Determination of thermodynamic properties of isotactic poly(1-butene) at infinite dilution using density and inverse gas chromatography

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Abstract

The partial molar volumes, V_1^M, and the molar volume of isotactic crystalline low-molecular-weight poly(1-butene), iPBu-1, V_1, have been calculated from the measured density of {iPBu-1 + solvent (*n*-hexane, *n*-heptane, *n*-nonane, *n*-decane, *p*-xylene, cyclohexane and chloroform)} systems. Some of the thermodynamic quantities were also obtained for the iPBu-1 with eight hydrocarbons (*n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tridecane, *o*-xylene, *m*-xylene, *p*-xylene) by the method of inverse gas chromatography at various temperatures. The weight fraction activity coefficients of the solvent at infinite dilution, Ω_2^∞, and the Flory-Huggins thermodynamic interaction parameters, χ_{21}^∞, between polymer and solvents were determined. The partial molar free energy, ΔG_2^∞, the partial molar heat of mixing, ΔH_2^∞, at infinite dilution and the polymer solubility parameter, δ_1, were calculated. Additionally, the (solid + liquid) binary mixtures equilibria, SLE, of iPBu-1 with three hydrocarbons (*n*-octane, *n*-decane and *m*-xylene) were studied by a dynamic method. By performing these experiments over a large concentration range, the *T*–*x* phase diagrams of the polymer–solvent systems were constructed. The excess Gibbs energy models were used to describe the nonideal behaviour of the liquid phase. The Ω_2^∞ were determined from the solubility measurements and were predicted by using the UNIFAC FV model.
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1. Introduction

Knowledge of the solubility of solvents in polymers is essential for many high-molecular-weight compound technologies. The thermodynamic information for the design of this process is the activity coefficient and – for a high polymer quality – the activity coefficient at very low concentration of the solvent (infinite dilution) in the polymer. Moreover, these experimental data offer the possibility to predict the thermodynamic properties of many polymer – solvent mixtures.

The present work is a continuation of our study on the application of isotactic poly(1-butene), iPBu-1, as an additive to gasoline or motor oils [1,2]. The interaction between iPBu-1 and hydrocarbons being representative of the petrol is very important for the improvement of physical properties of gasoline.

Isotactic poly(1-butene) (Fig. 1) is a crystalline polyolefin, one of the major commodity polymers, having excellent physical properties for improving the properties of the polymer blends. The polymorphic transformations [3–6] of isotactic iPBu-1 increase the possible uses of this polymer. Firstly, properly moulded and processed articles made from iPBu-1 show very good resistance to creep and environmental stress cracking [7]. Secondly, extruded iPBu-1 is generally used in the manufacture of the pipes and tubes because of its impact and corrosion resistance. Moreover, in certain cases such as applications at low temperature iPBu-1 is preferred to isotactic polypropylene and poly(4-methyl-1-pentene) for the production of house furnishing, electrical apparatus or
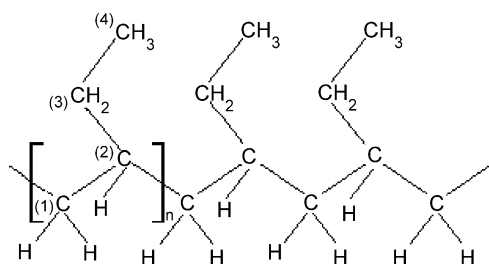
Fig. 1. The chemical structure of the isotactic poly(1-butene).

automotive parts where high impact resistance is needed [8]. It is also found that poly-butene group compound may be applied to waterproof telecommunication cables [9]. Finally, iPBu-1 can be used as a substance which improves lubricating properties of the gasoline and the motor oils.

Recent industrial applications of poly(1-butene) have increased the demand for physicochemical and thermodynamic data concerning this polymer. Inverse gas chromatography (IGC) has proved to be a rapid and consistent method to study polymer–solvent interactions [10–12]. It is well established that weight fraction activity coefficients [13] and heats of dilution may be derived accurately for these systems from IGC measurements [14–16].

The main focus of this work was to determine experimentally the molar volume of iPBu-1 from density measurements, the solvent activity coefficients at infinite dilution using IGC and the polymer solubility parameter from the retention data, using the current model based on Flory-Huggins theory [17–20]. Additionally, the (solid + liquid) phase diagrams, SLE, of (iPBu-1 + hydrocarbon) binary mixtures were under investigation.

2. Experimental

2.1. Materials

n-Hexane (+99%, 110-54-3), *n*-heptane (+99%, 142-82-5), *n*-octane (+99%, 111-65-9), *n*-decane (>99%, 124-18-5), *n*-undecane (99%, 1120-21-4), *n*-dodecane (99%, 112-40-3), *o*-xylene (97%, 95-47-6), cyclohexane (>99%, 110-82-7) and chloroform (99.9%, 67-66-3) were purchased from Aldrich Chemical Company. *n*-Nonane (>99%, 111-84-2), *p*-xylene (+99%, 106-42-3) and *n*-tridecane (97%, 629-50-5) were purchased from Fluka AG. Ethylbenzene (+99%, 100-41-4) and

m-xylene (+99%, 108-38-3) were purchased from Prolabo. All the solvents were fractionally distilled over different drying reagents to mass fraction purity better than 0.998 and 0.999. Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). The synthesis of the isotactic iPBu-1 has been described in a previous work [1]. The polymer characteristics are given in Table 1. Chromosorb® WHP 60/80 was purchased from Supelco Park.

