for the quantification of the hydrogen-bonding parameter. More recently Blanks and Prausnitz[3] suggested some illuminating methods of calculating polar and non-polar parameters for several polymers in a variety of solvents. While useful for nonpolar systems, polar polymers or polar solvents, they are not so reliable for systems wherein specific interactions obtain.

With the realization that at best δ is no more than a useful guide to predicting solubility behavior, we have determined this quantity by a variety of methods. Some of these were employed initially for the system rubber–solvent by Bristow and Watson,[4] while in criticizing certain facets of these, Mangaraj et al.[5] proposed modified procedures which they applied to the same system in addition to several others.[5-8] The method of Small,[9] whereby δ_p is calculated from attraction constants for the constituent groups in the polymer segment, has also enjoyed widespread use. References should be made to the original papers for the principal theoretical features of these procedures. In this work we have approached the subject in a fairly noncritical manner and have attempted to evaluate δ_p by as many different routes as possible.

PTHF is becoming an increasingly important polymer and may be incorporated into polyurethanes.[10] To the best of our knowledge the only previous communication concerning its solubility characteristics consists of some qualitative observations by Burrows and Crowe.[11] This present work constitutes part of a general programme on physico-chemical aspects of this polymer and its solutions. Our preliminary results have already been included in a recent review on PTHF by Dreyfuss and Dreyfuss.[12]

EXPERIMENTAL

Polymer

The crosslinked PTHF was kindly donated by Dr. D. Sims. The initial material had been prepared by the reaction between 1 g. of THF–PF_5 complex and 1 liter of THF under nitrogen for 24 hr. at room temperature.

The resultant polymer was dissolved in benzene and the catalyst fragments removed by washing the solution with water. After precipitation with methanol, the PTHF was cast into sheets and sealed in a glass tube under vacuum. This linear polymer was then irradiated for 500 min. at the rate of 10^6 rad/min. by using a 4 M.e.v. beam, the tube being water-cooled throughout. For the subsequent swelling and stress–strain measurements linear polymer was extracted for 24 hr. by benzene vapor in a Soxhlet apparatus. The specimen was finally dried *in vacuo* at 30°C. for 48 hr.

Esters

After preliminary drying over anhydrous K_2CO_3, the esters were purified by distillation, the middle fractions distilling within ±0.5°C. of the correct boiling point being retained. In the case of dibutyl phthalate and ethyl lactate, vacuum distillation was necessary.

Equilibrium Swelling

Strips (ca. 0.15 g.) of crosslinked polymer were suspended in about 50 ml. of the esters at 25°C. and the degree of swelling determined by conventional techniques.[4–8, 13] In all cases it was established that equilibrium swelling was attained after 3 days. The swelling coefficient Q (in millimeters solvent/gram polymer) was calculated from:

$$Q = (w - w_0)/w_0\rho_s \qquad (4)$$

where w_0, w, and ρ_s are respectively the mass of dry polymer, the mass of swollen polymer, and the density of the ester at 25°C.

Solution Viscosity

A purified fraction of linear PTHF which, from its intrinsic viscosity in toluene[14] had a $\bar{M}_n = 80,000$, was used throughout. The values of $[\eta]$ and the Huggins slope factor k' were obtained for the sample in each ester at 25°C. by using an Ubbelohde suspended-level viscometer with negligible kinetic-energy and end-effect corrections. In order to prevent degradation, an antioxidant (2,6 di-*tert*-butyl-*p*-cresol) was incorporated in all solvents and solutions at a concentration of 0.1% (w/v). No measurements could be performed with methyl formate in which the polymer is wholly insoluble.

Density of Polymer

Successive small volumes of a concentrated solution of linear polymer in chloroform were evaporated in a specific-gravity bottle until an air-free film occupying ca. 20% of the available volume was built up. The film was then dried for 1 week. The residual space was filled with *n*-heptane in which the polymer is entirely insoluble. The volume and hence the density of the polymer were then determined at 25°C.

Stress–Strain Measurements on Crosslinked Polymer

A strip having unstretched dimensions of 2.0 × 1.0 × 0.033 cm. was utilized and the measurements conducted at room temperature, 24°C. A bulldog clip was fixed firmly to each end of the strip. The upper clip was connected to a stand with copper wire and a fine iron wire was fastened to the lower one. Weights were attached to this iron wire and the corresponding movement of the lower clip measured with a cathetometer. No slipping of the clips or permanent deformation of the strip were verified by the observation that the lower clip returned to its original position when the weights were removed after considerable extension.

