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Estimation of Polymer Solubility Parameters by Inverse Gas Chromatography

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ABSTRACT: Inverse gas chromatography has been used to estimate solubility parameters (δ_2) for various homopolymers, copolymers, and blends of styrene and butyl methacrylate at 140 °C. Values of δ_2 were determined from the measured Flory–Huggins χ parameters for several hydrocarbon probes (at infinite dilution) in each of these stationary phases. In general, δ_2 values for the copolymers are a weak function of polymer composition and can be roughly approximated by a linear interpolation (in weight fraction) of the constituent polymers' properties. However, opposite deviations from additivity are observed for miscible blends (δ_2 values are lower than expected) and immiscible blends (δ_2 values are higher than expected).

Introduction

The solubility parameter concept based on regular solution theory has found many practical applications in the prediction of polymer solubility (e.g., in the selection of solvents for coating formulations). Hildebrand–Scatchard solution theory defines the solubility parameter, δ (cal$^{1/2}$ cm$^{-3/2}$), for any compound as the square root of the cohesive energy density (CED)

$$\delta = (\mathrm{CED})^{1/2} = (\Delta E_\mathrm{v}/V)^{1/2} \tag{1}$$

which is itself defined in terms of the molar energy of vaporization (ΔE_v) and the molar volume (V), both referred to the same temperature.[1] These parameters can be readily determined for low molecular weight species. Because of the negligible volatility of polymers, however, polymer solubility parameters have generally been deduced from swelling or viscosity measurements or have been estimated from group additivity contributions.[2]

Recently, DiPaola-Baranyi and Guillet demonstrated that the technique of inverse gas chromatography (IGC) can readily give consistent and realistic estimates for these parameters at infinite dilution of probe in polymer.[3,4] This method has been successfully applied by these and other workers to polystyrene,[3] poly(methyl acrylate),[3] poly(vinyl acetate),[4] some olefin polymers and copolymers,[5] and random copolymers of poly(vinyl acetate) and poly(vinyl chloride).[6]

This report presents new solubility parameter data obtained by IGC for various molten homopolymers, copolymers, and blends of styrene and butyl methacrylate.

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were used without further purification. The polystyrene samples (PS$_\mathrm{H}$: $\bar{M}_\mathrm{w}$ = 110 000, $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} < 1.06$; PS$_\mathrm{L}$: $\bar{M}_\mathrm{n}$ = 1709, $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} < 1.06$) were obtained from Polysciences and Pressure Chemical Co., respectively. Poly(*n*-butyl methacrylate) (PnBMA: $\bar{M}_\mathrm{w}$ = 320 000, $\bar{M}_\mathrm{n}$ = 73 500), poly(isobutyl methacrylate) (PiBMA: $\bar{M}_\mathrm{w}$ = 300 000, $\bar{M}_\mathrm{n}$ = 140 000), and poly(*sec*-butyl methacrylate) (PsBMA: density 1.052 g cm^{-3}) were obtained from Aldrich Chemical Co. Poly(styrene–*n*-butyl methacrylate) [P(S–nBMA): $\bar{M}_\mathrm{w}$ = 70 000–75 000, $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \simeq$ 2.0–2.3, MI = 15.5] and poly(styrene–isobutyl methacrylate) [P(S–iBMA): $\bar{M}_\mathrm{w}$ = 70 000] containing 58 and 80 wt % S, respectively, are random copolymers which were obtained from internal sources. Chromosorb G (AW-DMCS treated, 70–80 mesh) was obtained from Johns-Manville.

Columns. The columns were prepared in the usual manner. The polymers were coated from a benzene solution onto Chromosorb G (AW-DMCS treated, 70–80 mesh). After drying in a vacuum oven for ca. 48 h at 60 °C, the coated support was resieved and then packed into 48-mm-i.d. copper columns. The total percent loading of polymer (ca. 10%) on the support was determined by calcination using a suitable blank correction. The relative concentration of polymers in the blends is assumed to be identical with that in the original solution prior to deposition on the inert support. Columns were conditioned under nitrogen for 3 h at 100 °C above the glass transition of the polymer(s). A detailed description of the columns is found in previous publications.[7]

Instrumentation. The IGC measurements were carried out with a Hewlett-Packard 5830A gas chromatograph which was equipped with a dual flame ionization detector. The experimental setup and procedure have been described previously.[7]

