Estimation of Polymer Solubility Parameters by Gas Chromatography

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ABSTRACT: Partial molar heats of mixing ($\Delta\overline{H}_1^\infty$), partial molar free energies of mixing ($\Delta\overline{G}_1^\infty$), and the Flory–Huggins χ parameter have been determined for a wide variety of hydrocarbons in polystyrene (178 to 208 °C) and poly(methyl acrylate) (88 to 112 °C) by the gas chromatographic method. The Hildebrand–Scatchard solubility theory was used to calculate infinite dilution solubility parameters (δ_2^∞) from thermodynamic data for the polymer. In contrast to the poor correlation of heat of mixing data with solubility theory, the free-energy parameters ($\Delta\overline{G}_1^\infty$, χ) gave much better agreement with theory. In fact, the χ parameter yielded the most self-consistent and reasonable estimate of solubility parameters for both polymers: 7.6 ± 0.2 for polystyrene at 193 °C and 8.7 ± 0.3 for poly(methyl acrylate) at 100 °C. Values of δ_2^∞ for the polymers were also estimated at 25 °C, from χ values obtained by extrapolation of the high-temperature data. This procedure resulted in good agreement with literature values for δ_2 for these polymers obtained by conventional methods.

The solubility parameter concept based on regular solution theory has been used extensively in practical applications of polymers in various solvents and solvent mixtures. It has proven to be a valuable empirical tool in the paint and lacquer industry and in the prediction of adhesive interactions.

The solubility parameter, δ (units of $(\mathrm{cal/cm^3})^{1/2}$), for any compound is defined from Hildebrand–Scatchard solution theory as

$$\delta \equiv (\Delta E_\mathrm{v}/V_1)^{1/2} \qquad (1)$$

i.e., as the square root of the cohesive energy density, which is itself defined as the ratio of the energy of vaporization, ΔE_v, to the molar volume, V_1, both referred to the same temperature.[1]

Solubility theory gives the energy of mixing of two liquids at constant volume, ΔE_m, as follows:

$$\Delta E_\mathrm{m}/\phi_1\phi_2 = V_\mathrm{m}(\delta_1 - \delta_2)^2 \qquad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of the components, V_m is the average molar volume based on mole fractions, and δ_1 and δ_2 refer to the solubility parameter of each liquid. The theory has been particularly successful in describing, at least semiquantitatively, thermodynamic properties of dilute solutions, especially when the component liquids are nonpolar.

In addition to its role in the theory of solutions, the solubility parameter (or the closely related cohesive energy density) has been shown to be related to a number of physical properties, such as surface tension, wettability, glass transition temperatures of polymers, etc.

Since high polymers have no appreciable vapor pressure, and their molar volume is usually not well defined, there is at present no direct experimental determination of δ for a polymer. Therefore this value must be deduced from the measurements of swelling, solubility, and viscosity or calculated from an approximate theory. Although these methods are useful, they are often tedious and time consuming.

In principle, the technique of gas–liquid chromatography should be ideally suited for determining solubility parameters (δ_2) directly for polymer substrates from eq 2 (where δ_1 is known or can be calculated), since the method yields energies of mixing of polymer–solute systems. Moreover, the method is not restricted to the study of polymer–solvent systems but can also be used to investigate interactions between polymers and nonsolvents. In addition, the system is amenable to high, as well as to low, temperatures. The use of GLC data to determine solubility parameters for polymers was first proposed by Guillet,[2] but attempts to obtain consistent values have so far been unsuccessful.

Experimental Section

Materials. Solutes were used without further purification. *n*-Octane, *n*-dodecane, and ethylbenzene were obtained from BDH and *n*-decane, *n*-tetradecane, and naphthalene were obtained from Eastman Kodak. Ninety-nine percent pure samples of 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, 3,4,5-trimethylheptane, 3,3,4,4-tetramethylhexane, and *tert*-butylbenzene were obtained from Chemical Samples Co. (Columbus, Ohio). Cyclohexane, tetralin, benzene, and toluene were Fisher Certified ACS grade. Aldrich (99+%) *n*-butylcyclohexane and *n*-butylbenzene were used and *n*-hexadecane was obtained from J. T. Baker. *cis*- and *trans*-decalin were separated by preparative GC.

Anionic polystyrene ($\overline{M}_\mathrm{w}$ = 120 000, $[\eta]$ = 0.575) was obtained from Polymer Corp., and poly(methyl acrylate) ($\overline{M}_\mathrm{w}$ = 200 000, $\overline{M}_\mathrm{n}$ = 63 200) was obtained from Aldrich.

Columns. The polymers were first dissolved in a suitable solvent and deposited onto an inert chromatographic support by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for ca. 48 h, with slight heating, the chromatographic support was packed with the aid of a mechanical vibrator into 0.25 in. o.d. copper columns. The weight of the stationary phase (i.e., polymer) was determined by calcination, using suitable blank corrections.[3] Column parameters are described in Table I.

Instrumentation. Measurements were carried out on a Hewlett-Packard 5840A gas chromatograph, equipped with a dual flame ionization detector. Prepurified nitrogen was used as the carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time (0.01 min time base) was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at inlet and outlet of the column,[4] read from a mercury manometer (±0.05 mmHg), were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. The oven temperature was measured (to 0.01 °C) with a Hewlett-Packard quartz thermometer.

The solute molecules, including a small amount of methane marker, were injected manually with a 10 μL Hamilton syringe (<0.01 μL).

To check the precision of the retention data from the HP 5840A gas chromatograph, specific retention volumes for *n*-decane and *n*-dodecane on high-density polyethylene (linear MRLX-6050) were compared to literature values which had been previously obtained on the same column.[3] Retention volumes were reproduced to within 1–2% of the literature values.