THEORY AND RESULTS

Method 1: Direct Swelling Measurements

Application of the Scatchard-Hildebrand equation to swelling of amorphous crosslinked polymer yields the following expression for the heat of mixing $\Delta H_1{}^m$:

$$\Delta H_1{}^m = K V_s \phi_p{}^2 (\delta_s - \delta_p)^2 \tag{5}$$

in which V, ϕ, and δ denote molar volume, volume fraction, and solubility parameter respectively. Equilibrium swelling should be a maximum when $\Delta H_1{}^m \to 0$ and $\delta_s = \delta_p$. Hence, neglecting possible specific effects such as dipole and hydrogen-bonding interactions, a plot of the swelling coefficient
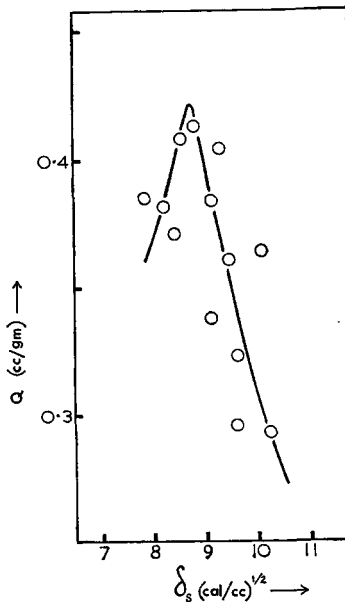

Fig. 1. Swelling coefficient vs. solubility parameter for crosslinked PTHF in esters at 25°C.

Q versus the solubility parameter of the liquid δ_s should yield a curve with a maximum at a value of δ_s, which equals the solubility parameter of the polymer.

This curve is illustrated in Figure 1, which, despite the considerable scatter, indicates that $\delta_p = 8.6 \pm 0.1$.

Method 2: Swelling Measurements Allowing for Molar Volume of Solvent

δ_p can be derived more accurately from an expression incorporating the molar volume of each liquid. Thus, Q is a Gaussian function of $V_s^{1/2} (\delta_s - \delta_p)$. The relationship may be expressed as:

$$Q = Q_{\max} \exp \{-KV_s(\delta_s - \delta_p)^2\} \tag{6}$$

Equation (6) can be recast in the form

$$[(1/V_s) \ln (Q_{\max}/Q)]^{1/2} = K^{1/2}(\delta_s - \delta_p) \tag{7}$$

Hence a plot of the left-hand side of eq. (7) (ordinate) versus δ_s (abscissa) should yield a straight line intersecting the abscissa axis at a value of δ_s, which equals the solubility parameter of the polymer.

The value of the maximum swelling coefficient $Q_{\max}$ was estimated from Figure 1 and the plot corresponding to eq. (7) is shown in Figure 2. From this, $\delta_p = 8.6 \pm 0.1$.
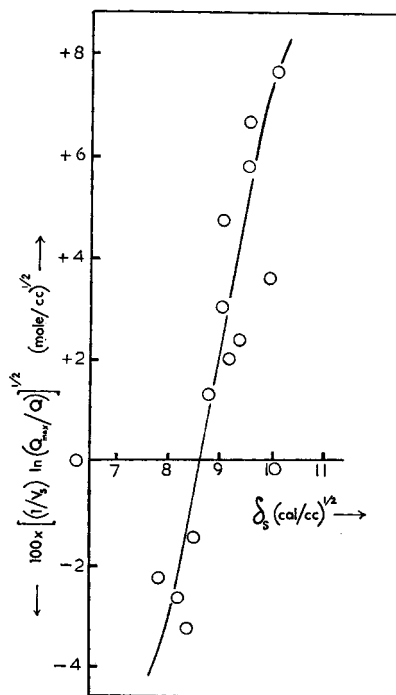

Fig. 2. Estimation of δ_p for crosslinked PTHF swollen in esters at 25°C.; via eq. (7).

