CHEMISTRY
A EUROPEAN JOURNAL

Phase Relationships and Thermodynamic Interactions of Isotactic Poly(1-butene) and Organic Solvent Systems**

Urszula Domańska* and Marta Karolina Kozłowska[a]

Abstract: Isotactic crystalline low-molecular-weight poly(1-butene), iPBu-1, was synthesised by using a metallocene catalyst. The molecular weight was determined by GPC. The chemical structure of iPBu-1 was verified by using high-temperature ^{13}C NMR spectroscopy and the thermal properties by differential scanning calorimetry (DSC). The (solid+liquid) equilibria, SLE, of iPBu-1 with different hydrocarbons (*n*-hexadecane, 1-heptene, 1-heptyne, cyclopentane, cyclohexane, cycloheptane, cyclooctane, benzene and propylbenzene) were studied by a dynamic method. By performing these experiments over a large concentration range, the temperature–mole fraction phase diagrams of the polymer–solvent systems could be constructed. From these diagrams it was found that iPBu-1 had the highest solubility in small-ring cycloalkanes and the lowest in *n*-hexadecane, 1-heptyne and benzene in the mole fraction range measured. The excess Gibbs energy models were used to describe the nonideal behaviour of the liquid phase and to estimate the solubility of iPBu-1 in the whole mole fraction range. Activity coefficients at infinite dilution of polymer and solvent were determined from the solubility measurements and were predicted by using the UNIFAC FV model and molecular Monte Carlo simulations.

Keywords: gasoline additives hydrocarbons • isotactic poly(1-butene) • phase diagrams • polymers • thermodynamics

Introduction

To predict the various thermodynamic properties of petroleum mixtures that are necessary for processing design in both the production and refining of crude oils, accurate knowledge of their basic physical properties and phase equilibria is important. Most of the methods used in the predictions and correlations of the thermodynamic properties of fuel additives, such as ethers or alcohols, which can enhance the octane rating and reduce pollution effects, may incur significant errors. The work described herein deals only with binary mixtures of a polymer additive, which can be used to enhance the lubricating properties of gasoline and motor oils. The properties investigated were the solid–liquid equilibria (SLE) and the activity coefficients in saturated solution. An accurate estimation of the solubilities of the polymer additives is important in a number of reservoir engineering calculations of the modified gasoline. Thus an estimation of the interactions between isotactic poly(1-butene) and hydrocarbons representative of petrol is very important if the physical properties of gasoline are to be improved.

Isotactic poly(1-butene), iPBu-1, is a crystalline polyolefin and is a major commodity polymer; it has excellent physical properties and can improve the properties of polymer blends. The polymorphic transformations[1] of isotactic iPBu-1 increase its possible applications. Firstly, properly moulded and processed objects made from iPBu-1 have very good resistance to creep and environmental stress cracking.[2a] Moreover, in some cases, such as in low temperature applications, iPBu-1 is preferred to isotactic polypropylene and poly(4-methyl-1-pentene) in the production of house furnishing, electrical apparatus and automotive parts in which high impact resistance is needed.[2b] It has also been found that the polybutene group compound can be applied to waterproof telecommunication cables.[2c]

Isotactic poly(1-butene) can exist in several different crystalline forms which differ in their chain conformation and, as a result, their unit-cell geometry and symmetry.[1e–l] However, only Forms I and II have been detected in melt-crystallised samples in quiescent conditions. Form I[1a,f,i] has a hexagonal unit cell and is obtained by the spontaneous crystal–

---

[a] Prof. Dr. U. Domańska, M. K. Kozłowska
Warsaw University of Technology
Faculty of Chemistry, Physical Chemistry Division
Noakowskiego 3, 00-664 Warsaw (Poland)
E-mail: ula@ch.pw.edu.pl

[**] Presented at CALCON 2003, 58th Annual Calorimetry Conference and Japan Society of Calorimetry and Thermal Analysis, Laie, Hawaii (USA), 27.07–01.08.2003.