2.2. Density measurements

An Anton Paar DMA 602 vibrating-tube densitometer, thermostated at $T = 293.15$ K was used to determine the density of pure solvents and iPBu-1/solvent systems and to determine V_1^M values. The densitometer's calibration was performed at atmospheric pressure using twice distilled and degassed water, high purity hexane and high purity cyclohexane. The vibrating-tube temperature was measured with an Anton Paar DM 100-30 digital thermometer and was regulated to within ± 0.01 K using a Bioblock Scientific Polyscience thermostat. The iPBu-1/solvent mixtures were prepared by weighing and by degassing in Bronson Ultrasonic Cleaner 1510E-DTM; the error in mole fraction being estimated as less than 5×10^{-4}. The results of measured densities of pure liquids compared with literature values are listed in Table 2.

2.3. Inverse gas chromatography

Measurements were carried out using a Shimadzu GC-8A gas chromatograph equipped with a heated on-column injector and a flame ionisation detector. The injector and detector temperatures were kept at 523.15 K during all experiments. The helium flow rate was adjusted to obtain adequate retention times. Exit gas flow rates were measured with a soap bubble meter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. A PC directly recorded detector signals and corresponding chromatograms were obtained using Borwin 2.1 software. Stationary phase used with packed columns were prepared by soaking the solid support (Chromosorb® WHP 60/80) in 10% iPBu-1 in cyclohexane solution. After the evaporation of cyclohexane (under vacuum), the support was equilibrated at 313.15 K during 5 h, then packed into stainless-steel column (i.d. 2.1 mm, length 1 m). The mass of the packing material was calculated from the mass of the packed and empty

Table 1

Physical constants of iPBu-1: number average molecular weight of iPBu-1 $\overline{M_n}$ (g mol^{-1}), weight average molecular weight of iPBu-1 $\overline{M_w}$ (g mol^{-1}), polydispersity index $\overline{M_w}/\overline{M_n}$, degree of polymerisation u, melting temperature of Form II $T_{\text{fus},1}$(II) (K) [1], solid–solid transition temperature (Form II → I') $T_{\text{tr},1}$ (K) [1], molar volume of Form II per unit V_{m1}(II)$^{298.15\,\text{K}}$ (cm^3 mol^{-1}) [1], molar volume of Form II per unit (this work) V_{m1}(II)$^{293.15\,\text{K}}$ (cm^3 mol^{-1}), melting temperature of Form I $T_{\text{fus},1}$(I) (K) [1], molar volume of Form I per unit V_{m1}(I)$^{298.15\,\text{K}}$ (cm^3 mol^{-1}) [1]

$\overline{M_n}$	$\overline{M_w}$	$\overline{M_w}/\overline{M_n}$	u	$T_{\text{fus},1}$(II)	$T_{\text{tr},1}$	V_{m1}(II)[a]	V_{m1}(II)[b]	$T_{\text{fus},1}$(I)	V_{m1}(I)[a]
18708	35102	1.88	333.43	363.55	349.60	61.41	66.02	376.83	49.13

[a] At 298.15 K.

[b] At 293.15 K. Obtained from extrapolation of V_1^M values to polymer mole fraction, x_1, equal to one.

Table 2
Densities ρ (g cm^{-3}) of pure solvents at 293.15 K

Solvent	ρ (this work)	ρ (reference)[a]	Solvent	ρ (this work)	ρ (reference)[a]
n-Hexane	0.65972	0.65947[b]	Cyclohexane	0.77832	0.77858[e]
n-Heptane	0.68333	0.68365[c]	Ethylbenzene	0.87181	0.8672
n-Nonane	0.71772	0.71785[d]	*p*-Xylene	0.86133	0.86073[f]
n-Decane	0.72972	0.7297	Chloroform	1.48758	1.4870[g]

[a] From Ref. [22].
[b] From Ref. [23].
[c] From Ref. [24].
[d] From Ref. [25].
[e] From Ref. [26].
[f] From Ref. [27].
[g] From Ref. [28].

column by using Thermogravimetric Analyzer TGA 2050 of TA Instruments and was checked during experiments. The injected volume of the sample vapour was 0.3 μl.

2.4. Dynamic method

(Solid + liquid) equilibrium temperatures were determined by using a dynamic method described in detail previously [21]. The samples (the mixtures of iPBu-1 and a solvent) placed in a thermostated, Pyrex glass cell were heated firstly fast to dissolution and after the crystallization in the solvent were heated again very slowly (at less than 2 K h^{-1} near the equilibrium temperature) with continuous stirring. The temperature of the crystal disappearance during the second or third heating was detected visually and measured with an electronic thermometer P 500 (DOSTMANN electronic GmbH) with probe totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of ITS-90. The accuracy of temperature measurements was ±0.01 K. The error in the mole fraction did not exceed $\delta_{x1} = 0.0005$.