Data Reduction. Specific retention volumes, V_g, were computed from the relation[5]

$$V_\mathrm{g} = (t_\mathrm{R}F/w_\mathrm{L})J_2^{\,3}(760/P_\mathrm{o}) \qquad (3)$$

where t_R is the net retention time, F is the flow rate at 273.16 K (760 mm), w_L is the mass of polymer, and $J_2^{\,3}$ is given by the relation[6]

$$J_n^{\,m} = (m/n)\{[(P_\mathrm{i}/P_\mathrm{o})^n - 1]/[P_\mathrm{i}/P_\mathrm{o})^m - 1]\} \qquad (4)$$

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Table I
Stationary Phases and Column Parameters

	Packing and column				
Polymer	Solvent	Inert support	Loading, %	Polymer mass, g	Length, ft
Polystyrene	Benzene	Chromosorb G, AW, DMCS, 70/80	5.55	0.5554	3
Poly(methyl acrylate)	Toluene	Chromosorb G, AW, DMCS, 70/80	4.87	0.4556	3

where $m = 3$, $n = 2$, and P_i and P_o are the inlet and outlet pressures.

Solute vapor pressures were computed from the Antoine equation

$$\log p_1{}^0 = A - B/(t + C) \qquad (5)$$

where $p_1{}^0$ is the solute vapor pressure in mmHg, t is the temperature (°C), and A, B, and C are constants taken from standard sources.[7]

Solute densities were obtained from various sources, including the compilations of Orwoll and Flory,[8] International Critical Tables,[9] and Timmermans' compilation.[10] If density data for a solute were not available in the required temperature range, then data from lower temperatures were extrapolated to the required range.

Second virial coefficients (B_{11}) were computed from[11]

$$B_{11}/\overline{V}_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{4.5} \qquad (6)$$

where $\overline{V}_c$ and T_c are critical volumes and temperatures, T is the temperature (K), and n is the number of carbon atoms of the n-alkane.

For the other hydrocarbons investigated, an effective number of carbon atoms, n_A, was estimated and replaced n in eq 4.[12] N_A takes on the value of n of the normal alkane having the same value for the vapor pressure parameter A, in

$$\ln (P_c/p) = A(T_c - T)T \qquad (7)$$

where P_c and T_c are the critical pressure (mm) and temperature (K) and p is the saturation vapor pressure (mm) at temperature T (K) of the solute.

Weight fraction activity coefficients $(a_1/w_1)^\infty$ at infinite dilution were then calculated from the following relationship:[13]

$$\ln (a_1/w_1)^\infty = \ln (273.16R/p_1{}^0V_gM_1) - p_1{}^0(B_{11} - V_1)/RT \qquad (8)$$

where V_1 and M_1 are the molar volume and molecular weight of the probe molecule, and R is the gas constant. χ parameters[14,15] were calculated wherever the specific volume (v_2) of the polymer was known, or could be estimated,

$$\chi = \ln (273.16Rv_2/p_1{}^0V_gV_1) - 1 - p_1{}^0(B_{11} - V_1)/RT \qquad (9)$$

The activity coefficient (at infinite dilution of solute) is related to the partial molar free energy of mixing by the relation[16]

$$\Delta\overline{G}_1{}^\infty = RT \ln (a_1/w_1)^\infty \qquad (10)$$

Results and Discussion

The experimental retention volumes, derived activity coefficients (weight fraction), and χ parameters for normal and branched alkanes, cycloparaffins, and aromatic solutes in polystyrene and poly(methyl acrylate) ($T > T_g$) were tabulated.[17] Volumetric data for polystyrene were obtained from Höcker et al.[18] Since no density data were available for poly(methyl acrylate) (in the temperature range of interest), specific volumes for the polymer were estimated from the Simha–Boyer relation.[19] It is interesting to note that the χ parameter is not very sensitive to errors in v_2. For example, an error of 0.002 cm^3/g in v_2 causes a difference in the derived χ parameter for n-butylcyclohexane in poly(methyl acrylate) of 0.0004. Retention volumes were obtained for at least 13 temperatures, over a temperature range of ca. 30 °C, for each solute (probe).

Table II
Weight Fraction Activity Coefficients, $(a_1/w_1)^\infty$, of Selected Solute–Polystyrene Systems at Several Temperatures[a]

	Temperature, °C		
	183	193	203
n-Decane	12.23	12.42	11.62
n-Dodecane	12.59	12.31	11.79
n-Tetradecane	12.93	12.65	12.27
n-Hexadecane	14.05	13.18	12.72
3,3,4,4-Tetramethylhexane[b]	9.90	9.16	8.71
Cyclohexane[b]	7.85	7.51	7.36
n-Butylcyclohexane[b]	8.36	8.15	7.90
cis-Decalin	5.47	5.32	5.23
trans-Decalin	5.94	5.76	5.61
Benzene[b]	4.98	4.91	4.88
n-Butylbenzene	5.29	5.29	5.19
Tetralin	3.83	3.80	3.79
Naphthalene	3.38	3.40	3.34

[a] The reliability of the present $(a_1/w_1)^\infty$ values, based on repeated measurements, is within 1–2%. [b] Values for $(a_1/w_1)^\infty$ given at 160, 170, and 180 °C.

Table III
Weight Fraction Activity Coefficients, $(a_1/w_1)^\infty$, of Selected Solute–Poly(methyl acrylate) Systems at Several Temperatures[a]

	Temperature, °C		
Solute	90	100	110
n-Octane	47.15	42.58	39.41
n-Decane[b]	60.40	53.83	47.65
n-Dodecane	80.70	71.29	63.31
n-Tetradecane	113.61	98.23	85.04
2,2,4-Trimethylpentane	46.53	40.40	35.49
2,2,5-Trimethylhexane	51.19	44.53	39.62
3,4,5-Trimethylheptane	45.81	40.25	36.42
3,3,4,4-Tetramethylhexane	33.87	30.14	27.36
Cyclohexane	22.02	20.19	18.27
n-Butylcyclohexane	38.79	35.22	31.82
cis-Decalin	26.23	23.33	21.15
trans-Decalin	28.76	25.39	23.08
Benzene	5.80	5.74	5.65
Toluene	6.84	6.65	6.62
n-Ethylbenzene	8.00	7.62	7.50
n-Butylbenzene	10.96	10.43	10.07
tert-Butylbenzene	9.74	9.38	9.05
Tetralin	8.61	8.32	7.94
Naphthalene		4.70	4.66

[a] The reliability of the present $(a_1/w_1)^\infty$ values, based on repeated measurements, is within 1–2%. [b] Values of $(a_1/w_1)^\infty$ are given at 88, 98, and 108 °C.