Method 3: Intrinsic Viscosity of Linear Polymer Solutions

The effective hydrodynamic volume or intrinsic viscosity $[\eta]$ is a measure of the size of a polymer molecule in solution. A high value of $[\eta]$ is encountered in a good solvent which induces pronounced polymer–solvent interactions and chain extension. When considering a group of liquids for the solvent power towards a polymer, it is expected from the theory of cohesive energy densities that the best solvent will be that possessing the solubility parameter closest to that of the polymer. The maximum $[\eta]$ is seen from Figure 3 to correspond to $\delta_p = 8.6 \pm 0.1$.
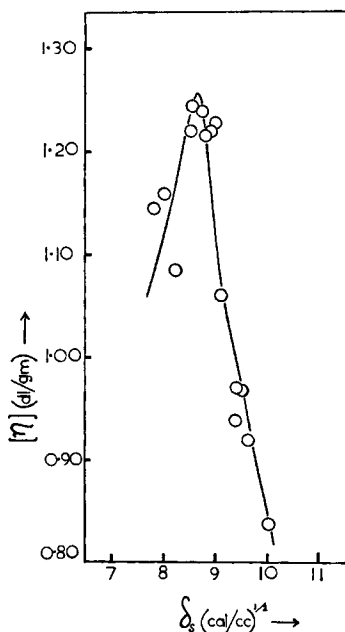

Fig. 3. Intrinsic viscosity of linear PTHF at 25°C. vs. solubility parameter of esters.

The effect of solvent power on the Huggins slope factor k' is approximately opposite to the effect on $[\eta]$. Normally k' is 0.3–0.4 in good solvents, whereas higher values obtain in poor ones. The points in a plot of k' (ordinate) versus δ_s (abscissa) are rather dispersed, but the general form is that of a curve with a minimum in the region of $\delta_s = 8.4–8.7$. Thus for $\delta_s = 8.45$, 8.5, and 8.65, the corresponding values of k' are 0.43, 0.40, and 0.43, respectively. Illustrative of the higher Huggins constants exhibited by poorer solvents on either side of this region are the values of 0.64 for both sec-butyl acetate ($\delta_s = 8.2$) and ethyl acetate ($\delta_s = 9.05$).

Method 4: Intrinsic Viscosity Allowing for Molar Volume of Solvent

By direct analogy with method 2, the results of intrinsic viscosity measurements may be interpreted more easily when recast into a linear form, thus:

$$[(1/V_s) \ln ([\eta]_{max}/[\eta])]^{1/2} = K^{1/2}(\delta_s - \delta_p) \qquad (8)$$

The value of the maximum intrinsic viscosity $[\eta]_{max}$ was estimated from Figure 3 and the appropriate plot of eq. (8) is shown in Figure 4. From this, $\delta_p = 8.6 \pm 0.1$.
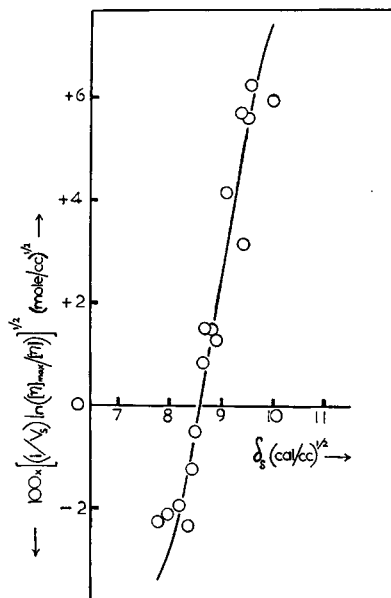

Fig. 4. Estimation of δ_p for linear PTHF from intrinsic viscosities; via eq. (8).

Method 5: Swelling in Conjunction with Stress–Strain

For a crosslinked polymer the applied load and the resultant extension are interrelated by the Rivlin equation:[15]

$$f = 2A_0 (\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \tag{9}$$

in which C_1 and C_2 are (in dynes per square centimeter) constants for the specimen; A_0 (in square centimeters) is the unstretched cross sectional area; f (in dynes) is the force, and the extension ratio λ is defined as the ratio of the extended to unstretched lengths of the strip. A graph of f versus $(\lambda - \lambda^{-2})$ is shown in Figure 5, the linearity indicating that C_2 is negligible. The slope, together with the value of A_0 (= 0.033 cm.^{2}), yield a value of 2.0×10^7 dyne/cm.^{2} for C_1.