Data Reduction. Specific retention volumes, V_g° (cm^3/g), were computed from the familiar expression of Littlewood et al.[8] Flory–Huggins χ parameters[9] at infinite dilution of probe were determined in the usual manner from the measured specific retention volumes for a variety of hydrocarbon probes in each of the pure[10] (χ_{12}) as well as mixed stationary phases[11] ($\chi_{1(23)}$). The literature sources for the solute parameters required for the calculations have been described previously.[7]

Results and Discussion

The IGC method for determining polymer solubility parameters is based on the principle that the Flory–Huggins χ parameter (a free energy parameter) can be readily determined from retention data for various small-molecule probes and that χ can be related to solubility parameters by combining Hildebrand–Scatchard solution theory[1] with Flory theory[9]

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

where V_1 refers to the probe's molar volume, δ_1 and δ_2 refer to the solubility parameter of the probe and polymer, respectively, and χ_S is an excess entropy term which is normally considered to be a constant near 0.3 for many polymers.[2,12,13] Equation 2 can be rewritten as

$$\left(\frac{\delta_1{}^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2{}^2}{RT} + \frac{\chi_S}{V_1}\right) \tag{3}$$

which is in a particularly useful form because if χ, V_1, and δ_1 are known, both δ_2 and χ_S can be determined graphically. If δ_2 has a constant value for all probes, a plot of $(\delta_1{}^2/RT - \chi/V_1)$ vs. δ_1 should yield a straight line with $2\delta_2/RT$ as the slope and $\delta_2{}^2/RT + \chi_S/V_1$ as the intercept. The validity of this approach has previously been demonstrated for several homopolymers[3–6] and a few copolymers.[5,6]

In the present work, IGC is used to determine and compare the solubility parameter, δ_2, for various molten styrene–butyl methacrylate homopolymers, copolymers, and blends at 140 °C. Only apolar probes are used in the present study. The χ data used in these calculations have been reported previously.[7] Solubility parameters for the volatile probes, δ_1, were determined from

$$\delta_1 = [(\Delta H_\mathrm{v} - RT)/V_1]^{1/2} \tag{4}$$

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Table I
Solute Parameters Used in Calculation of Polymer Solubility Parameters at 140 °C

solute	V_1, cm^3 mol^{-1}	δ_1, cal$^{1/2}$ cm$^{-3/2}$
n-octane	191.00	6.26
n-decane	223.99	6.51
n-dodecane	258.43	6.71
2,2,4-trimethylpentane	192.80	5.68
3,4,5-trimethylheptane	214.49	6.34
cyclohexane	127.88	6.73
methylcyclohexane	148.77	6.56
n-butylcyclohexane	197.23	6.90
carbon tetrachloride	113.80	7.13
benzene	104.91	7.56
toluene	123.83	7.34
ethylbenzene	140.24	7.49
n-butylbenzene	175.88	7.41
tert-butylbenzene	174.72	7.18

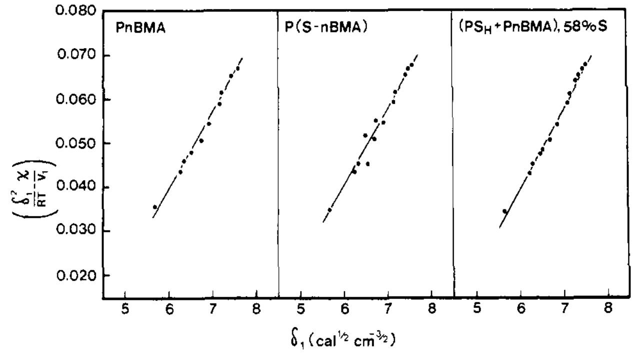

Figure 1. Estimation of polymer solubility parameters, δ_2, at 140 °C.

where ΔH_v, the heat of vaporization of the probe, and V_1, the liquid molar volume of the probe, were determined from literature vapor pressure data[14,15] and density data,[14-16] respectively. Calculated values of δ_1 at 140 °C are summarized in Table I. Literature sources give δ_1 only at 25 °C.[17]

A least-squares analysis of plots of $\delta_1^2/RT - \chi/V_1$ vs. δ_1 was carried out for each polymer system investigated. An excellent linear correlation coefficient (better than 0.995) is obtained in all cases. Figure 1 illustrates such plots for several apolar probes in a homopolymer (PnBMA), copolymer [P(S-nBMA)], and blend (PS$_H$-PnBMA) at 140 °C.

Polymer solubility parameters were calculated as outlined in the foregoing discussion. Table II summarizes δ_2 values obtained from the slope of such plots for all the homopolymers, copolymers, and blends investigated. These values are reliable to ±(0.10-0.15) cal$^{1/2}$ cm$^{-3/2}$. A closer inspection of the data in Table II follows.