Weight fraction activity coefficients (corrected for vapor-phase nonideality) of selected solutes in polystyrene and poly(methyl acrylate) at several temperatures are given in Tables II and III, respectively. In all cases, the activity coefficients decrease with increasing temperature, suggesting that the solubility of the hydrocarbons in the polymer increases accordingly. The largest activity coefficients were found for the n-alkanes. Similar trends were observed for the calculated χ parameters, which are given in Tables IV and V.

The partial molar heat of mixing ($\Delta\overline{H}_1{}^\infty$) of the solute at infinite dilution in the polymer is given by

$$\Delta\overline{H}_1{}^\infty = R\partial \ln (a_1/w_1)^\infty/\partial(1/T) \qquad (11)$$

Therefore $\Delta\overline{H}_1{}^\infty$ was obtained from the slope of the best straight line through a plot of the logarithm of the activity

Table IV
χ Parameters of Selected Solute–Polystyrene Systems at Several Temperatures[a]

Solute	Temperature, °C 183	193	203
n-Decane	1.011	1.016	0.937
n-Dodecane	1.086	1.056	1.004
n-Tetradecane	1.143	1.116	1.078
n-Hexadecane	1.215	1.180	1.139
3,3,4,4-Tetramethylhexane[b]	0.900	0.816	0.759
Cyclohexane[b]	0.620	0.564	0.534
n-Butylcyclohexane[b]	0.773	0.743	0.708
cis-Decalin	0.468	0.437	0.417
trans-Decalin	0.519	0.485	0.455
Benzene[b]	0.289	0.262	0.244
n-Butylbenzene	0.375	0.371	0.345
Tetralin	0.203	0.195	0.191
Naphthalene	0.129	0.130	0.109

[a] The precision on χ, as estimated from repeated measurements, is better than 5%. [b] Values of χ are given at 160, 170, and 180 °C.

Table V
χ Parameters of Selected Solute–Poly(methyl acrylate) Systems at Several Temperatures[a]

Solute	Temperature, °C 90	100	110
n-Octane	2.382	2.272	2.186
n-Decane[b]	2.680	2.558	2.430
n-Dodecane	3.000	2.870	2.746
n-Tetradecane	3.364	3.214	3.064
2,2,4-Trimethylpentane	2.353	2.204	2.067
2,2,5-Trimethylhexane	2.476	2.330	2.206
3,4,5-Trimethylheptane	2.443	2.308	2.202
3,3,4,4-Tetramethylhexane	2.172	2.050	1.947
Cyclohexane	1.720	1.624	1.514
n-Butylcyclohexane	2.337	2.236	2.130
cis-Decalin	2.066	1.945	1.844
trans-Decalin	2.128	2.000	1.901
Benzene	0.508	0.489	0.464
Toluene	0.667	0.631	0.619
n-Ethylbenzene	0.831	0.777	0.754
n-Butylbenzene	1.145	1.091	1.050
tert-Butylbenzene	1.034	0.992	0.951
Tetralin	1.035	0.998	0.948
Naphthalene		0.485	0.473

[a] The precision on χ, as estimated from repeated measurements, is better than 5%. [b] Values of χ are given at 88, 98, and 100 °C.

coefficient vs. the reciprocal of the absolute temperature, as determined by a linear least-squares analysis. Partial molar heats of 13 solutes in polystyrene and 19 solutes in poly(methyl acrylate) are given in Tables VI and VII, together with the corresponding heats of solution. Heats of solution (ΔH_s) were determined in a similar manner from the temperature dependence of the specific retention volumes:

$$\Delta H_s = -R\partial(\ln V_g)/\partial(1/T) \qquad (12)$$

The uncertainty limits stated in Tables VI and VII refer to standard errors in the slope, as given by the least-squares analysis. Values for naphthalene in polystyrene represent the average of two sets of measurements (in the given temperature range) on the same column. Since some sample size dependence was noted, results were extrapolated to zero sample size.

Table VI
Partial Molar Heats of Mixing and Heats of Solution of Several Hydrocarbons in Polystyrene

Solute	Temp range, °C	ΔH_1^{∞}, cal/mol	$-\Delta H_s$, cal/mol
n-Decane	168–218	966 ± 153	8380 ± 139
n-Dodecane	168–218	1000 ± 64	10220 ± 60
n-Tetradecane	168–218	1143 ± 35	11958 ± 34
n-Hexadecane	168–218	1370 ± 36	13575 ± 58
3,3,4,4-Tetramethylhexane	158–182	2575 ± 130	6591 ± 120
Cyclohexane	158–182	620 ± 182	5700 ± 184
n-Butylcyclohexane	158–182	988 ± 64	8731 ± 66
cis-Decalin	178–208	918 ± 76	8949 ± 79
trans-Decalin	178–208	1034 ± 77	8506 ± 75
Benzene	178–208	−10 ± 108	6489 ± 108
n-Butylbenzene	178–208	167 ± 80	9481 ± 77
Tetralin	178–208	268 ± 64	10213 ± 55
Naphthalene	178–208	121 ± 117	10703 ± 122

Table VII
Partial Molar Heats of Mixing and Heats of Solution of Several Hydrocarbons in Poly(methyl acrylate)