An attempt was made to evaluate C_2 by plotting $f/2A_0 (\lambda - \lambda^{-2})$ versus λ^{-1}, which should yield C_1 and C_2 from the intercept and slope, respectively. The variation was not uniform, presumably because of experimental error and the relatively small extensions obtained ($\lambda_{max} \simeq 1.1$). The straight line drawn through the intercept, i.e., the known value of C_1, and some of the coherently lying points indicates very small possible values of C_2 of the order of $C_1/100$. Accordingly C_2 was ignored.
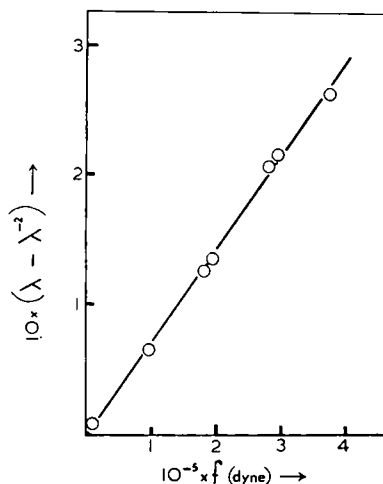
Fig. 5. Determination of C_1 from stress-strain measurements on crosslinked PTHF at 24°C.
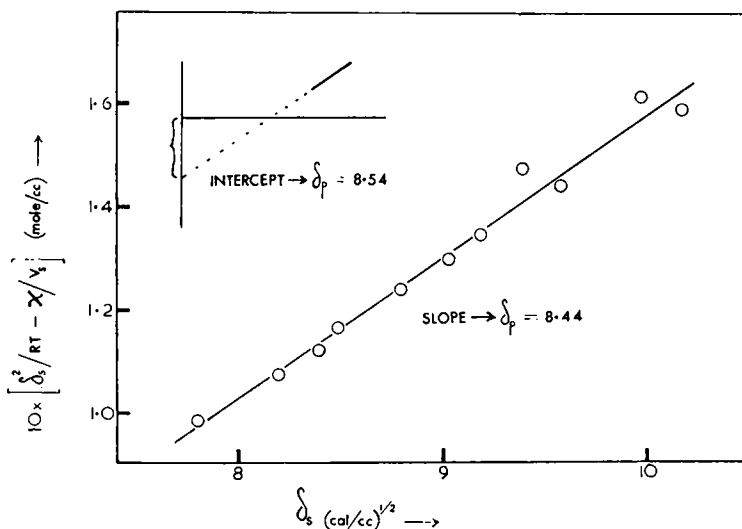

Fig. 6. Estimation of δ_p from slope of eq. (11) in which χ is obtained from swelling and stress–strain measurements. The inset shows extension of graph to $\delta_s = 0$ yielding δ_p from the intercept.

The constant C_1 was required in order to obtain values of the polymer–solvent interaction parameter χ via the Flory-Rehner equation:[16]

$$-RT \ln (1 - \phi_p) + \phi_p + \chi\phi_p{}^2 = 2V_sC_1(\phi_p{}^{1/3} - 0.5\phi_p) \qquad (10)$$

where each χ appertains to the ester (of molar volume V_s) in which the volume fraction of polymer in the swollen crosslinked sample is ϕ_p. Assuming that the density of 1.02 g./cm.[3] found for the linear polymer applies also

to the crosslinked sample, then $\phi_p = Q/(1.02 + Q)$. Values of χ were determined by using the values of Q already obtained in method 1 and δ_p obtained graphically in Figure 6 from the Huggins relationship.

$$\delta_s^2/RT - \chi/V_s = (2\delta_p/RT) - \delta_p^2/RT - \beta/V_s \qquad (11)$$

The slope yields $\delta_p = 8.44 \pm 0.05$, and the negative intercept has a value of $\delta_p^2/RT + \beta/V_s$, in which the dimensionless quantity β depends on the entropy of mixing. If the latter term, and hence β/V_s, is neglected, then a value of $\delta_p = 8.54 \pm 0.05$ is derived from the intercept. Since β/V_s is only $<3\%$ of δ_p^2/RT, the value of δ_p from the intercept when β is neglected is in good agreement with that derived directly from the slope.

Method 6: Incorporating χ Derived from Flory Θ Condition

The method just described may also be treated via a different approach to the interaction parameter χ. It is readily shown[17] that

$$1 - 2\chi = (\alpha^5 - \alpha^3)/C_m M^{1/2} \qquad (12)$$

where M is the molecular weight of the polymer; α is the expansion factor by which the linear chain dimensions are increased owing to intramolecular interactions; C_m is a characteristic of the polymer–solvent system and is defined as

$$C_m = (3^3/2^{5/2}\pi^{1/2})(\bar{v}_p^2/V_s N_A)(M/\overline{r_0^2})^{3/2} \qquad (13)$$