With regards to the butyl methacrylate homopolymers investigated, δ_2 appears to be insensitive to geometric isomerism of the butyl side chains. Values of δ_2 lie between 7.15 and 7.20. Within the experimental uncertainty, both the low and high molecular weight polystyrene (PS$_L$ and PS$_H$, respectively) have a similar solubility parameter (i.e., 7.49 vs. 7.55, respectively). The solubility parameter determined for each copolymer is similar to that obtained by a linear interpolation (in weight fraction) of the corresponding homopolymer values. To this point, the results are not unusual.

Table II
Polymer Solubility Parameters and Entropic Contribution at 140 °C

polymer	δ_2[a]	χ_S/V_1
PnBMA	7.18	0.0026
PiBMA	7.15	0.0025
PsBMA	7.20	0.0025
PS$_H$	7.55	0.0031
PS$_L$	7.49	0.0025
P(S-nBMA)	7.41	0.0020
P(S-iBMA)	7.41	0.0031
PS$_H$ + PnBMA		
30 wt % PS$_H$	7.35	0.0025
58 wt % PS$_H$	7.51	0.0025
PS$_L$ + PnBMA		
15 wt % PS$_L$	6.99	0.0032
27 wt % PS$_L$	7.08	0.0029
30 wt % PS$_L$	7.15	0.0022
35 wt % PS$_L$	7.03	0.0034
40 wt % PS$_L$	7.10	0.0031
58 wt % PS$_L$	7.30	0.0026
80 wt % PS$_L$	7.27	0.0028

[a] ±(0.10-0.15) cal$^{1/2}$ cm$^{-3/2}$.

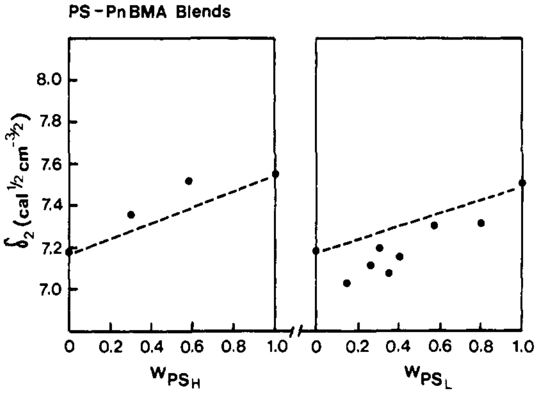

Figure 2. Comparison of δ_2 values at 140 °C for immiscible and miscible blends.

The results for the polymer blends, however, are more unusual. Previous work has shown that while PS$_H$-PnBMA blends are immiscible, the corresponding PS$_L$-PnBMA blends are miscible over the whole composition range.[7] It was therefore very interesting to observe opposite deviations from additivity for each type of blend (Figure 2). Whereas the δ_2 values for the immiscible blends are slightly higher than expected, the δ_2 values for the miscible blends are consistently lower than expected. However, since some of the measurements are on the border of experimental uncertainty, no firm conclusions can be drawn at this time regarding the relationship between polymer-polymer miscibility and trends in δ_2. The generality of these trends will have to be determined by examining other polymer blends.

In addition to calculation of δ_2 values from the slope of plots such as those illustrated in Figure 1, values of χ_S/V_1 were estimated from the observed intercepts. These values are summarized in Table II. In all the present systems, the estimated value of χ_S/V_1 at 140 °C lies between 0.002 and 0.003. If V_1 is taken as 170 cm^3 mol^{-1} (i.e., average of V_1 values in Table I), χ_S values between 0.3 and 0.5 are obtained. This is in good agreement with previous estimates for this parameter[5,12,13] and represents a significant entropic contribution to the experimentally determined χ value.

