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Thermodynamic study of polystyrene–*n*-alkane systems by inverse gas chromatography

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ABSTRACT

Phase diagrams of systems containing high-carbon-number *n*-alkanes (up to *n*-pentatriacontane) and polystyrene were studied in the temperature range from 190 to 250°C. Experimental data obtained for low-carbon-number alkanes by inverse gas chromatography were extrapolated taking advantage of the linear relationships between ln V_g^0 (specific retention volume at 0°C) and the inverse of the temperature and between ln V_g^0 and the number of carbon atoms for homologous series. The resulting activity coefficients and interaction parameters were typical of systems with a poor compatibility. The Gibbs free energy of mixing (ΔG_m) for polystyrene–alkane systems was calculated, with the Flory–Huggins χ parameter assumed to be independent of the composition. The ΔG_m *vs.* alkane volume fraction curves exhibited a shape corresponding to solution instability at low concentrations of both components. On this basis the phase diagram of the system polystyrene–alkanes was calculated.

INTRODUCTION

A description of the phase behaviour of binary polymer–solvent systems is useful for optimal equipment design in the polymer industry. Polymer devolatilization, purification and plastification are examples of manufacturing operations in which knowledge of the solubility relations is one of the key requirements.

In the present work the solubility limits of high-carbon-number *n*-alkanes in polystyrene at elevated temperatures were studied. Owing to the physical characteristics of these alkanes (high melting point, very low vapour pressure), it was impossible to find a method for the direct measure of the polystyrene–solute phase diagram. Therefore, the thermodynamic characterization of these systems was obtained by extrapolating experimental data from low- to higher-carbon-number alkanes.

Polymer–solute interactions in highly concentrated polymeric solutions were measured by inverse gas chromatography, thus obtaining the mass fraction infinite dilution activity coefficient (Ω^∞) of nine alkanes from hexane (C_6) to tricosane (C_{23}) at temperatures ranging from 150 to 210°C. Thermodynamic data of alkanes up to 35 carbon atoms at temperatures up to 250°C were obtained by extrapolating the chromatographic data.

Finally, Flory polymer–solvent interaction parameters at infinite dilution (χ^∞) were calculated, and phase diagrams were drawn following the Flory–Huggins theory, assuming that the χ^∞ parameter depends on the temperature, but not on the concentration.

EXPERIMENTAL

Materials

Polystyrene (Edistir N1280) was supplied by Enichem Polimeri (Mantova, Italy). Its mass-average molecular mass and its glass transition temperature (T_g) were 300 000 and 98°C, respectively.

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TABLE I

EXPERIMENTAL MASS FRACTION ACTIVITY COEFFICIENTS AND FLORY-HUGGINS χ PARAMETERS AT INFINITE DILUTION FOR POLYSTYRENE-*n*-ALKANE SYSTEMS AT TEMPERATURES RANGING FROM 150°C TO 210°C

	$T = 150°C$		$T = 170°C$		$T = 190°C$		$T = 210°C$	
	Ω^∞	χ^∞	Ω^∞	χ^∞	Ω^∞	χ^∞	Ω^∞	χ^∞
C_6	12.51	0.88	11.80	0.78	11.58	0.69	9.95	0.45
C_7	12.37	0.92	11.35	0.80	10.73	0.71	10.03	0.59
C_{10}	11.98	1.03	11.06	0.94	10.36	0.85	9.95	0.79
C_{12}	12.16	1.09	11.25	1.00	10.50	0.92	9.96	0.85
C_{14}	12.65	1.16	11.59	1.06	10.71	0.97	10.17	0.91
C_{15}	12.70	1.17	11.77	1.09	10.87	1.00	10.31	0.94
C_{16}			12.09	1.12	11.13	1.03	10.46	0.96
C_{18}					10.82	1.02	10.13	0.95
C_{23}							11.79	1.13

Hexane (C_6), heptane (C_7), decane (C_{10}), dodecane (C_{12}), tetradecane (C_{14}), pentadecane (C_{15}), hexadecane (C_{16}), octadecane (C_{18}) and tricosane (C_{23}) were supplied by Carlo Erba (Italy) and were used without further purification.