Solute	Temp range, °C	$\Delta \bar{H}_1^{\infty}$, cal/mol	$-\Delta H_s$, cal/mol
n-Octane	88–112	2676 ± 88	6117 ± 78
n-Decane	78–108	3215 ± 60	7840 ± 73
n-Dodecane	88–112	3379 ± 34	9679 ± 27
n-Tetradecane	88–112	4120 ± 39	11132 ± 38
2,2,4-Trimethylpentane	88–112	3842 ± 130	3627 ± 124
2,2,5-Trimethylhexane	88–112	3576 ± 80	4936 ± 72
3,4,5-Trimethylheptane	88–112	3066 ± 60	6854 ± 50
3,3,4,4-Tetramethylhexane	88–112	3083 ± 42	7038 ± 42
Cyclohexane	88–112	2490 ± 72	4557 ± 70
n-Butylcyclohexane	88–112	2740 ± 16	7954 ± 25
cis-Decalin	88–112	2893 ± 49	8291 ± 40
trans-Decalin	88–112	3087 ± 56	7741 ± 44
Benzene	88–112	340 ± 48	6875 ± 50
Toluene	88–112	416 ± 50	7781 ± 44
Ethylbenzene	88–112	930 ± 58	8180 ± 53
n-Butylbenzene	88–112	1182 ± 31	9816 ± 24
tert-Butylbenzene	88–112	1001 ± 24	9327 ± 22
Tetralin	88–112	1165 ± 35	10663 ± 31
Naphthalene	98–122	345 ± 20	11796 ± 25

Whereas the values of $\Delta \bar{H}_1^{\infty}$ for aromatic solutes vary from 0.3 to 1.1 kcal/mol in poly(methyl acrylate), and from −0.01 to 0.3 in polystyrene, the corresponding values for saturated hydrocarbons are 2.5 to 4.1 and 0.6 to 2.5 kcal/mol. These trends are those expected for solvent–polymer and nonsolvent–polymer systems, respectively.

A comparison of results given in Tables VI and VII for the *n*-alkanes, cyclohexane, *n*-butylcyclohexane, benzene, and *n*-alkyl-substituted derivatives reveals a general increase in $\Delta \bar{H}_1^{\infty}$ with an increase in the hydrocarbon chain length.

Solubility Parameter Theory. Solubility parameters (δ_1) were calculated for the various solutes (probes) from the relation

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \qquad (13)$$

where R is the universal gas constant, and V_1 is the solute molar volume corresponding to temperature, T (K), which was chosen as the midpoint of the temperature range investigated for each polymer–solute system (100 °C for poly(methyl acrylate), 193 °C for polystyrene); ΔH_v is the molar enthalpy of vaporization for the solute at temperature T. The units of δ

Table VIII
Solute Solubility Parameters at 25, 100 and 193 °C

Solute	$\delta_{25^\circ C}$	$\delta_{100^\circ C}$	$\delta_{193^\circ C}$
n-Octane	7.6	6.7	
n-Decane	7.7	7.0	5.9
n-Dodecane	7.8	7.1	6.1
n-Tetradecane	7.9	7.2	6.2
n-Hexadecane	8.0		6.3
2,2,4-Trimethylpentane	6.9	6.1	
2,2,5-Trimethylhexane	7.0	6.2	
3,4,5-Trimethylheptane	7.4	6.7	
3,3,4,4-Tetramethylhexane	7.6	6.9	6.2
Cyclohexane	8.2	7.2	6.4[a]
n-Butylcyclohexane	8.0	7.2	6.2[a]
cis-Decalin	8.7	8.0	7.0
trans-Decalin	8.4	7.7	6.8
Benzene	9.2	8.1	7.1[a]
Toluene	8.9	8.0	
Ethylbenzene	8.8	7.9	
n-Butylbenzene	8.6	7.8	6.8
tert-Butylbenzene	8.4	7.6	
Tetralin	9.5	8.7	7.8
Naphthalene	9.9	9.2	8.2

[a] $\delta_{170^\circ C}$.

are $(\mathrm{cal/cm^3})^{1/2}$. These calculated values are summarized in Table VIII.[20]

Heats of vaporization for the solutes (at 100 and 193 °C) were obtained from the heats of solution and heats of mixing in Tables VI and VII as follows:[21]

$$\Delta H_v = \Delta \overline{H}_1{}^\infty - \Delta H_s \tag{14}$$

The experimental heat of vaporization for *n*-octane at 100.5 °C is 8.691 kcal/mol.[22] The value used in the present work at 100 °C is 8.79 ± 0.17 kcal/mol, which is in excellent agreement with the experimental value. Derived heats were assumed constant over the temperature range of interest. This fact has already been well established.[5,23,24]

Since the heat of vaporization decreases and the molar volume increases with increasing temperature, the solubility parameters of compounds decrease with increasing temperature. For a polymer one expects the variation of δ_2 to be smaller than for δ_1, because of the relatively small coefficient of thermal expansion of the polymer. The solubility parameters for poly(methyl acrylate) and polystyrene at 25 °C are in the range of 9.8 to 10.4 and 8.5 to 10.5, respectively.[25]

If one assumes zero volume change on mixing, the Hildebrand–Scatchard equation (eq 2) can be rewritten in terms of the partial molar heat of mixing as follows:

$$\Delta \overline{H}_1{}^\infty = V_1(\delta_1 - \delta_2)^2 \tag{15}$$

which suggests that as the solubility parameters of both components become equal, the heat of mixing should approach zero. Therefore on extrapolation of a plot of $\Delta \overline{H}_1{}^\infty$ vs. the solubility parameter of the probe (δ_1), to $\Delta \overline{H}_1{}^\infty = 0$, a reasonable solubility parameter for the polymer (δ_2) should be obtained (at the temperature for which $\Delta \overline{H}_1{}^\infty$ and δ_1 were calculated). The results of such plots for both the polystyrene and poly(methyl acrylate) systems are illustrated in Figure 1. Data points fall in a general region, which when extrapolated to zero partial molar heat of mixing yield a broad range of possible δ_2 values, although the probes used in the present study are nonpolar, saturated, and unsaturated hydrocarbons, which should not show any specific interactions (e.g., hydrogen bonding) with the polymers used. This method does not appear to be very useful.

