

Analysis

Chromatographic Determination of Polymer Solubility Parameters

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SUMMARY

Weight fraction activity coefficients (Ω_1^∞) and interaction parameters χ have been determined for seven different solvents in Polyarylate at three temperatures by the gas chromatographic method (inverse gas chromatography). Data have been used to calculate infinite dilution solubility parameters according to the method proposed by DiPaola-Baranyi and Guillet. The validity of the plots involved in the above mentioned method is also discussed.

INTRODUCTION

Gas chromatographic methods have shown promise in the making of a wide range of physical measurements. More recently, GC has been employed to investigate the structure and interactions of polymeric materials. The experimental measurements we are dealing with here refer to those where the polymeric material under study is employed as the stationary phase in a gas chromatographic column. The method allows us to determine glass transition temperatures, crystallinity, solvent activity coefficients in molten homopolymers, adsorption isotherms, polymer-polymer miscibility, curing processes in non-volatile thermosetting systems, etc. Several reviews have been published summarizing the different applications of this technique to polymer science (GRAY 1977).

Several years ago, DIPAOLA-BARANYI and GUILLET (1978) reported a method for estimating polymer solubility parameters by inverse gas chromatography. The method is based on the HILDEBRAND-SCATCHARD solubility theory (HILDEBRAND and SCOTT 1950). In the above mentioned work, the authors identified

$$\chi^\infty = (V_1/RT) (\delta_1 - \delta_2^\infty)^2 \quad (1)$$

where χ^∞ is the interaction parameter at infinite dilution of the solvent, as deduced in IGC experiments from the specific retention volume V_g^0 . δ_1 is the solvent solubility parameter and δ_2^∞ is the polymer solubility parameter in the chromatographic conditions. V_1 is the molar volume of the solvent. Rearranging this equation (1)

$$\delta_1^2/RT - \chi/V_1 = 2\delta_2\delta_1/RT - \delta_2^2/RT \quad (2)$$

So, a plot of the first member of equation (2) against δ_1 allows us to calculate δ_2^∞ from the slope or the intercept. Assuming a linear dependence of the solubility parameter on temperature, DIPAOLA-BARANYI and GUILLET (1978)

calculated δ_2^∞ at 25°C, the reference temperature in tabulations of these parameters. The method has also been used, among others, by this laboratory (FERNANDEZ-BERRIDI et al. 1982), calculating the solubility parameter of Poly(ethylene oxide). In all cases, and as DIPAOLA-BARANYI and GUILLET (1978) pointed out in their original paper, there is "an astonishing consistency of the data when plotted according to equation (2)".

In this paper, we point out some comments with reference to this method and its validity. These remarks have appeared during our chromatographic investigation of a sample of a commercial Polyarylate (PAR), a copolymer of an equimolar mixture of isophthalic and terephthalic acids and bisphenol-A.

EXPERIMENTAL

The Polyarylate sample employed in this work was a low molecular weight fraction ($M_w=7,000$), obtained from a commercial Polyarylate (Arylef U-100) kindly supplied by Solvay & Cie (Brussels, Belgium). Its glass transition temperature was 120°C, which allows us to make experimental determinations in liquid-liquid equilibrium at temperatures above 140°C. Experimental conditions and data reduction have been detailed elsewhere (DIPAOLA-BARANYI and GUILLET 1978). Our chromatographic column was a 110 cm. column in which the polymer was coated onto an inert support. 0.3513 g. of PAR were dissolved in chloroform and deposited onto the support by slow evaporation of the solvent. The final loading was 6%. Data of the solvents have been taken from the usual data compilations also detailed in previous works (FERNANDEZ-BERRIDI et al. 1982). Data of the polymer have been taken from a recent paper of ZOLLER (1982), in which equation-of-state parameters of different modern thermoplastics were obtained according to the model proposed by SIMHA et al. (1974,1975).

The solvents used in this work were Ethylbenzene, Tetraline, o-Dichlorobenzene (ODCB), Chlorobenzene, p-Xylene, n-Dodecane and Diethylene glycol diethyl ether (DEGDEE).