Column preparation

Polystyrene was coated on the inert support (Chromosorb W DMCS 80–100 mesh, Carlo Erba) by evaporation from its chloroform solution.

The coated support was dried to constant weight in a vacuum oven at 50°C, then it was packed in a stainless-steel column (130 cm × 4 mm I.D. × 6 mm O.D.). The amount of column loading was measured by thermal gravimetric analysis using the appropriate blank correction. The final coverage ratio was 15.17%.

Equipment

Chromatographic analyses were carried out on a Carlo Erba HRGC 5300 Mega Series gas chromatograph, equipped with a flame ionization detector. Helium was used as carrier gas. Flow-rates ranging from 12 to 30 ml/min were chosen, and were measured with a soap bubble flow meter at the detector outlet.

Three different flow-rates were tested for each sample and temperature, in order to check the influence of flow-rate on the specific retention volume. The pressure drop in the column was measured with a mercury manometer. To keep the sample size as small as possible, the probes were usually injected in the vapour form. Tricosane and octadecane were dissolved in hexane

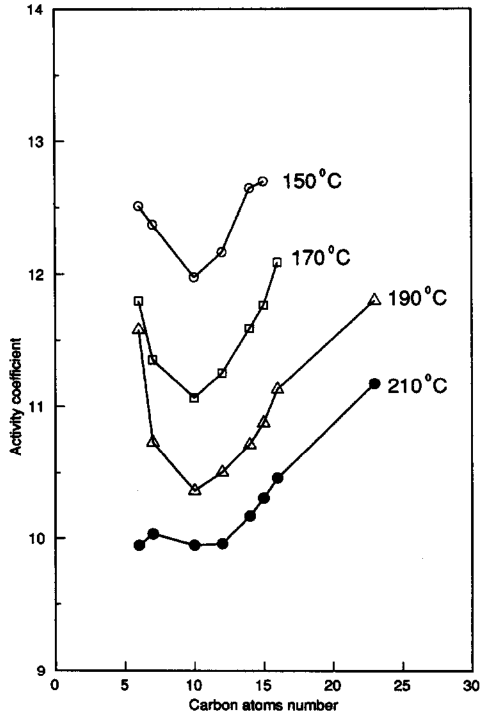

Fig. 1. Experimental mass fraction activity coefficients at infinite dilution as a function of carbon atom number at the indicated temperatures.

and the obtained solutions were injected using a 1-μl Hamilton syringe.

RESULTS AND DISCUSSION

Chromatographic data reduction

The elution behaviour of volatiles in gas chromatographic columns can be described by the specific retention volume, usually referred to a column temperature of 0°C [1]:

$$V_g^0 = \frac{J \cdot 273.15 \cdot (t_p - t_m) \cdot F}{T_{room} \cdot W} \tag{1}$$

where V_g^0 is the specific retention volume at 0°C, J is the James–Martin pressure correction term, t_p is the probe retention time, t_m is the marker retention term, F is the flow-rate of the carrier gas, measured at room temperature (T_{room}), and W is the mass of stationary phase in the column.

The mass fraction activity coefficient of the solute probe at infinite dilution (Ω^∞) can be calculated from the equation:

$$\ln \Omega^\infty = \ln\left(\frac{273.15 \cdot R}{V_g^0 \cdot p_1^0 \cdot M_1}\right) - \frac{p_1^0 \cdot (B_{11} - V_1)}{R \cdot T} \tag{2}$$

where R is the universal gas constant, p_1^0 is the vapour pressure, M_1 is the molecular mass, B_{11} is the second virial coefficient and V_1 is the molar volume of the solute.

