Polymer Solubility Parameters of Poly(propylene oxide) Rubber from Inverse Gas Chromatography Measurements

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ABSTRACT: Inverse gas chromatography was used to measure partial molar heats of mixing ΔH_1^x of several solutes on poly(propylene oxide) rubber. Flory-Huggins interaction parameter interaction parameters χ_{12} and its enthalpic and entropic contributions were also calculated at 354.1, 359.0, and 363.0 K. Polymer solubility parameters were deduced by the method of DiPaola-Baranyi from Flory-Huggins χ_{12} interaction parameters. Solubility parameters δ_1 for the solutes were also reported.

KEY WORDS Inverse Gas Chromatography / Poly(propylene oxide) / Solubility Parameters /

The concept of solubility parameter is useful for many practical applications such as solvent selection and prediction of phase equilibrium. The solubility parameter of a polymer, δ_2 , can not be determined directly because polymers can not be vaporized without decomposition. Therefore δ_2 is defined as the same as that of a solvent in which the polymer will mix in all proportions without heat effect and without volume change. Experimental determination of δ_2 is possible from solubility measurements (midpoint of solubility range with a solvent group) or from swelling values of sparsely crosslinked polymers. In this paper we used inverse gas chromatography for the evaluation of the solubility parameter of a polymeric stationary phase, from measurements of interaction parameters. The Hildebrand-Scatchard theory¹ predicts that solubility parameters (δ_i) of substances at a given temperature T may be calculated with the expression:

$$\delta_i = [(\Delta H_v - RT)/V_i]^{1/2} \quad (1)$$

where ΔH_v is the molar enthalpy of vaporization of substance at temperature T , and R is the universal gas constant.

Polymers cannot be vaporized without decomposition, and therefore it is not possible to calculate solubility parameters using eq 1. However Guillet² has shown that inverse gas chromatography is a useful method for determining this parameter at a given temperature. If one assumes zero volume change on mixing, the Hildebrand-Scatchard equation can be rewritten in terms of the partial molar heat of mixing ΔH_1^x ³ as:

$$\Delta H_1^x = V_1(\delta_1 - \delta_2)^2 \quad (2)$$

At constant pressure it is the free energy, and not the heat of mixing, that is given directly by the solubility parameters,^{3,4} and eq 2 therefore becomes:

$$\Delta G_1^x = V_1(\delta_1 - \delta_2)^2 \quad (3)$$

Combining the Flory treatment⁵ with the Hildebrand-Scatchard theory and bearing in mind that the interaction parameter χ_{12} has free energy characteristics, with enthalpic ($\chi_{12,H}$) and entropic ($\chi_{12,S}$) contribution terms, the following expression may be written⁶:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1} = \frac{2\delta_2}{RT} \delta_1 - \frac{\delta_2^2}{RT} - \frac{\chi_{12,S}}{V_1} \quad (4)$$

Representation of the term in the left hand side *versus* δ_1 yields a straight line which slope allow an estimation of δ_2 . It has to be noted that δ_2 values obtained under this circumstances represent infinite dilution solubility parameters. δ_2 values usually fall well within the temperature range for a polymer; but up to now the relationship between δ_2 and δ_2 obtained from another techniques is still not certain.

Poly(propylene oxide) rubber has been reported to have good solubility in most aliphatic and aromatic solvents.⁷ In this paper we measured the solubility parameter δ_2 at infinite dilution of poly(propylene oxide) rubber from Flory-Huggins thermodynamic interaction parameter χ_{12} data.

EXPERIMENTAL

Materials

Solvents were reagent grade (Merck) and were used without further purification. The following solvents of very different characteristics were used: *n*-heptane, *n*-octane, *n*-nonane, benzene, toluene, ethanol, propanol, ethyl acetate, and *N,N*-dimethylformamide. Poly(propylene oxide) samples were obtained from BF Goodrich Company (Parel 58). The polymer was purified by precipitation in distilled water from acetone solutions, then dried under vacuum during 48 h at 353 K.

Columns

The polymer were first dissolved in a suitable solvent (acetonitrile) and deposited on Chromosorb G 60–80 mesh support (4% loading) by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for *ca.* 48 h with slow heating, the coated support was resieved and packed into 1 m length, 0.25 in o.d. stainless-steel columns with the aid of an ultrasonic bath. The weight of stationary phase was determined by thermogravimetric analysis (Mettler TA3000) system, using a suitable blank correction. Columns were conditioned under nitrogen 24 hours at 373 K.

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Instrumentation

The gas chromatographic (IGC) measurements were run on a modified Perkin-Elmer 3920B gas chromatograph equipped with an integrator Spectra-Physics SP4290 fitted with a dual flame ionization detector. Dried nitrogen was used as carrier gas. Five different flow rates were employed, in the range of 15–30 cm³ min⁻¹, measured with a soap bubble flow meter at the end of the column. The inlet and outlet pressures were monitored by a precision digital manometer. Experiments were run at 354.1, 359.0, and 363.9 K. A 10 µl syringe was used to inject the probes. To avoid saturation the syringe was emptied three times, and only the amount remaining in the needle was injected. Nevertheless it was found that under these conditions the retention time was a function of the amount of sample injected. In order to avoid these situations several injections were made and the peak area was extrapolated to zero sample size for following calculations. Methane was used as a non-retained substance for the measurement of the dead time.