RESULTS AND DISCUSSION

The solubility parameter δ (units of $(\text{cal/cc})^{-1/2}$) for any compound is defined from the HILDEBRAND-SCATCHARD theory as

$$\delta = (\Delta E_v/V_1)^{1/2} \quad (3)$$

or the square root of the ratio of the energy of vaporization to the molar volume of the substance. ΔE_v is usually calculated as the heat of vaporization minus RT ($\Delta E = \Delta H - RT$) and the heat of vaporization may be calculated as

$$\Delta H_v = -R \partial \ln P_1^0 / \partial (1/T) \{ P_1^0 (B_{11} - V_1) / T \} \quad (4)$$

from pressures and second virial coefficients data at different temperatures. The second quantity in the right hand term is the correction for the non-ideality of the vapour probe.

In connection with IGC papers, it is interesting to remark that some authors have suggested the possibility of determining δ_1 by inverse gas chromatography from

$$\Delta H_v = \Delta H_1^\infty - \Delta H_s \quad (5)$$

where ΔH_1^∞ and ΔH_s are accessible from chromatographic data,

$$\Delta H_1^\infty = R\{\partial \ln(\Omega_1)^\infty / \partial (1/T)\} \quad (6)$$

$$\Delta H_s = -R\{\partial \ln v_g^0 / \partial (1/T)\} \quad (7)$$

with

$$\ln(\Omega_1)^\infty = \ln\{273.2 R/v_g^0 M_1 P_1^0\} - (P_1^0/RT)(B_{11}-V_1) \quad (8)$$

However, a close inspection of equations (5), (6), (7) and (8) shows that the determination of ΔH_v in this way does not depend on chromatographic measurements. A combination of these equations gives the above mentioned equation (4). In these expressions ΔH_1^∞ is the partial molar enthalpy at infinite dilution, ΔH_s is the solution heat and $(\Omega_1)^\infty = a_1/w_1$ is an activity coefficient based on weight fractions.

Since high polymers have no appreciable vapour pressure and their molar volumes are usually not well defined, there is not, at the present, direct determinations of δ for a polymer. Therefore, it is necessary to use other methods based on various kinds of measurements in combination with an adequate theory about the relation between the solubility parameter and experimentally measurable magnitudes. Among others, measurements such as the swelling of a crosslinked polymer or intrinsic viscosities of the same polymer in a variety of solvents have been used. In both cases, the assumption is that the extent of the swelling and the intrinsic viscosity will show a maximum when the δ value of the polymer matches that of the solvent. This implies, with the aid of the usual concepts in polymer solution theories, a minimum in the interaction parameter χ . An identical suggestion is made in equation (1). Modern theories, however, give a free-energy character to the interaction parameter so, the solubility parameter δ_2 obtained from this equation loses its original definition as internal energy. Moreover, it is well known that the maximum of the solubility of a polymer in a solvent has not to be obligatorily identified with a zero value of the interaction parameter. For this reason, some authors prefer to write

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \beta \quad (9)$$

PATTERSON (1967) showed that this expression allows qualitative predictions on polymer solutions. It even allows the prediction of both lower (LCST) and upper (UCST) critical solution temperatures. PATTERSON concluded that there is an evident parallelism between this expression and his resumed free volume theory. However, it is only an speculation to identify the β parameter with the entropic component of the interaction parameter, χ_s . In any event, equation (9) can be also rearranged in a similar manner to equation (2). In principle, a similar plot allows one to determine δ_2^∞ and β , from the slope and the intercept, respectively.

Using these equations, it is necessary to know the interaction parameter χ^∞ , which may be chromatographically determined by means of the expression (GRAY, 1977).

$$\chi^\infty = \ln\{273.2 R v_{sp,2} / P_1^0 v_g^0 V_1\} - 1 - (P_1^0/RT)(B_{11}-V_1) \quad (10)$$

where $v_{sp,2}$ is the specific volume of the polymer. Table I gives weight fraction activity coefficients and interaction parameters of Polyarylate with different solvents at three temperatures.

These data, as derived in IGC experiments, give a qualitative evaluation of the solvency power of the different molecular probes. Within the experimental error and taking into account the concentration and temperature depen-

dences of the interaction parameter, the solvency power is inversely proportional to the magnitude of χ .

TABLE I

Weight fractions activity coefficients and interaction parameters of several probes with Polyarylate at three temperatures.