The infinite dilution Flory–Huggins interaction parameter (χ^∞) can be determined from experimental inverse gas chromatogaphic data by the relation:

$$\chi^\infty = \ln \Omega^\infty + \frac{V_1}{M_n \cdot v_2} - \ln \frac{v_1}{v_2} - 1 \tag{3}$$

where v_1 and v_2 are solute- and polymer-specific volume, respectively, and M_n is the number-average molecular mass of the polymer.

Experimental Ω^∞ and χ^∞ of nine alkanes were calculated by eqns. 1–3, for temperatures ranging from 150 to 210°C. The solute vapour pres-

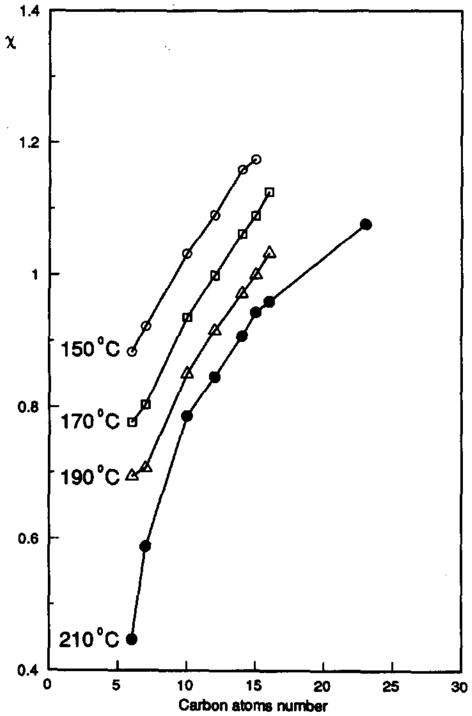

Fig. 2. Experimental Flory–Huggins χ parameters at infinite dilution as a function of carbon atom number at the indicated temperatures.

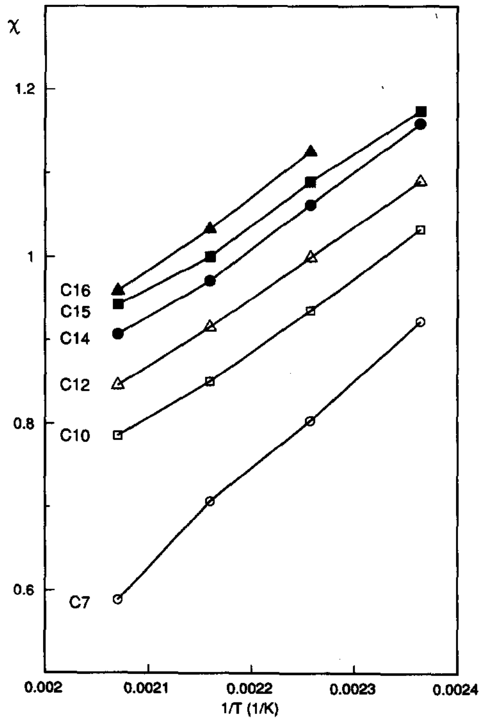

Fig. 3. Experimental Flory–Huggins χ parameters at infinite dilution as a function of $1/T$.