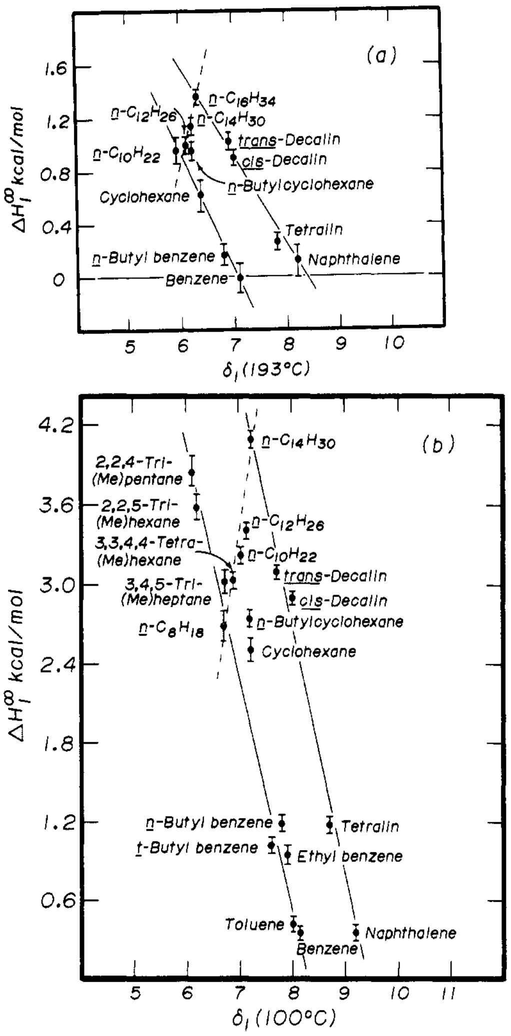

Figure 1. Partial molar heat of mixing vs. solubility parameter of the hydrocarbon: (a) in polystyrene at 193 °C; (b) in poly(methyl acrylate) at 100 °C.

It is interesting to note, however, the linearity within families of compounds (e.g., *n*-alkanes, branched alkanes, and alkyl-substituted benzene derivatives). It is also interesting that, of the solutes tested, the partial molar heat of mixing for the normal alkanes (n-$C_8 \rightarrow n$-C_{16}) increases with increasing solubility parameter. One would expect a decrease in partial molar heats of mixing as the value of δ_1 approaches that of δ_2.

Although solubility theory gives the energy of mixing (ΔE_m) (eq 2), it is given at constant volume.[1] It is often assumed that the heat of mixing at constant pressure (ΔH_m) would be approximately the same. If a suitable correction can be made to constant pressure, then the usual heat of mixing can be substituted in the Hildebrand–Scatchard equation. At constant pressure it is the free energy, and not the heat of mixing, which is given directly by the solubility parameters.[1,26] Therefore, replacing $\Delta \overline{H}_1{}^\infty$ by $\Delta \overline{G}_1{}^\infty$ in eq 15, the Hildebrand–Scatchard equation becomes

$$\Delta \overline{G}_1{}^\infty = V_1(\delta_1 - \delta_2)^2 \tag{16}$$

A plot of the partial molar free energy of mixing, $\Delta \overline{G}_1{}^\infty$, vs. δ_1 should therefore show less scatter and from this one expects that when the free-energy change is 0, $\delta_1 = \delta_2$. This is illustrated in Figure 2. The free-energy change on mixing was calculated from the weight fraction activity coefficient according to eq 10, and the results are summarized in Table IX. As expected, the scatter is less pronounced, and the free energy seems more suited to fit the Hildebrand–Scatchard equation. This is in agreement with Patterson's suggestion

Table IX
Molar Volumes and Partial Molar Free Energies of Mixing of Hydrocarbons in Polystyrene and Poly(methyl acrylate)

	Polystyrene			Poly(methyl acrylate)		
Solute	Temp, °C	V_1, cm³/mol	$\Delta\bar{G}_1^\infty$, cal/mol	Temp, °C	V_1, cm³/mol	$\Delta\bar{G}_1^\infty$, cal/mol
n-Octane				100	179.90	2798
n-Decane	193	243.20	2348	93	211.19	2964
n-Dodecane	193	277.30	2340	100	246.97	3183
n-Tetradecane	193	312.43	2365	100	281.10	3422
n-Hexadecane	193	348.37	2403	100		
2,2,4-Trimethylpentane				100	182.60	2759
2,2,5-Trimethylhexane				100	199.33	2831
3,4,5-Trimethylheptane				100	204.69	2756
3,3,4,4-Tetramethylhexane	170	215.81	981	100	198.47	2540
Cyclohexane	170	134.53	1786	100	120.19	2241
n-Butylcyclohexane	170	203.57	1859	100	189.40	2656
cis-Decalin	194	180.60	1558	100	165.27	2349
trans-Decalin	193	186.13	1632	100	170.39	2412
Benzene	170	110.46	1410	100	98.73	1304
Toluene				100	116.94	1413
n-Ethylbenzene				100	133.61	1515
n-Butylbenzene	194	186.72	1555	100	168.78	1749
tert-Butylbenzene				100	167.52	1670
Tetralin	193	157.21	1245	100	145.44	1580
Naphthalene	193	145.45	1140	110	134.30	1179

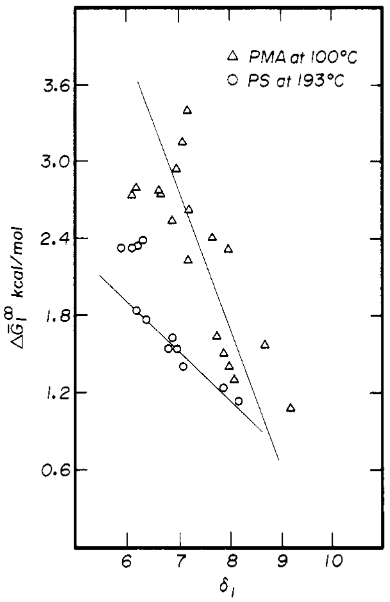

Figure 2. Partial molar free energy of mixing vs. solubility parameter of the hydrocarbon: (○) in polystyrene at 190 °C; (△) in poly(methyl acrylate) at 100 °C.

that better correlations are obtained for the free energy with solubility parameter theory, which remains the most generally useful method of approximately predicting polymer solubility.[26] Scott[27] suggested that the heat and entropy, separately, are affected by secondary factors of which the most important is normally the volume change on mixing; the free energy is, however, very insensitive to these factors.