	140		170		200	
	$(\Omega_1)^\infty$	χ^∞	$(\Omega_1)^\infty$	χ^∞	$(\Omega_1)^\infty$	χ^∞
Ethylbenzene	9.64	0.82	8.11	0.62	7.17	0.48
Tetraline	7.88	0.75	7.11	0.64	6.70	0.57
ODCB	4.96	0.59	4.18	0.41	3.70	0.27
Chlorobenzene	5.69	0.54	5.06	0.40	4.68	0.30
p-Xylene	9.92	0.84	7.85	0.58	6.58	0.39
n-Dodecane	19.2	1.34	17.8	1.28	17.4	1.24
DEGDEE	12.0	1.08	9.24	0.80	7.45	0.56

Data resumed in Table I are in good agreement with solubility tests carried out at room temperature and low polymer concentrations. PAR is soluble in chlorobenzene and ODCB; it swells in tetraline and it is insoluble in the others solvents, even when heated.

We have also determined δ_2^∞ from the slope of the plots of $\delta_1^2/RT - \chi/V_1$ against δ_1 . The results are 7.89(140), 7.69(170) and 7.48(200), which follow a linear relation with the temperature. The extrapolated value at 25°C was 8.66 far from the value obtained according to the VAN KREVELEN (1976) contribution group method, which gave a value of 9.89 at 25°C.

However, we have some comments to make about the validity of such plots. Our argument begins with an analytical solution of equation (1), the expression used by DIPAOLA-BARANYI and GUILLET (1978). It is clear that there are two solutions for δ_2^∞ in equation (1), i.e.

$$\delta_2^\infty = \delta_1 \pm (RT\chi/V_1)^{1/2} \quad (11)$$

Assuming that a polymer should have a higher solubility parameter, because of its higher cohesive energy, we have calculated the higher values which satisfy equation (11). At 140°C, the results showed that the solubility parameters so obtained, were dependent on the solvent solubility parameter as can be inferred from data in Table II. Moreover, the average value (and one may doubt the validity of such average) was 9.78 at 25°C, far from the value deduced from the slope of the above mentioned plots. A similar behaviour can be obtained if the data of DIPAOLA-BARANYI and GUILLET (1978) for Polystyrene and Poly(methyl acrylate) are used in a similar manner, according to equation (11).

Our opinion is that the differences between the linear plot and the analytical solutions arise from the incorrectness of equation (1). If χ has a free energy character, δ_2^∞ should reflect the interactions between the polymer and the solvent. Consequently, the solubility parameter, defined in equation (1), is not a unique magnitude, characteristic of the polymer,

but an index, not clearly defined, of the interactions of the polymer with the corresponding solvent. Consequently, equation (2) cannot be treated as a linear plot, in spite of its apparent good correlation. In fact, a plot of δ_1^2/RT against δ_1 gives a slope, an intercept and a correlation near to those obtained from a strict application of equation (2). However, it is clear that the relationship δ_1^2/RT vs δ_1 is a parabolic curve.

TABLE II

Values of the PAR solubility parameter at 140°C, according to equation (11). The solubility parameter was taken as the higher solution of equation (11).

	δ_1	δ_2^∞
Ethylbenzene	7.47	9.66
Tetraline	8.29	10.30
ODCB	7.94	10.65
Chlorobenzene	8.11	10.06
p-Xylene	7.48	9.68
n-Dodecane	6.68	8.75
DEGDEE	7.26	9.34

A similar conclusion is applicable to the use of the expression derived from equation (9). In this case, we can assume that δ_2^∞ is the correctly defined solubility parameter of the polymer, but then β will depend on the solvent and the temperature. Consequently, the equation can be satisfied with different $\delta_2^\infty - \beta$ pairs, given the inaccuracy inherent in the use of linear plots. Another possibility is to use the same assumption as that employed in swelling and viscometric determinations, i.e., the solubility parameter of the polymer will be that of the solvent showing the lowest interaction parameter. Given the usual agreement in tabulating values of the solubility parameter at 25°C, this would be limited to polymers with low T_g , allowing chromatographic determinations in liquid-liquid conditions at room temperature. In any case, it is again assumed that β is a constant in the involved series of solvents, an hypothesis difficult to maintain.

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