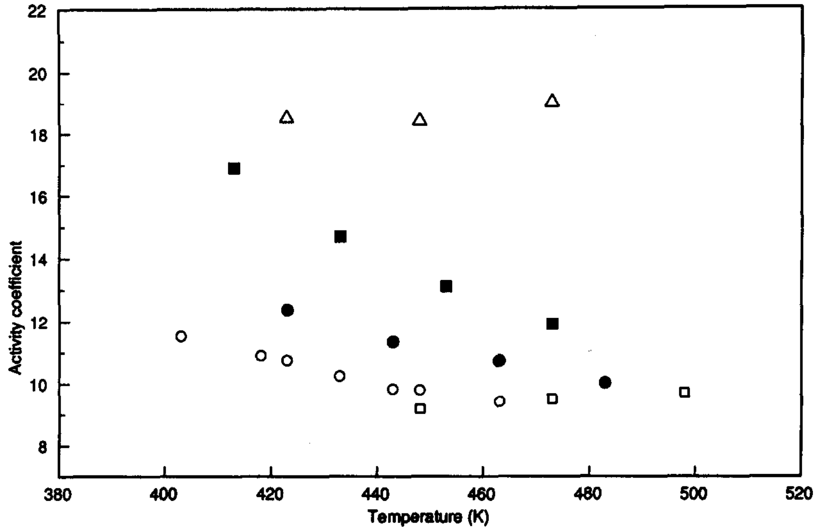

Fig. 4. Comparison of experimental mass fraction activity coefficients obtained by several authors by inverse gas chromatography. ○ = Ref. 9; □ = ref. 7; △ = ref. 6; ● = this work; ■ = ref. 8.

sure p_1^0 was obtained by the Antoine equation, using the constants taken from literature sources [2,3], the second virial coefficients (B_{11}) were calculated by the method of Hayden and O'Connell [4] and the saturated liquid density by the method of Yen and Woods [5]. Critical constants of alkanes were taken from ref. 2.

Table I summarizes our experimental results. Figs. 1 and 2 show the relationship between Ω^∞, χ^∞ and the number of carbon atoms of alkanes. The elevated values of Ω^∞ and χ^∞ are typical of systems with a poor compatibility; the increasing value of Ω^∞ with the number of carbon atoms indicates a reduction in the affinity with polystyrene increasing the chain length. A minimum can be observed between heptane and decane, as already observed by other authors [6]. In Fig. 3, the temperature dependence of χ^∞ of heptane, decane, dodecane, tetradecane, pentadecane, hexadecane is shown. A remarkable linearity between χ^∞ and $1/T$ can be noted. Moreover, the lower the temperature, the lower is the affinity of alkanes with polystyrene.

Inverse gas chromatography has been used by several authors [6–9] in order to obtain thermodynamic data in polystyrene–alkane systems. In Fig. 4 infinite dilution activity coefficients of heptane in polystyrene reported in literature are compared with those obtained in this study. Our data are lower than those reported by Lipatov and Nesterov [6] and Galin and Rupprecht [8], and higher than those reported by Stiel and Harnish [7] and Schuster *et al.* [9]. A significant disagreement exists between the results obtained

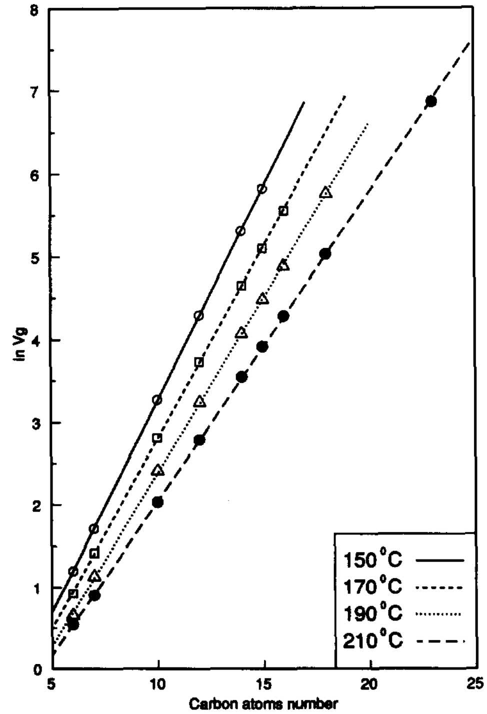

Fig. 5. Plot of ln V_g^0 as a function of carbon atom number.

by different authors, particularly at low temperatures.

Chromatographic data extrapolation

In order to obtain χ^{∞} for alkanes with a carbon atom number between 23 and 35 at elevated temperatures, the experimental specific retention volumes were extrapolated taking advantage of the linear relationships between ln V_g^0 and $1/T$ and between ln V_g^0 and the number of carbon atoms for homologous series [1].