3. Results and discussion

3.1. Density measurements

The densities of pure solvents (Table 2) and of the seven mixtures of {iPBu-1 (1) + hydrocarbon (2) (*n*-hexane, *n*-heptane, *n*-nonane, *n*-decane, *n*-cyclohexane, *p*-xylene and chloroform)} have been measured over a large composition range at 293.15 K under atmospheric pressure by using a vibrating-tube densitometry. These data were used to determine the partial molar volumes, V_1^M, which were calculated according to the following equations:

$$V_S = \frac{M_1 x_1 + M_2 x_2}{\rho_S} \tag{1}$$

$$V_S = x_1 V_1 + x_2 V_2 \tag{2}$$

$$V_1^M = \frac{M_2 x_2}{x_1} \left(\frac{1}{\rho_S} - \frac{1}{\rho_2} \right) + \frac{M_1}{\rho_S} \tag{3}$$

where V_S is the molar volume of binary solution, M_1 and M_2 the polymer and solvent molecular weights, respectively, x_1 and x_2 the polymer and solvent mole fractions, respectively, V_1 and V_2 the polymer and solvent molar volumes, respectively, ρ_S and ρ_2 are the solution and solvent densities, respectively. The molar volume of iPBu-1, V_1, (Table 1) was obtained from extrapolation of V_1^M values of (iPBu-1 + hydrocarbon) systems (Fig. 2) to polymer mole fraction, x_1, equal to one. It can be seen from Table 1 that the density measurements allowed the estimation of the polymer molar volume, V_1.

3.2. Inverse gas chromatography

The retention data determined with inverse chromatography experiments were used to calculate the thermodynamic functions of the solute dissolution in iPBu-1 as well as Hildebrand's solubility parameter. The probe specific retention volume, V_g^0, corrected to 273.15 K were calculated (Table 3) from the standard chromatographic relation:

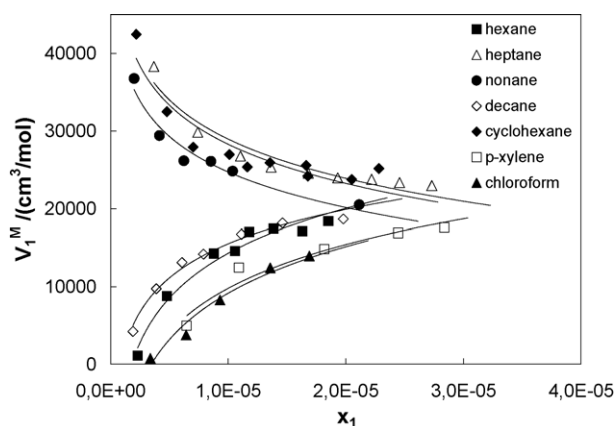$$V_g^0 = \frac{t_R' F 273.15}{wT} \frac{3}{2} \frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \tag{4}$$

Fig. 2. Partial molar volume of polymer for: (iPBu-1 + solvent) systems at 293.15 K.

Table 3

Temperature T (K), specific retention volume V_g^o (cm^3 mol^{-1}), experimental weight fraction activity coefficient of solvent (2) at infinite dilution $\Omega_{2\,\text{exp}}^\infty$, predicted (with the UNIFAC-FV model) weight fraction activity coefficient at infinite dilution $\Omega_{2\text{pred}}^\infty$, partial molar free energies of mixing at infinite dilution ΔG_2^∞ (kJ mol^{-1}) and Flory-Huggins interaction coefficient at infinite dilution χ_{21}^∞