A third approach is to combine the Flory treatment[28] with Hildebrand–Scatchard theory to give the following relationship for the interaction parameter, χ[26]

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{17}$$

where χ has free-energy characteristics, i.e.,

$$\chi = \chi_H + \chi_S \tag{18}$$

Table X
Solubility Parameters of Polystyrene and Poly(methyl acrylate) at 193 and 100 °C

	δ_2		
	χ(eq 17)	$\Delta\bar{G}_1^\infty$(eq 16)	$\Delta\bar{H}_1^\infty$(eq 15)
	Polystyrene, 193 °C		
Slope	7.6 ± 0.2	7.1 ± 0.5	8.0 ± 0.6
Intercept	7.6 ± 0.2	7.6 ± 0.4	8.2 ± 0.4
	Poly(methyl acrylate), 100 °C		
Slope	8.5 ± 0.3	8.4 ± 0.4	10.4 ± 0.6
Intercept	8.8 ± 0.2	9.1 ± 0.4	10.5 ± 0.4

Polymer solubility parameters should be obtained from eq 17 for poly(methyl acrylate) and polystyrene at 100 and 193 °C (which correspond to the midpoint of temperature range investigated).

Equation 17 can be rewritten as

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2^2}{RT} \tag{17a}$$

Therefore a plot of $[(\delta_1^2/RT) - (\chi/V_1)]$ vs. δ_1 of probe should yield a straight line with a slope of $2\delta_2/RT$ and an intercept of $-(\delta_2)^2/RT$.

The results are illustrated in Figure 3. An excellent linear correlation is found (13 data points for PS, 19 points for PMA). Slopes and intercepts were obtained from a linear least-squares analysis. Derived values of δ_2 for the polymers are listed in Table X. The solubility parameters estimated in this manner for polystyrene and poly(methyl acrylate) are 7.6 ± 0.2 and 8.7 ± 0.3 at 193 and 100 °C, respectively. Although there are no experimental values in the literature at these elevated temperatures, these values seem to be of the correct magnitude. Slightly higher δ_2 values would have been expected, however, since the thermal expansion coefficient of polymers is generally lower than that of small molecules.

The astonishing consistency of the data when plotted according to eq 17a is worthy of some additional comment. To our knowledge, this is the first time that consistent results for the solubility parameter of a polymer have been obtained with

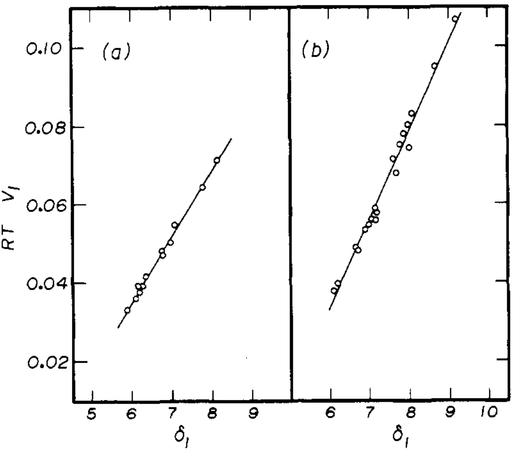

Figure 3. Estimation of solubility parameter (δ_2) of the polymer from the χ parameter: (a) in polystyrene at 193 °C; (b) in poly(methyl acrylate) at 100 °C.

Table XI
Trouton Constants (Entropies of Vaporization)

Solute	$\Delta H_v/T_{bp}$, cal/°C/mol
n-Octane	20.5
n-Decane	20.9
n-Dodecane	21.3
n-Tetradecane	21.6
n-Hexadecane	21.9
2,2,4-Trimethylpentane	19.9
2,2,5-Trimethylhexane	20.3
3,4,5-Trimethylheptane	20.3
3,3,4,4-Tetramethylhexane	20.3

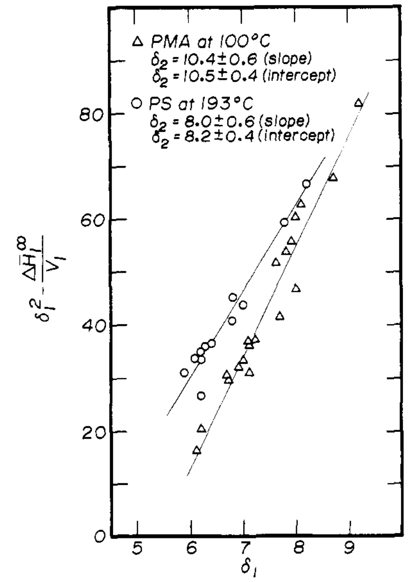

Figure 4. Estimation of solubility parameter (δ_2) of the polymer from partial molar heat of mixing, $\Delta\bar{H}_1^\infty$: (○) in polystyrene at 193 °C; (△) in poly(methyl acrylate) at 100 °C.

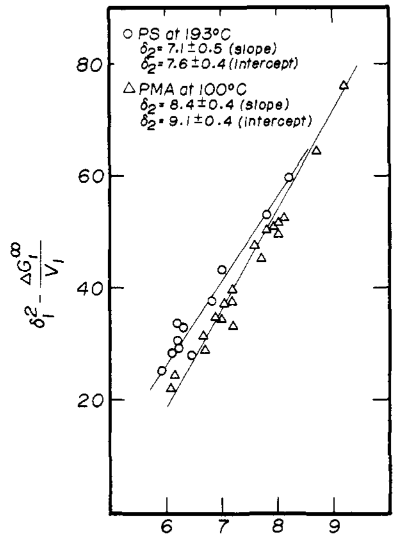

Figure 5. Estimation of solubility parameter (δ_2) of the polymer from partial molar free energy of mixing, $\Delta\bar{G}_1^\infty$: (○) in polystyrene at 193 °C; (△) in poly(methyl acrylate) at 100 °C.

such a wide variety of solvents. This must imply a special relationship between the χ parameter (at infinite dilution of the probe) and the solubility parameter δ_1 of the probe molecule. As has been pointed out recently by Guillet and Purnell[29] the χ^∞ parameter as defined in these studies is, in fact, the work function (Helmholtz free energy) associated with the polymer–probe interaction. It is therefore a parameter of rather fundamental significance.