From Fig. 5 it is evident that a remarkable correlation exists between our experimental ln V_g^0 data and the carbon atom number for all the tested temperatures. Moreover, Fig. 6 shows the linearity of experimental ln V_g^0 *versus* $1/T$. The results of the double extrapolation, up to 35 carbon atoms and 250°C, are shown in Fig. 7.

With V_g^0 available, Ω^{∞} and χ^{∞} were easily obtained using eqns. 2 and 3. In this case the second term on the right-hand side of eqn. 2 was neglected, owing to the very low vapour pressure of alkanes with more than 20 carbon atoms. The saturated vapour pressures of the long-chain alkanes were calculated by the Kudchadker–Zwolinski correlation [3]. The densities were calculated by the method of Elbro *et al.* [10], instead of the method of Yen and Woods [5], as the critical constants were not available.

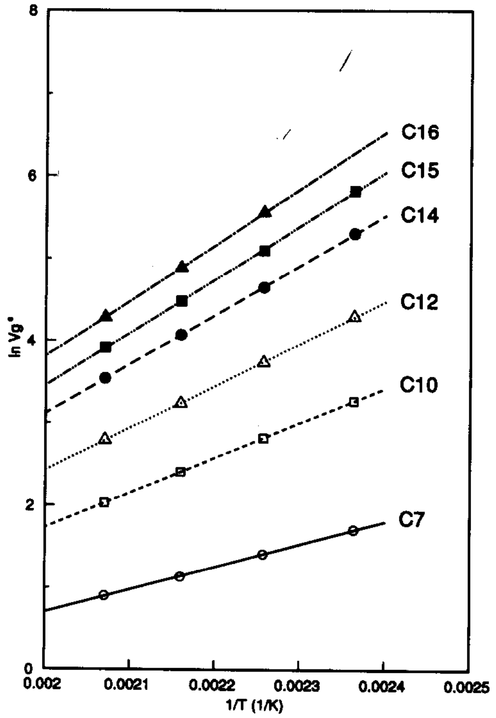

Fig. 6. Retention plot for several *n*-alkanes in polystyrene.

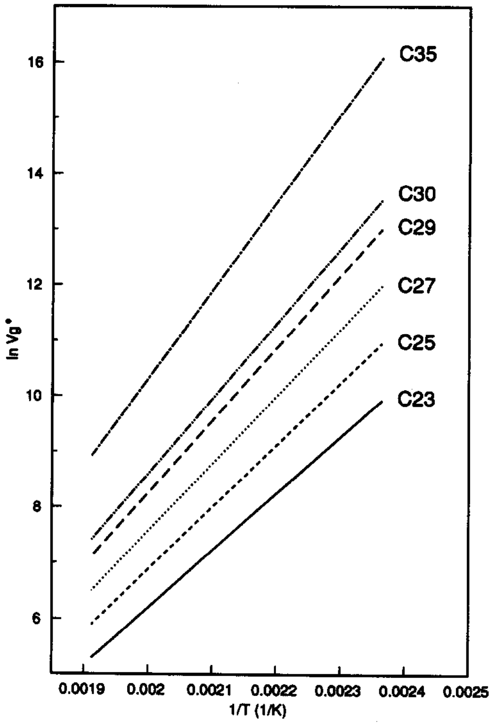

Fig. 7. Specific retention volumes obtained from a two-step extrapolation of experimental data (see text).

As an example, Fig. 8 shows Ω^{∞} for the homologous series with number of carbon atoms ranging from 6 to 35, whereas Fig. 9 shows the relationship between χ^{∞} and the inverse of the temperature.