In eq. (13), $\bar{v}_p$ is the partial specific volume of the polymer in a solvent of molar volume V_s; N_A is Avogadro's number and $\overline{r_0^2}$ is the mean square unperturbed end-to-end distance. On solving eq. (12) for χ it is seen that a knowledge of α and C_m is required for each system, viz:

$$\chi = 0.5 - (\alpha^5 - \alpha^3)/(2C_m M^{1/2}) \qquad (14)$$

Denoting Flory Θ conditions by a subscript Θ, then

$$\alpha^5 - \alpha^3 = ([\eta]/[\eta]_\Theta)[([\eta]/[\eta]_\Theta)^{2/3} - 1] \qquad (15)$$

Furthermore, partial evaluation of C_m from eq. (13) yields

$$C_m = 1.4 \times 10^{-24}(\bar{v}_p^2/V_s)(M/\overline{r_0^2})^{3/2} \qquad (16)$$

The constant ratio $(M/\overline{r_0^2})$ is accessible, as it is equal to Φ/K_Θ, where Φ is the universal parameter introduced by Flory and K_Θ is the constant in the following expression prevailing under Θ conditions:

$$[\eta]_\Theta = K_\Theta M^{1/2} \qquad (17)$$

Hence we may now write the interaction parameter in the convenient form

$$\chi = 0.5 - ([\eta]/[\eta]_\Theta)[([\eta]/[\eta]_\Theta)^{2/3} - 1](V_s/A) \qquad (18)$$

in which

$$A = (2M^{1/2} \times 1.4 \times 10^{-24} \times \Phi)/(K\bar{v}_p^2) \qquad (19)$$
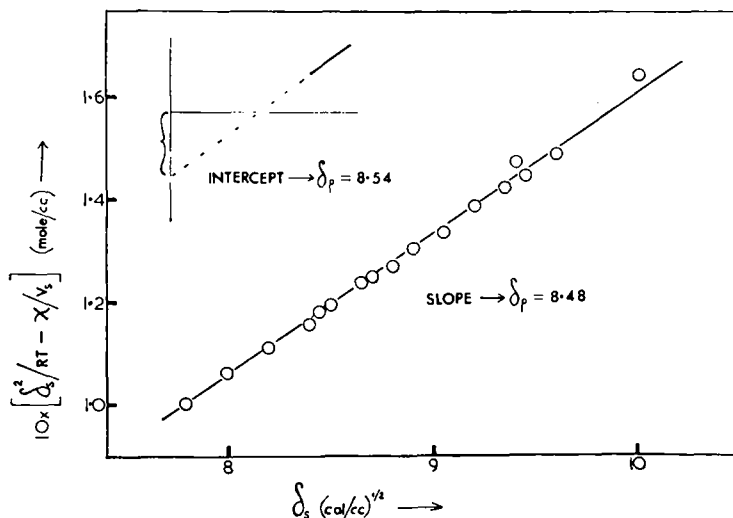
Fig. 7. Estimation of δ_p from slope of eq. (11) in which χ is obtained from the chain expansion factor α. The inset shows extension of graph to $\delta_s = 0$, yielding δ_p from the intercept.

When $(\overline{r_0^2})^{1/2}$ and $[\eta]$ are expressed in units of centimeter and deciliters per gram, respectively, the best accepted value of Φ is 2.87×10^{21}. Subsidiary phase separation studies[18] yield a mean value of 2.3×10^{-3} dl./g. for K_Θ. Unpublished results[19] indicate that $\bar{v}_p$ depends markedly on the con-

TABLE I
Molar Volumes and Solubility Parameters of Esters, and Interaction
Parameters χ of PTHF–Ester Systems

Ester	δ_s, (cal./cc.)$^{1/2}$	V_s at 25°C., cc./mole	χ
Isobutyl n-butyrate	7.8	167	0.441
n-Butyl n-butyrate	8.0	165	0.337
sec-Butyl acetate	8.2	134	0.387
Isopropyl acetate	8.4	116	0.406
n-Amyl acetate	8.45	148	0.325
n-Butyl acetate	8.5	132	0.335
n-Amyl formate	8.65	130	0.345
Ethyl n-butyrate	8.7	132	0.355
n-Propyl acetate	8.8	115	0.376
Ethyl propionate	8.9	115	0.366
Ethyl acetate	9.05	97.8	0.429
n-Propyl formate	9.2	97.8	0.386
Ethyl acetate–methyl acetate (1:1, v/v)	9.35	88.1	0.464
Dibutyl phthalate	9.4	226	0.353
Ethyl formate	9.45	80.2	0.454
Methyl acetate	9.6	80.0	0.467
Ethyl lactate	10.0	114	0.463