On the other hand, the molar excess heat of mixing, $\Delta\bar{H}_1^e$, is defined in terms of models of ideal solutions which may not be relevant to the experimental situation. It is worth pointing out that since the pure liquid is one standard reference state, we are measuring differences of free energy between pure liquid probe and probe molecules at infinite dilution in the polymer phase. It is usual to assume that the entropy of vaporization is nearly the same for all probe molecules and that differences of free energy are primarily related to enthalpy differences between the initial and final states. However, recent studies by Patterson and Botherel have shown that considerable order exists in the liquid states of pure *n*-alkanes and hence their entropy of vaporization must be greater than for branched alkanes.[30] This is also shown by inspection of the Trouton constants for comparable branched and linear alkanes (Table XI). Furthermore, this order increases with the length of the alkyl chain and could well explain the anomalous results for linear alkanes shown in Figure 1. This would explain why free-energy relations give better correlations with solubility parameters than enthalpies alone. The reason for the special virtue of the χ parameter must await further study of a variety of polymer–probe systems.

It is, however, worth pointing out that the solubility parameter defined by eq 17 is not identical to that conventionally measured by swelling, solubility, and surface tension data, since these are at concentrations where the probe is highly concentrated and possibly associated, whereas in this case the probe is at infinite dilution in the polymer. One might hope that a direct relation could be found between δ_2^∞ and δ_2, but this must await further experimental studies. In any case, δ_2^∞ is of both practical and theoretical interest, since it relates directly to the force fields which surround a probe molecule in a polymer matrix. It should also be related to diffusional mobility and the removal of trace amounts of small molecules from polymer films. An analogous approach has been used to estimate solubility parameters for styrene–acrylonitrile copolymers,[31] polyethylene glycol,[32] and some surfactants.[33]

For comparative purposes, eq 15 and 16 were rewritten thus:

$$\delta_1^2 - (\Delta\bar{H}_1^\infty/V_1) = (2\delta_2)\delta_1 - \delta_2^2 \quad (15a)$$

$$\delta_1^2 - (\Delta\bar{G}_1^\infty/V_1) = (2\delta_2)\delta_1 - \delta_2^2 \quad (16a)$$

and analyzed in a similar manner. Results are graphically illustrated in Figures 4 and 5. These plots show extra scatter

Table XII
Temperature Dependence of the χ Parameter of Selected Solutes in Polystyrene

Solute	Slope (β)	Correlation coeff	Intercept (α)	Temp range, °C
n-Decane	724.2	0.946 34	−0.5600	168–218
n-Dodecane	680.7	0.988 75	−0.4124	168–218
n-Tetradecane	709.9	0.996 82	−0.4086	168–218
n-Hexadecane	800.7	0.997 17	−0.5426	168–218
3,3,4,4-Tetramethylhexane	1416.6	0.986 54	−2.365	158–182
Cyclohexane	528.7	0.849 54	−0.6185	158–182
n-Butylcyclohexane	582.2	0.980 18	−0.5735	158–182
cis-Decalin	536.1	0.965 51	−0.7063	178–208
trans-Decalin	597.9	0.968 38	−0.7955	178–208
Benzene	222.8	0.754 13	−0.2345	178–208
n-Butylbenzene	188.0	0.760 11	−0.0369	178–208
Tetralin	180.5	0.812 95	−0.1871	178–208
Naphthalene	210.1	0.753 56	−0.3313	178–208

Table XIII
Temperature Dependence of the χ Parameter of Selected Solutes in Poly(methyl acrylate)

Solute	Slope (β)[a]	Correlation coeff	Intercept (α)[a]	Temp range, °C
n-Octane	1469.7	0.995 45	−1.661	88–112
n-Decane	1702.1	0.996 34	−2.030	78–108
n-Dodecane	1777.2	0.997 86	−1.889	88–112
n-Tetradecane	2138.0	0.997 44	−2.521	88–112
2,2,4-Trimethylpentane	2041.9	0.992 37	−3.277	88–112
2,2,5-Trimethylhexane	1897.7	0.996 94	−2.748	88–112
3,4,5-Trimethylheptane	1622.9	0.996 17	−2.038	88–112
3,3,4,4-Tetramethylhexane	1634.3	0.999 07	−2.325	88–112
Cyclohexane	1384.2	0.996 42	−2.090	88–112
n-Butylcyclohexane	1442.3	0.999 55	−1.634	88–112
cis-Decalin	1506.7	0.997 88	−2.082	88–112
trans-Decalin	1607.3	0.998 61	−2.300	88–112
Benzene	295.2	0.957 00	−0.3055	88–112
Toluene	317.8	0.964 62	−0.2139	88–112
n-Butylbenzene	660.0	0.995 72	−0.6722	88–112
tert-Butylbenzene	569.9	0.997 55	−0.5368	88–112
Tetralin	625.0	0.994 64	−0.6835	88–112
Naphthalene	218.2	0.987 02	−0.09691	98–112

[a] The data were fitted to an equation of the form $\chi = \alpha + \beta/T$.