Solvent	T	V_g^o	$\Omega_{2\,\text{exp}}^{\infty\ \text{a}}$	$\Omega_{2\,\text{exp}}^{\infty\ \text{b}}$	$\Omega_{2\text{pred}}^\infty$	ΔG_2^∞	χ_{21}^∞
n-Octane	365.85	144.07	3.847	4.803	3.754	4.10	−0.209
	368.85	138.39	3.629	4.800	3.757	3.95	−0.280
	371.90	132.63	3.437	4.796	3.759	3.82	−0.347
	379.25	142.52	2.520	4.788	3.764	2.92	−0.688
	385.15	134.31	2.261	4.782	3.768	2.61	−0.818
n-Decane	365.85	667.69	3.402	3.828	3.465	3.72	−0.265
	368.85	623.69	3.202	3.831	3.467	3.57	−0.338
	371.90	560.56	3.150	3.834	3.468	3.55	−0.366
	379.25	555.33	2.397	3.842	3.473	2.76	−0.666
	385.15	509.52	2.101	3.847	3.476	2.38	−0.820
n-Undecane	365.85	1413.0	3.267	–	3.368	3.60	−0.280
	368.85	1309.0	3.081	–	3.369	3.45	−0.350
	371.90	1214.2	2.900	–	3.371	3.29	−0.422
	379.25	1113.6	2.306	–	3.374	2.63	−0.678
	385.15	995.02	2.033	–	3.377	2.27	−0.825
n-Dodecane	365.85	2892.4	3.257	–	3.288	3.59	−0.260
	368.85	2708.8	3.001	–	3.289	3.37	−0.352
	371.90	2450.9	2.858	–	3.290	3.25	−0.413
	379.25	2211.5	2.247	–	3.292	2.55	−0.680
	385.15	1936.2	1.976	–	3.294	2.18	−0.828
n-Tridecane	365.85	6117.4	3.575	3.050	–	3.88	−0.149
	368.85	5524.4	3.361	3.057	–	3.72	−0.222
	371.90	5062.0	3.126	3.064	–	3.52	−0.305
	379.25	4284.8	2.520	3.081	–	2.91	−0.546
	385.15	3644.0	2.189	3.094	–	2.51	−0.708
o-Xylene	365.85	308.50	3.423	–	–	3.74	−0.045
	368.85	286.95	3.312	–	–	3.67	−0.089
	371.90	274.43	3.122	–	–	3.52	−0.159
	379.25	286.70	2.339	–	–	2.68	−0.473
	385.15	275.65	2.007	–	–	2.23	−0.646
m-Xylene	365.85	254.37	3.513	6.140	3.656	3.82	−0.047
	368.85	244.02	3.303	6.113	3.650	3.66	−0.120
	371.90	229.45	3.161	6.086	3.644	3.56	−0.175
	379.25	244.96	2.328	6.024	3.632	2.66	−0.507
	385.15	231.26	2.042	5.977	3.622	2.29	−0.658
p-Xylene	365.85	247.61	3.507	–	3.686	3.82	−0.055
	368.85	237.24	3.303	–	3.680	3.66	−0.126
	371.90	229.60	3.085	–	3.674	3.48	−0.205
	379.25	240.47	2.320	–	3.661	2.65	−0.517
	385.15	233.41	1.982	–	3.651	2.19	−0.695

[a] Calculated from Eq. (5) using IGC data.

[b] Calculated from Wilson's eq. assuming $x_2 = 0$.

where t_R' is the difference between the retention times of the probe and that of the air, F the flow rate of the carrier gas measured at room temperature T, w the mass of the polymeric stationary phase and P_i and P_o are the inlet and outlet pressures, respectively.

Generally, V_g^0 decreases with an increase of temperature in all investigated systems as expected for an exothermic sorption process.

The weight fraction activity coefficient, Ω_2^∞, the partial molar free energy, ΔG_2^∞ (Table 3) and the average partial molar enthalpy, ΔH_2^∞ (Table 4) at infinite dilution of the

Table 4

Partial molar enthalpy at infinite dilution for hydrocarbons in iPBu-1 ΔH_2^∞ (kJ mol^{-1}) at 365.85–385.15 K

Solvent	ΔH_2^∞
n-Octane	32.5
n-Decane	29.3
n-Undecane	28.8
n-Dodecane	30.3
n-Tridecane	29.4
o-Xylene	32.5
m-Xylene	33.0
p-Xylene	34.7

Table 5
Physical constants of solvents: molar volume V_m (cm^3 mol^{-1}), critical volume V_c (cm^3 mol^{-1}), critical temperature T_c (K), critical pressure P_c (bar)

Solvent	V_m[a]	V_c[b]	T_c[b]	P_c[b]
n-Octane	163.51	492	568.9	24.9
n-Decane	195.95[c]	624	617.7	21.1
n-Undecane	212.67	689	639.0	19.8
n-Dodecane	228.59[d]	754	658.2	18.0
n-Tridecane	244.94[e]	823	675.8	16.1
o-Xylene	121.20	370	630.3	36.8
m-Xylene	123.47[e]	375	617.1	34.9
p-Xylene	123.90	378	612.2	34.7

[a] From ref. [29] at 298.15 K.
[b] From ref. [30].
[c] From ref. [31].
[d] From ref. [32].
[e] From ref. [33].

solvents were calculated according to the following equations [10]:

$$\Omega_2^\infty = \frac{273.15R}{V_g^0 P_2^0 M_2} \exp\left(\frac{-P_2^0(B_{22} - V_2)}{RT}\right) \quad (5)$$

$$\Delta G_2^\infty = RT\ln\Omega_2^\infty \quad (6)$$

$$\Delta H_2^\infty = R\frac{\partial \ln(\Omega_2^\infty)}{\partial(1/T)} \quad (7)$$

where B_{22} is the second virial coefficient of the solute in the gaseous state, P_2^0 the solute vapour pressure at temperature, T (K), V_2 the molar volume of the solute (Table 5) and M_2 is the molecular weight of the solute. The values of B_{22} have been calculated using the equation proposed by *C*. Blake, presented in [34]. The critical quantities used to calculate of B_{22} are reported in Table 5.