centration but the limiting value for dilute solution in a number of solvents is 1/1.02 ml./g. at 25°C. For PTHF in THF at the same temperature, Sims[20] quotes $\bar{v}_p$ = 1/1.025 ml./g. As the density was found to be 1.02 g./ml., we have taken $\bar{v}_p$ = 1/1.02 ml./g., whence A [via eq. (19)] and thence χ [via eq. (18)] may be calculated for linear PTHF in each of the esters. For the sample, $[\eta]_\Theta$ = 0.620 dl./g. in the Θ solvent diethyl malonate at 33.5°C. The results are tabulated in Table I.

These values of χ have been incorporated into a graphical procedure for estimating δ_p in a similar manner to that utilized in method 5. The appropriate plot of eq. (11) is shown in Figure 7. The slope yields δ_p = 8.48 ± 0.05 and, when the term β/V_s is neglected, a value of δ_p = 8.54 ± 0.05 is derived from the intercept.

Method 7: Calculation by Using Molar Attraction Constants

From the results of vapor-pressure measurements on volatile compounds Small[9] has tabulated group and bond attraction constants F. The solubility parameter of a polymer is given by

$$\delta_p = (\Sigma F)/V_p \qquad (20)$$

where the molar volume of the polymer $V_p = M/\rho$, ρ = density.

For the repeat segment in PTHF, M = 72.1 and

$$\Sigma F = (4F_{CH_2}) + (4F_O)$$

From Small's tabulated data, ΣF = 602.

With regard to the density of the polymer there is a variety of values available, the divergence among them depending to some extent on the crystallinity of the sample. Some of these literature values have been collected and reported elsewhere.[12] Our measurements yield a value of 1.02 g./ml. at 25°C. as do other unpublished ones on a sample prepared differently.[21]

On taking, then, 1.02 g./ml. as the density of the PTHF, eq. (20) yields

$$\delta_p = 602/[(72.1/1.02)] = 8.52.$$

DISCUSSION

The experiments were conducted in the order of swelling, stress–strain, viscosity. As not all the esters were available initially, the reason for the smaller number of swelling compared to viscometric data will be apparent. Rather dispersed points are observed in Figure 1, particularly, because of the uniformly low values of Q which confer low accuracy. The maximum swelling coefficient was 0.48 which, in this instance, represents only a 43% increase in weight of the strip in its equilibrium swelling condition. Clearly it would have been preferable had a less highly crosslinked specimen been made available.

It is known that an irregular variation of Q (and $[\eta]$) with δ_s is obtained if measurements are made on a random group of liquids selected solely for the

range of their solubility parameters. The optimum characteristic is that they be structurally interrelated and akin to the polymer segment $+(CH_2)_2$— O—$(CH_2)_2+$. The closest analog of this would be found in a series of ethers, R_1—O—R_2. However, as a sufficiently wide range of these is not readily available nor are all the δ_s values known, it was decided to utilize the reasonably closely related (although more polar) esters R_1—CO—O—R_2, for which calculated solubility parameters are available in the literature. Molar volumes V_s were calculated from the densities of the esters at 25°C. The value calculated for the ethyl acetate–methyl acetate mixed solvent (1:1, v/v) is an approximate one based on additivity of volumes neglecting the effect of partial molar volumes.

The values for χ deduced from viscometric measurements in the esters at 25°C. coupled with $[\eta]_\theta$ lie within the range 0.32–0.47. These are typical results expected for moderately good solvents. $[\eta] = 1.69$ dl./g. (25°C., toluene) for the same sample, from which result we have $\chi = 0.29$, which confirms that toluene is a better solvent than all the esters. The agreement among the values found for δ_p is gratifyingly close and is indeed somewhat better than the accord commonly encountered in determining this quantity by different methods.[22,23] It should be noted, however, that the figure of 8.52 $(cal./cc.)^{1/2}$ calculated via Small's attraction constants (method 7) is critically dependent on the value utilized for the density of the polymer. Thus if this is taken as 1.03 g./ml., δ_p becomes 8.60 $(cal./cc.)^{1/2}$. Apart from some unpublished swelling data[20] indicating that $\delta_p \simeq 8.5$ $(cal./cc.)^{1/2}$, there do not appear to be any literature values available for purposes of comparison.

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