DOI: 10.1002/chem.200400309

crystal transformation of Form I′ or II. Form I exhibits a high crystalline density and a melting temperature about 13 K higher than that of Form II. Form II[1e,g] has a tetragonal unit cell and is the kinetically favoured form obtained by melt crystallisation. Upon ageing at room temperature, it slowly transforms into the more stable Form I.[1b,d] Form I′ has an untwinned hexagonal unit cell and can be obtained by melt crystallisation of an iPBu-1 solution or by polymerisation of 1-butene.[1d] The crystal forms and possible transformations of iPBu-1 as well as the influence of *n*-alkanes on polymer behaviour have been discussed in a previous paper.[3]

Recent industrial applications of poly(1-butene) have increased the demand for physicochemical and thermodynamic data for this polymer. The thermodynamic phase behaviour of a polymer–solvent system is very important in every polymer application. Phase diagrams of many polymer–solvent diluent systems have been determined visually or by other optical techniques, such as optical microscopy and light scattering,[4] and also by differential scanning calorimetry (DSC).[5] Furthermore, of these methods, being fast and precise, thermal analysis is the most convenient one by which to study the transformations of iPBu-1 in polymer solutions. DSC is a well-known experimental technique by which to study (solid+liquid) demixing (crystallisation)[4c] and the vitrification[4a,5b,5d] of (liquid+liquid) demixed polymer solutions. Berghmans and co-workers[5] have also used DSC to determine the (liquid+liquid) equilibrium temperature. Their results were in very good agreement with the optical observations.

Abstract in Polish: *Przeprowadzono syntezę izotaktycznego, krystalicznego poli(1-butenu), iPBu-1, o niskim ciężarze cząsteczkowym stosując katalizator metalocenowy. Wyznaczono rozkład ciężarów cząsteczkowych za pomocą chromatografii żelowej (GPC). Strukturę nowo otrzymanego polimeru zweryfikowano przy użyciu wysokotemperaturowego* ^{13}*C NMR oraz różnicowej kalorymetrii skaningowej (DSC). Następnie zbadano stosując metodę dynamiczną rozpuszczalność iPBu-1 w 9 różnych węglowodorach (n-heksadekan, 1-hepten, 1-heptyn, cyklopentan, cykloheksan, cykloheptan, cyklooktan, benzen, n-propylobenzen), będących związkami modelowymi składników benzyny. Dla tych układów otrzymano wykresy fazowe T - x, z których wynika, iż iPBu-1 wykazuje najlepszą rozpuszczalność w cykloalkanach o małym pierścieniu, a najgorszą w n-heksadekanie, 1-heptynie lub benzenie. Do opisu odchyleń od doskonałości fazy ciekłej zastosowano modele nadmiarowej energii Gibbsa. Mając parametry korelacji krzywych likwidusu wyznaczono rozpuszczalność iPBu-1 we wszystkich węglowodorach w całym zakresie ułamka molowego. Wyznaczano także współczynniki aktywności polimeru i rozpuszczalnika w rozcieńczeniu nieskończenie wielkim z pomiarów rozpuszczalności oraz z przewidywania modelem UNIFAC FV i metodą symulacji molekularnej Monte Carlo.*

The main focus of this work was to obtain a low-molecular-weight isotactic poly(1-butene) and to determine experimentally the (solid+liquid) phase diagrams of the SLE of iPBu-1 with different hydrocarbons at normal pressure by using a dynamic method. The organic solvents that have been studied are important components of gasoline and motor oils. One of the challenges in engineering is to predict solid–liquid phase transitions in poly(1-olefin) solutions. These data are usually difficult to predict or correlate with the equations of state. The SAFT equation of state has been found to represent fluid–liquid and solid–liquid phase transitions only in high-pressure polyolefin solutions.[6] Group-contribution activity coefficient models have been used to describe the nonideal behaviour of the liquid phase of semicrystalline polymers with different degrees of crystallinity and molecular weight in different solvents.[7] Recently, new entropic polymer models which predict solvent activity coefficients in binary systems that contain polymers have been developed.[8] The shape of the phase diagrams of polymer blends is strongly influenced by the molecular-weight distribution of the polymers, especially for low-molecular-weight polymers. A useful discussion has been presented on the use of group-contribution activity coefficient models [the UNIFAC and entropic-FV (free volume) models] to predict the solubility and liquid-phase nonideality of polymers.[7] The main aim of the work described herein was to use excess Gibbs energy models to correlate the liquidus curve of a semicrystalline polymer in solvent and to estimate the polymer solubility for the whole mole fraction from 0 to 1. Finally, the polymer activity coefficients are discussed.