RESULTS AND DISCUSSION

The specific retention volumes V_g^0 (cm³ g⁻¹) is characteristic of a particular solute, stationary phase and carrier gas. It is defined as the net retention volume at 0°C for unit weight of stationary phase, and is given by:

$$V_g^0 = t_n F J / w_L \quad (5)$$

where t_n is the net retention time for the probe, J is the James–Martin correction factor for gas compressibility,⁸ w_L is the weight of polymer in the column and F is the carrier gas flow rate at 0°C and 1 atm which is obtained from:

$$F = 273.16 F_0 (P_a - P_w) / 760 (273.16 + T_A) \quad (6)$$

where P_a is the atmospheric pressure (mmHg), F_0 is the flow rate measured from the end of the column (cm³ min⁻¹) and P_w is the water pressure (mmHg) at temperature T_A (°C) of the flowmeter.

From the Flory–Huggins treatment of solutions thermodynamics^{9,10} one can obtain the χ_{12} parameter, which is a measure of the residual free energy of interaction between solute and polymer. χ_{12} is determined from the relationship:

$$\chi_{12} = \ln(273.16 R v_2) / V_g^0 p_1^0 V_1 - (1 - V_1 / M_2 v_2) - p_1^0 (B_{11} - V_1) / RT \quad (7)$$

where V_1 is the molar volume of pure (liquid) solute, p_1^0 is its vapor pressure at temperature T , R is the gas constant, v_2 is the specific volume of the polymer, M_2 is its number average molecular weight, and B_{11} is the second virial coefficient which is used to correct for vapor phase non-ideality of the probe. Values of B_{11} were obtained from Dymond and Smith compilation.¹¹ For *n*-nonane and *N,N*-dimethylformamide B_{11} were computed from the expression¹²:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (8)$$

where V_c and T_c are critical volume and temperature, T is the temperature (K), and n is the number of carbon atoms of the *n*-alkane, or alternatively an effective number of carbons (the value of n of the normal alkane having the same value for the vapor pressure A), in the equation¹³:

$$\ln(P_c/P) = A(T_c - T)/T \quad (9)$$

where P_c and T_c are the critical pressure (mmHg) and temperature of the solute. Solute vapor pressures were obtained from Riddick and Bunger tabulations.¹⁴ Solute densities were obtained from various sources, including the compilations by Orwoll and Flory¹⁵ and Timmermans.¹⁶ At infinite dilution of the probe and for high molecular weight polymers the second term of eq 3 approaches one.

Weight fraction infinite dilution activity coefficients Ω_1^∞ was calculated from the relation¹⁷:

$$\ln \Omega_1^\infty = \ln(273.16 R / p_1^0 V_g M_1) - p_1^0 (B_{11} - V_1) / RT \quad (10)$$

being M_1 the molecular weight of the probe.

Calculated values of χ_{12} y $\ln \Omega_1^\infty$ at the three temperatures tested are shown in Table I. χ_{12} values are in all cases smaller than unity, as expected for polymer-solvent systems. In all cases χ_{12} values becomes lower, or more negative, as temperature increases, except for *N,N*-dimethylformamide, where this relation is not so clear, a linear relation being observed between χ_{12} and $1/T$ (Figure 1). Comparison of χ_{12} values show that hydrocarbons are less miscible in PPO as chain length increases, the system becomes more miscible in probes like aromatics and ethyl acetate, being immiscible in alcohols.

Weight fraction infinite dilution activity coefficients Ω_1^∞ are positive being the higher values those obtained

Table 1. Experimental values of χ_{12} y $\ln \Omega_1^\infty$

Solute	T = 354.1 K		T = 359.0 K		T = 363.9 K	
	χ_{12}	$\ln \Omega_1^\infty$	χ_{12}	$\ln \Omega_1^\infty$	χ_{12}	$\ln \Omega_1^\infty$
<i>n</i> -Heptane	-0.267	1.201	-0.382	1.094	-0.459	1.023
<i>n</i> -Octane	0.466	1.902	0.326	1.767	0.191	1.638
<i>n</i> -Nonane	0.824	2.232	0.762	2.177	0.711	2.131
Benzene	-0.341	0.874	-0.450	0.771	-0.561	0.666
Toluene	-0.285	0.934	-0.353	0.873	-0.390	0.841
Ethanol	0.464	1.815	0.426	1.747	0.361	1.687
Propanol	0.752	2.041	0.588	1.883	0.477	1.777
Ethyl acetate	-0.586	0.614	-0.416	0.754	-0.313	0.902
<i>N,N</i> -Dimethylformamide	0.840	1.960	0.872	1.997	0.911	2.040

Figure 1. Variation of χ_{12} with reciprocal temperature (K) for the PPO/*n*-octane system.