It has been proposed that $\Omega_2^\infty > 5$ are indicative of poor polymer–solvent systems while lower values characterise good solubility for such a system [35]. It can be seen from Table 3 that Ω_2^∞ values for all systems are lower than 5. Thus, alkanes and xylenes are good solvents for iPBu-1. According to the partial molar free energy, relatively low values of ΔG_2^∞ were obtained (Table 3). This results from the relatively good miscibility of the hydrocarbons with investigated low-molecular-weight polymer. Positive values of ΔH_2^∞ (Table 4) indicate that the interaction between the molecules of hydrocarbons with those of polymer is endothermic reaction.

According to the Flory-Huggins theory, the parameter χ_{21}^∞ characterizes the interactions between the vapour-phase of the solute and the polymeric stationary phase was calculated (Table 3) according to the following equation:

$$\chi_{12}^\infty = \ln\left(\frac{273.15R\upsilon_1}{V_g^0 P_2^0 V_2}\right) - P_2^0\frac{(B_{22} - V_2)}{RT} \quad (8)$$

where R is the gas constant and υ_1 is the specific volume of the stationary phase which was estimated using the Tait equation [36] (see Table 6).

Table 6
Specific volume of iPBu-1 υ_1 (m^3 kg^{-1}) at inlet pressure P_i (Pa) and temperature T (K)

T	P_i	υ_1
365.85	0.90E+05	1.2197E−03
368.85	0.91E+05	1.2220E−03
371.90	0.91E+05	1.2244E−03
379.25	1.19E+05	1.2301E−03
385.15	1.11E+05	1.2348E−03

According to Klein and Jeberien [37] values of χ_{21}^∞ greater than 0.5 represent unfavourable polymer–solvent interactions while values lower than 0.5 indicate that these interactions are favourable for solvent dissolution. As is shown in Table 3, that parameter again indicates that alkanes and xylenes are good solvents for iPBu-1.

Assuming that the interaction parameter can be expressed in function of the solubility parameters of the solute and of the stationary phase [38]:

$$\chi = \frac{V_2(\delta_2 - \delta_1)^2}{RT} \quad (9)$$

where δ_1 and δ_2 are the solubility parameters, then, the solubility parameter of the stationary phase, δ_1, can be calculated by fitting χ_{21}^∞ and δ_2 to the following equation:

$$\left(\frac{\delta_2^2}{RT} - \frac{\chi_{21}^\infty}{V_2}\right) = \left(\frac{2\delta_1}{RT}\right)\delta_2 - \frac{\delta_1^2}{RT} \quad (10)$$

The interaction parameters, χ_{21}^∞ extrapolated to 298.15 K as well as the solvent solubility parameters, δ_2, are given in Table 7.

If the left-hand side of Eq. (10) is plotted against δ_2, a straight line having a slope of $2\delta_1/RT$ and an intercept of $-\delta_1^2/RT$ is obtained (see Fig. 3). The solubility parameter of the stationary phase, δ_1, was determined from both the slope and the intercept of the straight line [41–43] and was compared with value predicted by using the method of Hoftyzer and van Krevelen [44] (Table 8). As can be seen from Table 8 this method overestimates the experimental value of polymer solubility parameter, obtained from inverse gas chromatography data. However, it should be noted that this is group contribution method and gives rather approximate estimates.

Table 7
Flory-Huggins interaction coefficient at infinite dilution extrapolated to 298.15 K χ_{21}^∞, solubility parameter of solvent at 298.15 K δ_2 (MPa)$^{0.5}$

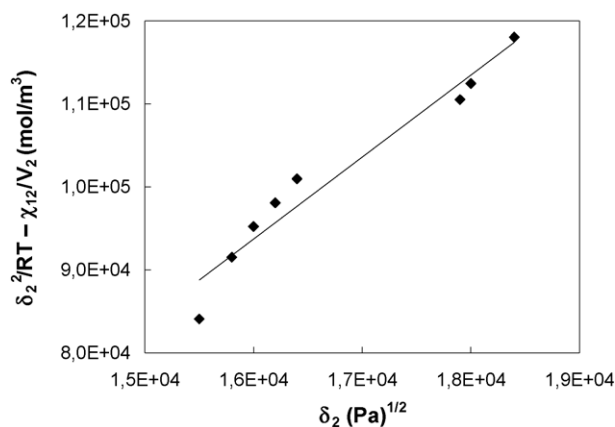| Solvent	χ_{21}^∞	δ_2[a]
n-Octane	2.10	15.5
n-Decane	1.80	15.8
n-Undecane	1.71	16.0[b]
n-Dodecane	1.78	16.2[b]
n-Tridecane	1.84	16.4[b]
o-Xylene	2.25	18.4
m-Xylene	2.25	18.0
p-Xylene	2.32	17.9

[a] From ref. [39].
[b] From ref. [40].

Fig. 3. Determination of the solubility parameter of iPBu-1 at 298.15 K from Eq. (11).