Table XIV
Extrapolated χ Values at 25 °C for Various Probes in Poly(methyl acrylate) and Polystyrene

Solute	V_1, cm^3/mol	χ	
		PMA	PS
n-Octane	163.53	3.267	
n-Decane	195.90	3.678	1.869
n-Dodecane	228.58	4.071	1.870
n-Tetradecane	261.27	4.650	1.972
n-Hexadecane	294.08		2.143
2,2,4-Trimethylpentane	166.08	3.571	
2,2,5-Trimethylhexane	182.38	3.616	
3,4,5-Trimethylheptane	188.44	3.405	
3,3,4,4-Tetramethylhexane	182.80	3.155	2.385
Cyclohexane	108.74	2.551	1.155
n-Butylcyclohexane	176.31	3.203	1.379
cis-Decalin	154.81	2.971	1.091
trans-Decalin	158.83	3.090	1.209
Benzene	89.40	0.684	0.513
Toluene	106.85	0.852	
n-Butylbenzene	156.78	1.541	0.593
tert-Butylbenzene	155.63	1.374	
Tetralin	136.82	1.412	0.418
Naphthalene	126.69	0.635	0.373

of experimental points, especially for the heat of mixing data (Figure 4). Results of a least-squares analysis of such plots are also summarized in Table X.

The partial molar free energy of mixing (eq 16a) yields average δ_2 for PS and PMA of 7.4 ± 0.4 and 8.8 ± 0.4, in good agreement with values derived from the χ parameter. On the other hand, δ_2 estimated from the heat of mixing data is higher. In fact, the solubility parameter derived from the heat of mixing for PMA appears to be much too high, being higher than the literature value at 25 °C, which is not very likely. Of the methods tested, the χ parameter seems to give by far the most self-consistent estimate of polymer solubility parameters.

In view of the consistency of the data from a wide variety of probe molecules, it is tempting to speculate further on the nature of the solubility parameter determined by the GC procedure. Since the solubility parameter δ_1 for the probe has a unique thermodynamic definition via eq 1 one may define an infinite dilution solubility parameter δ_2^∞ for the polymer in terms of measureable thermodynamic quantities by:

$$\chi^\infty \equiv (V_1/RT)(\delta_1 - \delta_2^\infty)^2 \qquad (19)$$

As pointed out earlier, χ^∞ is a Helmholtz free energy, the work function relating the free energy required to remove a probe (solute) molecule from a polymer matrix at infinite dilution to that required to remove the same molecule from pure solute at the same temperature. δ_2^∞ thus has an unambiguous thermodynamic definition via eq 19. One must then ask if δ_2^∞ has any relationship to the value of δ_2 estimated by conventional procedures.[25]

Table XV
Estimated Solubility Parameters of Polystyrene and Poly(methyl acrylate) at 25 °C

	δ_2	
	PS	PMA
Slope	9.7 ± 0.2	9.9 ± 0.4
Intercept	9.8 ± 0.2	10.2 ± 0.3
Lit.[a]	8.5–10.5	9.8–10.4

[a] Reference 25.

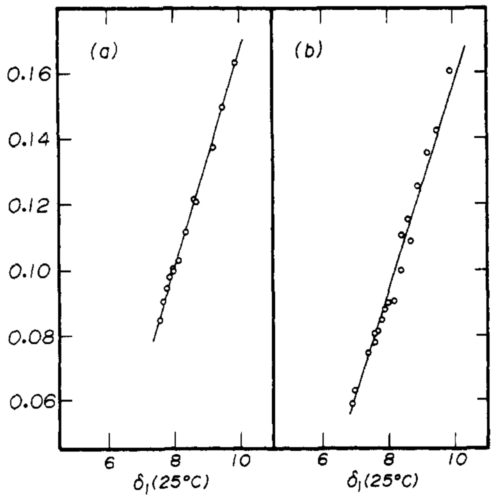

Figure 6. Estimation of solubility parameter (δ_2) of the polymer from the χ parameter: (a) in polystyrene at 25 °C; (b) in poly(methyl acrylate) at 25 °C.

In the first place, δ_2^∞ is measured at the temperature of the GC column, which is often 100 °C or more above room temperature where most values of δ_2 are measured and reported. A correction must therefore be made to bring both values to the same temperature.

The temperature dependence of the χ parameter in the ranges investigated fits an equation of the form

$$\chi = \alpha + \beta/T \qquad (20)$$

where α and β are the intercept and slope of the line and T is the absolute temperature. The constants were evaluated from a least-squares analysis of the data and are summarized in Tables XII and XIII. In most cases, the linear correlation is excellent. If one assumes that this relationship remains valid at lower temperatures (which is not too unreasonable), then values of χ can be estimated at 25 °C (for each solute–polymer system) from extrapolation of the high-temperature data. The χ values so obtained are listed in Table XIV. Literature values for V_1, the molar volumes of the solutes, are also included.

Using the solubility parameter for the solutes at 25 °C from Table VIII values of δ_2^∞ for the polymers were obtained from the slope and intercept of a plot of $[(\delta_1^2/RT) - (\chi/V_1)]$ against δ_1. The plots are shown in Figure 6. The numerical values of δ_2^∞ obtained in this manner (Table XV) are in good agreement with δ_2 values obtained by other methods. This suggests that the infinite dilution polymer solubility parameters (δ_2^∞) measured by GLC may well be useful in deriving fundamental information about polymer solubility, even at finite concentrations.

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(21) Since from the temperature variation of the retention volume both the excess enthalpy and entropy of mixing, ΔH_m^e and ΔS_m^e, can be determined:

$$\ln \gamma_1^\infty = \Delta G_m^e/RT = (\Delta H_m^e/RT) - (\Delta S_m^e/R) \qquad (14a)$$

where γ_1^∞ is the activity coefficient. By differentiating

$$V_g = 273.16R/p_1^0\gamma_1^\infty M_2 \qquad (14b)$$

$$\partial(\ln V_g)/\partial T = -(\partial \ln \gamma_1^\infty/\partial T) - (\partial \ln p_1^0/\partial T) \qquad (14c)$$

since

$$\partial \ln p_1^0/\partial T = \Delta H_v/RT^2 \qquad (14d)$$

where ΔH_v is the enthalpy of vaporization of the solute. It follows that

$$\partial \ln V_g/\partial(1/T) = (\Delta H_v - \Delta H_m^e)/R = -\Delta H_s/R \qquad (14e)$$

$\Delta H_v - \Delta H_m^e$ is the heat of evaporation from solution, equal, but of opposite sign, to the heat of solution, ΔH_s.
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