The temperature dependence of the experimentally determined χ parameter for each polymer-solute system fits an equation of the form

$$\chi = \alpha + \beta/T \qquad (5)$$

where T is the absolute temperature. The constants α and β were evaluated from a least-squares analysis of the data and are summarized for PS$_H$, PS$_L$, and PnBMA in supplementary Tables I-III. Although eq 5 is strictly valid

Table III
Extrapolated Flory-Huggins Interaction Parameters for Various Solute-Homopolymer Systems at 25 °C

solute	χ PS$_H$	χ PS$_L$	χ PnBMA
n-octane	1.88	1.48	1.16
n-decane	1.78	1.44	1.17
n-dodecane	1.79		
2,2,4-trimethylpentane	1.87	1.80	1.01
3,4,5-trimethylheptane	1.48	1.41	0.84
cyclohexane	0.83	1.06	0.86
n-butylcyclohexane	1.21		1.05
carbon tetrachloride	0.76	0.52	0.52
benzene	0.38	0.33	0.31
n-butylbenzene	0.43		0.38
tert-butylbenzene	0.57		0.27

for the experimental temperature range only (170–190 °C for PS$_H$, 110–150 °C for PS$_L$, and 120–150 °C for PnBMA), previous work[3-6] has shown that this extrapolation procedure yields χ data, which although crude, can still be used to provide reasonable estimates for polymer solubility parameters outside this temperature range. Table III summarizes the χ data which were used to estimate δ_2 values at 25 °C. Values of V_1, ΔH_v, and δ_1 which were required for these calculations were obtained from the literature.[16,17]

There is good agreement between the δ_2 values calculated from the experimental IGC data (at infinite dilution of probe) and literature values (at finite concentration of solvent) for these homopolymers. The extrapolated δ_2 values for PS$_H$, PS$_L$, and PnBMA are 9.1, 9.0, and 8.5 cal$^{1/2}$ cm$^{-3/2}$, respectively. The corresponding values quoted in the literature are 9.1 cal$^{1/2}$ cm$^{-3/2}$ for polystyrene[17] and 8.7 cal$^{1/2}$ cm$^{-3/2}$ for poly(*n*-butyl methacrylate).[17]

Conclusion

New solubility parameter measurements are reported for several homopolymers, copolymers, and blends of styrene and butyl methacrylate at 140 °C. In addition to an apparent insensitivity of polymer solubility parameters to geometrical isomerism of the butyl side groups of PBMA, δ_2 values are not very sensitive to differences in polymer molecular weight (PS$_H$, PS$_L$). Although the solubility parameters of the copolymers investigated can be roughly approximated by a linear interpolation (in weight fraction) of the homopolymer values, a close examination of the data on the polymer blends reveals opposite deviations from additivity for the immiscible PS$_H$–PnBMA blends (δ_2 values are higher than expected) and the miscible PS$_L$–PnBMA blends (δ_2 values are lower than expected). The generality of these trends will be determined by examining other polymer blends.

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Supplementary Material Available: Temperature dependence of χ for selected solutes in PS$_H$ between 170 and 190 °C (supplementary Table I), temperature dependence of χ for selected solutes in PS$_L$ between 110 and 150 °C (supplementary Table II), and temperature dependence of χ for selected solutes in PnBMA between 120 and 150 °C (supplementary Table III) (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Hildebrand, J. H.; Scott, R. L. "The Solubility of Non-Electrolytes", 3rd ed.; Reinhold: New York, 1950.
(2) Blanks, R. F. *Polym.-Plast. Technol. Eng.* **1977**, *8*, 13.
(3) DiPaola-Baranyi, G.; Guillet, J. E. *Macromolecules* **1978**, *11*, 228.
(4) DiPaola-Baranyi, G.; Guillet, J. E.; Klein, J.; Jeberien, H.-E. *J. Chromatogr.* **1978**, *166*, 349.
(5) Ito, K.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1163.
(6) Merk, W.; Lichtenthaler, R. N.; Prausnitz, J. M. *J. Phys. Chem.* **1980**, *84*, 1694.
(7) (a) DiPaola-Baranyi, G. *Macromolecules* **1981**, *14*, 683. (b) DiPaola-Baranyi, G.; Degrē, P. *Ibid.* **1981**, *14*, 1456.
(8) Littlewood, A. B.; Phillips, C. S. G.; Price, D. T. *J. Chem. Soc.* **1955**, 1480.
(9) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(10) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356.
(11) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(12) Scott, R. L.; Magat, M. *J. Chem. Phys.* **1945**, *13*, 172. *J. Polym. Sci.* **1949**, *4*, 555.
(13) Bristow, G. M.; Watson, W. F. *Trans. Faraday Soc.* **1958**, *54*, 1731, 1742.
(14) Dreisbach, D. R. *Adv. Chem. Ser.* **1955**, *No. 15*. *Ibid.* **1959**, *No. 22*. *Ibid.* **1961**, *No. 29*.
(15) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1. *Ibid.*, 1965, Vol. 2.
(16) "International Critical Tables"; McGraw-Hill: New York, 1928; Vol. 3.
(17) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley: New York, 1975.