3.3. (Solid + liquid) equilibria

The solubility of the polymer was measured in three hydrocarbons (*n*-octane, *n*-decane, *m*-xylene) over a large concentration range at 285–361 K by the dynamic method. These systems are shown in Fig. 4 together with (iPBu-1 + *n*-tridecane) binary mixture, published previously [1]. The experimental points correspond to the crystalline modification (Form I) of iPBu-1. The results of the solubility measurements are listed in Table 9 in form of the equilibrium temperature, $T_{(I)}$ and the mole fraction of the crystallographic Form I of iPBu-1, x_1.

The experimental phase diagram (Fig. 4) of SLE investigated in this work is characterized mainly by the following: (i) the solubility of iPBu-1 decreases with an increase of the number of carbon atoms of the solvent; (ii) the polymer shows better solubility in *n*-alkanes than in *m*-xylene; (iii) differences between the solubilities of iPBu-1 in various hydrocarbons at the measured mole fraction range are noticeable but very small.

3.4. Correlation of (solid + liquid) phase equilibrium

From the equality of the fugacities of the polymer in the crystalline (S) and solution (L) phases we have:

$$f^S = x_1 \gamma_1 f^L \tag{11}$$

where x_1 the mole fraction of the polymer, γ_1 the activity coefficient of the polymer in the solution, f^S the fugacity of the solid polymer, and f^L is the fugacity of the subcooled liquid polymer, which is used as the standard state fugacity to which γ_1 refers.

Table 8
Values of the iPBu-1 solubility parameter δ_1 (MPa)$^{0.5}$ at 298.15 K

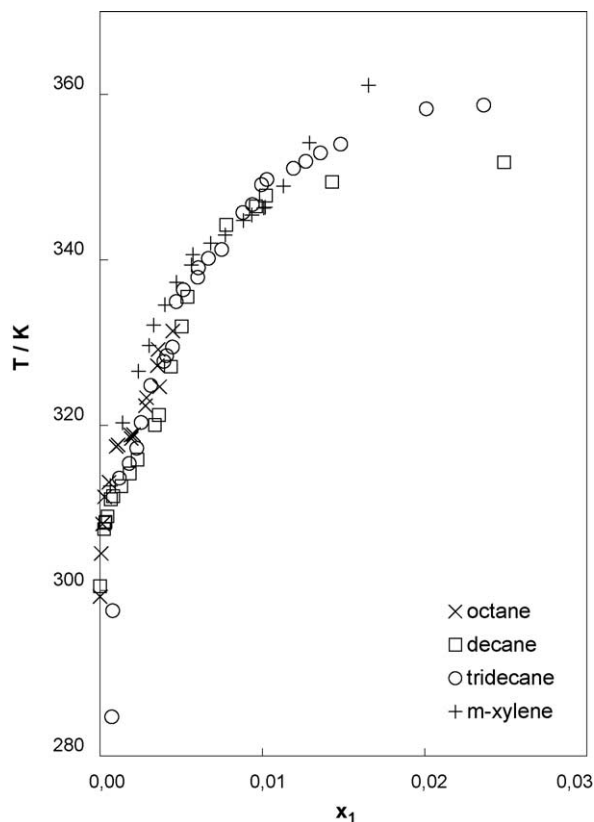| Intercept	Slope	δ_1 from intercept	δ_1 from slope	$\delta_1{}^a$
−6.429E+04	9.875	12.6	12.2	16.9

^{a} Calculated from ref. [44].

Fig. 4. Comparison between the solubilities of iPBu-1 in four hydrocarbons (*n*-octane, or *n*-decane, or *n*-tridecane [1], or *m*-xylene).

Table 9
Experimental solid–liquid equilibrium temperatures, T_I (K) (Form I) for {iPBu-1 (1) + hydrocarbon (2)} systems

x_1	$T_{(I)}$	x_1	$T_{(I)}$	x_1	$T_{(I)}$
n-Octane					
0.0000	299.3	0.0011	317.6	0.0035	327.2
0.0001	304.5	0.0019	318.8	0.0036	329.2
0.0002	308.1	0.0019	318.4	0.0037	324.6
0.0003	311.3	0.0021	318.9	0.0045	331.4
0.0006	313.1	0.0028	322.4	1.0000	376.8^a
0.0010	317.5	0.0029	323.3		
n-Decane					
0.0000	300.5	0.0013	312.6	0.0054	335.5
0.0003	307.4	0.0018	314.2	0.0078	344.2
0.0003	308.2	0.0023	315.9	0.0096	346.5
0.0004	308.3	0.0034	320.0	0.0102	347.8
0.0005	309.0	0.0036	321.2	0.0143	349.4
0.0007	311.0	0.0044	327.1	0.0249	351.8
0.0008	311.4	0.0050	331.9	1.0000	376.8^a
m-Xylene					
0.0006	312.7	0.0056	339.4	0.0102	346.4
0.0014	320.3	0.0057	340.6	0.0113	348.9
0.0024	326.5	0.0068	342.0	0.0129	354.1
0.0030	329.6	0.0077	343.0	0.0165	361.1
0.0033	332.1	0.0088	344.7	1.0000	376.8^a
0.0040	334.6	0.0094	345.4		
0.0047	337.3	0.0101	346.3		

^{a} DSC measurements [1].