Phase diagram

Flory–Huggins χ parameter can be used to predict the equilibrium behaviour of two liquid phases containing a polymer and a solvent. Following the classical Flory–Huggins theory [11], with χ parameter and density available, it is possible to calculate the Gibbs free energy of mixing (ΔG_m) as a function of the solute volume fraction:

$$\Delta G_m = RT\left(\frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2 + \chi\varphi_1\varphi_2\right) \qquad (4)$$

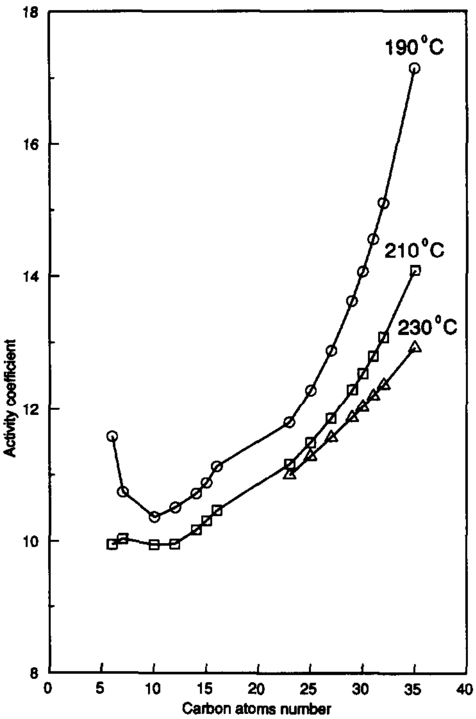

Fig. 8. Plot of mass fraction activity coefficients for the examined homologous series showing experimental (C_6–C_{23}) and calculated (C_{25}–C_{35}) data.

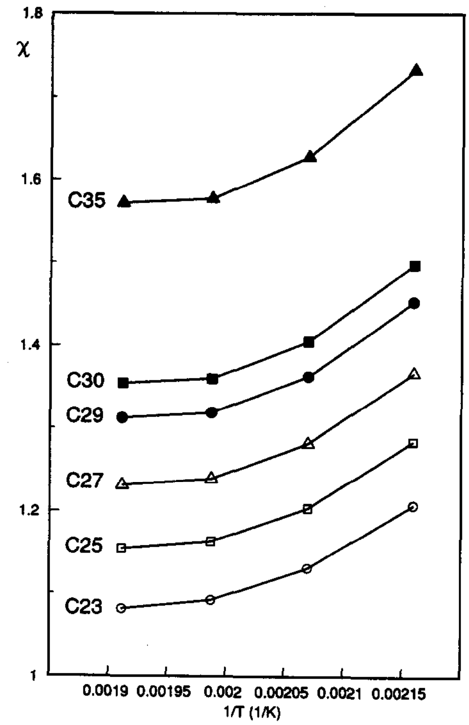

Fig. 9. Calculated Flory–Huggins χ parameters at infinite dilution as a function of $1/T$ for some high-carbon-number alkanes.

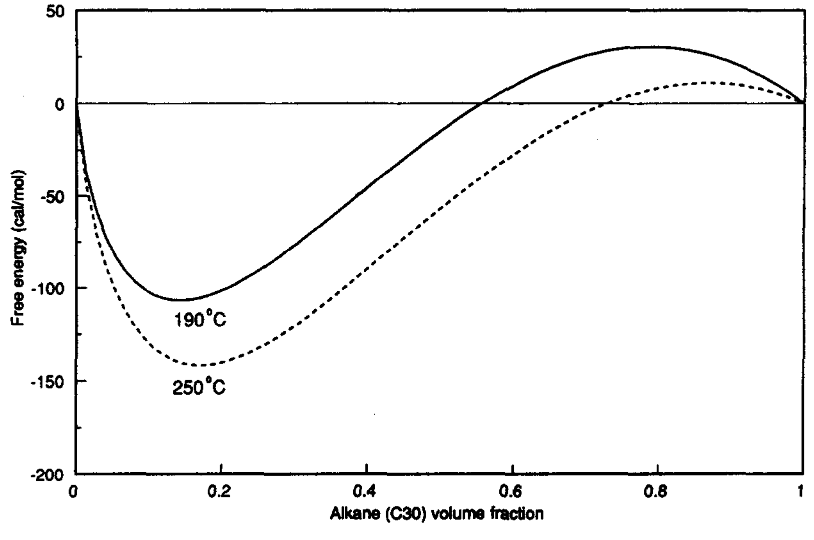

Fig. 10. Example of relationship between Gibbs free energy and alkane volume fraction for *n*-triacontane (C_{30}) at two different temperatures. 1 cal = 4.14 J.