Figure 2. Variation of $\ln \Omega_1^\infty$ with reciprocal temperature (K) for the PPO/ethanol system.

for *n*-nonane.

The solubility parameters δ_1 for the solutes were calculated from the expression

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \quad (11)$$

where R is the gas constant and V_1 is the molar volume of the solute at temperature T . At infinite dilution ΔH_v is transformed into ΔH_v^∞ .

The molar enthalpies of vaporization ΔH_v^∞ were obtained by applying the expression:

$$\Delta H_v^\infty = \Delta H_1^\infty - \Delta H_s \quad (12)$$

where ΔH_1^∞ is the partial molar heat of mixing of the solute at infinite dilution in the polymer, calculated from:

$$\Delta H_1^\infty = -R d(\ln \Omega_1^\infty)/d(1/T) \quad (13)$$

Therefore ΔH_1^∞ was obtained from the slope of the best straight line through a plot of the logarithm of the activity coefficient vs. the reciprocal of the temperature, as de-

Table II. Partial heat of mixing, heat of solution, and molar enthalpies of vaporization of probes in poly(propylene oxide)

Solute	ΔH_1^∞ kcal mol ⁻¹	ΔH_s kcal mol ⁻¹	ΔH_v^∞ kcal mol ⁻¹
<i>n</i> -Heptane	4.80	-2.36	7.17
<i>n</i> -Octane	3.90	-2.12	6.03
<i>n</i> -Nonane	1.21	-7.44	8.66
Benzene	7.09	-1.72	8.81
Toluene	2.74	-5.90	8.65
Ethanol	1.91	-6.11	8.02
Propanol	3.62	-3.37	6.99
Ethyl acetate	-9.78	-14.86	5.08
<i>N,N</i> -Dimethylformamide	-1.04	-12.40	11.35

Table III. Solubility parameter δ_1 (cal cm⁻³)^{1/2} extrapolated at 298.16 K

Solute	δ_1
<i>n</i> -Heptane	6.68
<i>n</i> -Octane	5.76
<i>n</i> -Nonane	6.69
Benzene	9.6
Toluene	8.68
Ethanol	11.25
Propanol	9.23
Ethyl acetate	6.75
<i>N,N</i> -Dimethylformamide	11.79

Figure 3. Estimation of solubility parameter δ_2 of poly(propylene oxide) from χ_{12} parameter at 363.9 K.

termined by a least-squares analysis (Figure 2).

The corresponding heats of solution ΔH_s were obtained in a similar way from the temperature dependence of the specific retention volume V_g^0

$$\Delta H_s = -R d(\ln V_g^0)/d(1/T) \quad (14)$$

Values of ΔH_1^∞ , ΔH_s and ΔH_v^∞ obtained are given in Tables II and III compiles solute solubility parameters extrapolated to 298.16 K.

Infinite dilution solubility parameter δ_2^∞ for the polymer where obtained from the slope of the plot $(\delta_1^2/RT) - (\chi_{12}/V_1)$ against δ_1 (Figure 3). Table IV compiles values obtained for δ_2^∞ and $\chi_{12,s}/V_1$ at the

Table IV. Infinite dilution solubility parameter δ_2 and $\chi_{12,s}/V_1$ terms for poly(propylene oxide)

	δ_2 (cal cm ⁻³) ^{1/2}	$\chi_{12,s}/V_1$
PPO, 354.1 K	7.96	-0.0030
PPO, 359 K	7.90	-0.0037
PPO, 363.9 K	7.88	-0.0041

three temperatures tested.

The values of δ_2 decreases slightly as temperature increases. Linear extrapolation to 298.16 K gives a value of 8.41 (cal cm⁻³)^{1/2} for δ_2 . The value is in the range of those reported in the literature for this polymer (7.5–9.9 cal cm⁻³)^{1/2}.¹⁸ Nevertheless it has to be pointed out that solubility parameter δ_2 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. However δ_2 data obtained are of both practical and theoretical interest, since it relates directly to the force fields which surrounds a probe molecule in a polymer matrix and should also be related to diffusional mobility and the removal of trace amounts of small molecules from polymer films.

Values obtained for $\chi_{12,s}/V_1$ term indicate that the contribution of entropic term to the value of interaction parameter χ_{12} is negative, thus contributing to negative values of χ_{12} , being higher in absolute values as temperature grows up. Values of $\chi_{12,s}$ estimated from these $\chi_{12,s}/V_1$ results, are in the range of -0.19 to -0.44, which will make an important contribution to the χ_{12} parameter, particularly when χ_{12} is small, as in the present case.

CONCLUSIONS

From this study it is concluded that inverse gas

chromatography procedure is a rapid and useful method of estimating the solubility parameter of a polymer δ_2 , at infinite dilution of the probe molecule. Entropic contribution to χ_{12} interaction parameter are negative at the three temperatures tested, thus improving miscibility characteristics of this polymer, even with low interacting solutes.

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