The solubility of a polymer 1 in a liquid showing solid–solid phase transition before fusion may be expressed in a very general manner by Eq. (12). The solubility equation for temperatures below that of the phase transition must include the effect of the transition [45]. The result for the first-order transition is

$$-\ln x_1 \gamma_1 = \frac{\Delta_{\text{fus}} H_1}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{fus},1}}\right) + \frac{\Delta_{\text{tr}} H_1}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{tr},1}}\right)$$
$$- \frac{\Delta_{\text{fus}} Cp_1}{R}\left(\ln \frac{T}{T_{\text{fus},1}} + \frac{T_{\text{fus},1}}{T} - 1\right) \quad (12)$$

where x_1, γ_1, $\Delta_{\text{fus}} H_1$ [1], $\Delta_{\text{fus}} Cp_1$ [1], $T_{\text{fus},1}$ and T stand for mole fraction, activity coefficient, enthalpy of fusion (100% crystallinity), difference in polymer heat capacity between the solid and liquid at the melting temperature, melting temperature of the polymer (1) and equilibrium temperature, respectively. The $\Delta_{\text{tr}} H_1$ (100% crystallinity) [1], and $T_{\text{tr},1}$ stand for the enthalpy of solid–solid transition and transition temperature of the polymer, respectively. Eq. (12) is valid for simple eutectic mixtures with complete immiscibility in the solid phase. The values of $T_{\text{fus},1}$ and $T_{\text{tr},1}$ are presented in Table 1. The values of $\Delta_{\text{fus}} Cp_1$ for two crystallographic forms (II) and (I) were calculated as a difference of solid and liquid heat capacities at melting temperature [1]. For the semicrystalline polymer Eqs. (11) and (12) may be presented as follow [46,47]

$$\ln \frac{f^{\text{S}}}{f^{\text{L}}} = \ln x_1 \gamma_1 = cu\left(\ln \frac{f^{\text{S}}}{f^{\text{L}}}\right)_{\text{cryst.unit}} \quad (13)$$

where c is the degree of the crystallinity of solid semicrystalline polymer and u is the degree of polymerisation (see Table 1). The chemical potential of polymer and the $\ln x_1 \gamma_1$ is proportional to the degree of polymerisation u.

In this study three methods were used as the correlation equations that describe the Gibbs excess energy, (G^{E}): the Wilson [48], UNIQUAC [49] and NRTL [50] models. The exact mathematical forms of the equations have been presented in our previous paper [51]. Eq. 12 was used for the correlation of the experimental points with the assumption that the mixtures under study are simple eutectic systems. This point was confirmed in our previous work, where the solubilities of iPBu-1 with the n-alkanes were measured by the DSC method [1]. The eutectic point for system (iPBu-1 + n-tricosane) was described [1].

The infinite dilution activity coefficients may be also obtained by extrapolating values of the correlation of the experimental data. Using the Wilson equation the "experimental" activity coefficients at infinite dilution of solvent, $\gamma_{2\,\text{exp}}^{\infty}$ were calculated for $x_2 = 0$. For infinite dilution of the solvent, the mole fraction activity coefficient and the weight fraction activity coefficient are related according to the following equation:

$$\frac{\Omega_{2\,\text{exp}}^{\infty}}{\gamma_{2\,\text{exp}}^{\infty}} = \frac{M_1}{M_2} \quad (14)$$