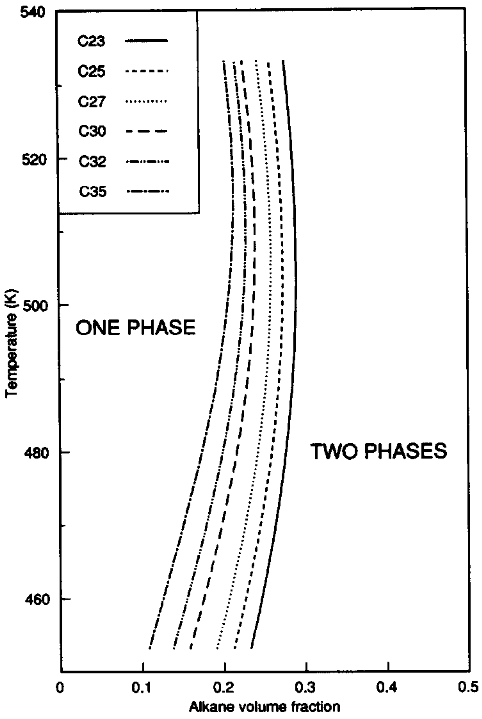

Fig. 11. Phase diagram for the system polystyrene–long-chain alkanes (x-axis is reduced for clarity).

where φ_1 and φ_2 are volume fractions and r_1 and r_2 are the number of segments of the molecules calculated with respect to a reference volume which, in this case, is the solvent molar volume.

Complete miscibility occurs when ΔG_m is less than the Gibbs energy of the components, and the solution maintains its homogeneity only as long as ΔG_m remains less than the Gibbs free energy of any two possible coexisting phases. As an example in Fig. 10 ΔG_m is plotted *versus* the volume fraction for the system polystyrene–C_{30} calculated by eqn. 4 at two different temperatures (190 and 250°C). The free energy–composition curve has a shape that clearly shows how two liquid phases coexist; one of them is the pure solvent. Such a behaviour has already been observed for the system acetone–polystyrene [12].

The analogous curves and the solubility limits for the long-chain alkanes were calculated at temperatures ranging from 190 to 250°C, using the extrapolated interaction parameter, assumed to be independent of the composition, and a molecular mass of 300 000 for polystyrene.

The results of these calculations are collected in Fig. 11: the solubility limits range between 10 and 25% volume for temperatures between 180°C and 260°C, and the conjugated phase is always the pure alkane.

REFERENCES

1 J.R. Conder and C.L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, Chichester, 1979.
2 T.E. Daubert and R.P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals—Data Compilation*, Hemisphere, Washington, DC, 1989.
3 A.P. Kudchadker and B.J. Zwolinski, *J. Chem. Eng. Data*, 11 (1966) 253.
4 J.G. Hayden and J. O'Connell, *Ind. Eng. Chem. Proc. Des. Dev.*, 14 (1975) 209.
5 L.C. Yen and S.S. Woods, *AIChE J.*, 12 (1966) 95.
6 Y.S. Lipatov and A.E. Nesterov, *Macromolecules*, 8 (1975) 889.
7 L.I. Stiel and D.F. Harnish, *AIChE J.*, 22 (1976) 117.
8 M. Galin and M.C. Rupprecht, *Polymer*, 19 (1978) 506.
9 R.H. Schuster, H. Grater and H.J. Cantow, *Macromolecules*, 17 (1984) 619.
10 H.S. Elbro, A. Fredenslund and P. Rasmussen, *Ind. Eng. Chem. Res.*, 30 (1991) 2576.
11 P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY and London, 1953.
12 A.A. Patwardhan and L.A. Belfiore, *J. Polym. Sci.: Polym. Phys.*, 24 (1986) 2473.