Many combinatorial-free-volume expressions have been proposed for the last 10 years for polymer solutions. The UNIFAC-FV model, was used in this work for the prediction of the solvent weight fraction activity coefficients at infinite dilution, $\Omega_{2\text{pred}}^{\infty}$ [52,53]. The solvent weight fraction activity coefficients, $\Omega_{2\text{exp}}^{\infty}$ (form Wilson equation) and $\Omega_{2\text{pred}}^{\infty}$ were calculated and are presented in Table 3 together with other $\Omega_{2\text{exp}}^{\infty}$ values obtained form inverse gas chromatography and
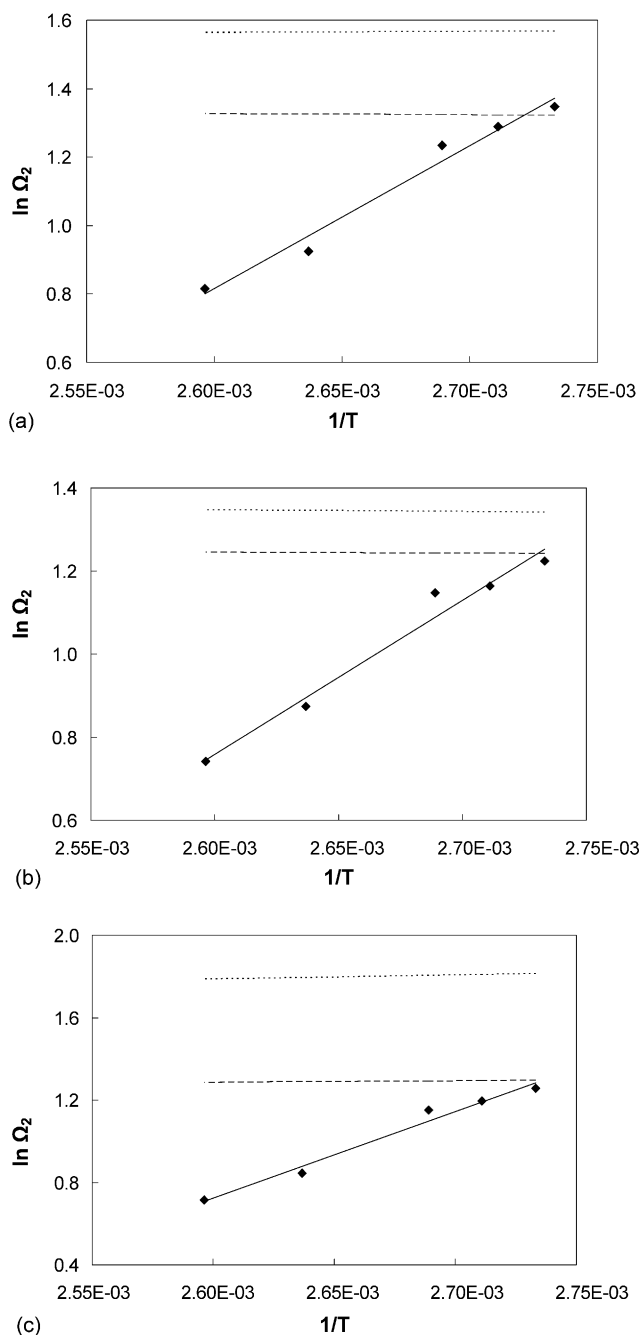

Fig. 5. Solvent weight fraction activity coefficients at infinite dilution for: (a) iPBu-1 + n-octane, or (b) iPBu-1 + n-decane, or (c) iPBu-1 + m-xylene systems. Solid line, calculated by the linear regression; dashed line, calculated by UNIFAC-FV model; dotted line, calculated by the Wilson equation.

discussed above. In Fig. 5, the predictions with UNIFAC-FV model are compared with the experimental infinite dilution weight activity coefficients obtained from IGC data and from Wilson's equation for (iPBu-1 + *n*-octane, or *n*-decane, or *m*-xylene) binary systems, as an example. For all polymer/solvent systems the $\Omega_{2\,exp}^{\infty}$ (from Wilson's eq.) and Ω_{2pred}^{∞} values are nearly constant at the measured temperature range, while the $\Omega_{2\,exp}^{\infty}$ values obtained from IGC data decrease with an increase in the temperature (see Table 3 and Fig. 5). In the case of all iPBu-1 systems, the values of solvent activity coefficients obtained from UNIFAC-FV model and especially by the Wilson equation are overestimated with the exception of *n*-tridecane (Wilson's equation; see Table 3). However, UNIFAC-FV model works in the same way in PIB systems [54]. UNIFAC-FV model yields better results than Wilson's equation {$\Omega_{2pred}^{\infty} = 3.656$ and $\Omega_{2\,exp}^{\infty} = 6.140$ for (iPBu-1 + *m*-xylene) system at 365.85 K} because free-volume differences play an important role in polymer solutions. Nevertheless, the results given by Wilson are acceptable (with exception of *m*-xylene).

4. Conclusions

The molar volume of isotactic poly(1-butene), iPBu-1, as a hypothetically subcooled liquid at 293.15 K was derived from density measurements of polymer–solvent systems. This value does not differ significantly from the value estimated by group contribution method and this method appears to be a simple and good method to obtain polymer molar volumes. The inverse gas chromatography technique was successfully applied to determine the thermodynamic data at infinite dilution concerning polymer–solvent interactions: the solvent weight fraction activity coefficient, Ω_2^{∞}, the partial molar free energy, ΔG_2^{∞}, the partial molar enthalpy, ΔH_2^{∞}, the Flory-Huggins interaction parameter, χ_{21}^{∞}. The results indicated a good miscibility of hydrocarbons with iPBu-1. Hildebrand's solubility parameter of iPBu-1 was calculated from these data and compared with value obtained from the method of Hoftyzer and van Krevelen [44]. The solubility of polymer was very similar in different solvents, considered as model components of gasoline. For those systems the miscibility gap in the liquid phase was not observed within the range of the experiments. The well known "simila similibus solvuntur" (like dissolves like) applies to the tested mixtures. It was shown that a correlation of the SLE in polymer solution with activity coefficients models is indeed possible with the reasonable accuracy. The UNIFAC-FV model was used to predict Ω_2^{∞}. These values are very close with those obtained from IGC data.

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