Results and Discussion

Synthesis of poly(1-butene): Isotactic iPBu-1 (Figure 1) was produced as fine white granules of various diameters. The high-temperature ^{13}C NMR spectrum of the product is shown in Figure 2. There are four peaks in the aliphatic region. The peaks observed at $\delta = 40.0$ and 34.8 ppm have been assigned to the main chain carbons C1 and C2, respectively. The peak observed at $\delta = 27.6$ ppm was assigned to C3, which is the side chain methylene carbon directly bonded to the main chain of the isotactic structure. The peak observed at $\delta = 10.4$ ppm was assigned to C4, which is the methyl carbon in the ethylene side chain. This data is in

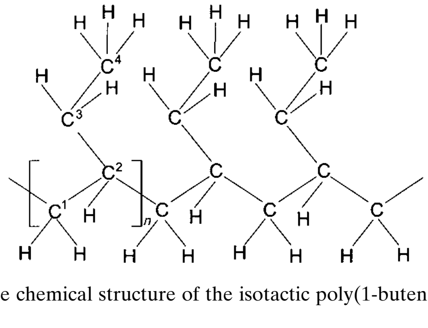

Figure 1. The chemical structure of the isotactic poly(1-butene).

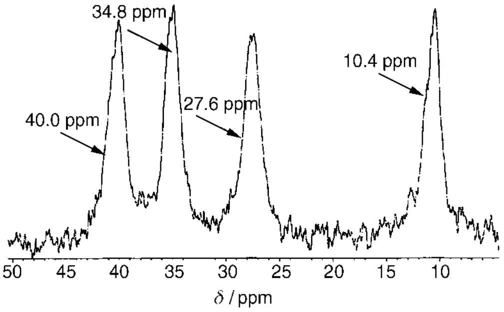

Figure 2. High-temperature ^{13}C NMR spectrum of iPBu-1.

good agreement with the low-temperature ^{13}C NMR spectrum of iPBu-1 reported in the literature.[9] Thus the main information on the isotacticity of the synthesised polymer is provided by the ^{13}C NMR spectra and the melting temperature of the isomer. It is well known that the melting temperature is strongly dependent on the configurational regularity of the chain. The melting temperature of the syndiotactic poly(1-butene) is about 325 K,[9] whilst isotactic poly(1-butene) (Form II) melts at 363.5 K.[3] The molecular-mass distribution of iPBu-1 obtained after 24 h of reaction, as determined by gel-permeation chromatography, is presented in Table 1.

Table 1. Molecular characteristics of iPBu-1.[a]

t [h]	24
M_n [Da]	18708
M_w [Da]	35102
M_w/M_n	1.8760

[a] t, reaction time in hours; M_n, number average molecular weight of polymer; M_w, weight average molecular weight of polymer; M_w/M_n, polydispersity index.

Differential scanning calorimetry: Multiple endotherms were detected in the first heating cycle of the DSC experiments performed on pure iPBu-1.[3] This was attributed to the solid–liquid phase transition at the melting temperature and to the solid–solid phase transition of the well-known polymorphic forms: Form II→Form I′. After the next few heating cycles for the same sample, one new endotherm was detected,[3] which was attributed to the transformation of iPBu-1 into the new high-temperature crystalline form: Form I. Table 2 lists the melting parameters for the (solid+liquid) phase transition of Form I: the onset temperature and enthalpy were obtained from the DSC thermogram after the fifth heating cycle of pure iPBu-1 of 100% crystallinity per unit of polymer.[3] The melting parameters for the (solid+liquid) and solid–solid phase transitions of Form II→Form I′ and the onset temperatures and enthalpies, were discussed in our previous paper.[3] The molar volume for the twinned hexagonal modification (Form I) was assumed to be 20% lower [$V_{\mathrm{m1}}(\mathrm{I})_{\mathrm{sc}}=49.13$ cm^{3}mol^{-1}] than the molar volume of the tetragonal modification (Form II) [$V_{\mathrm{m1}}(\mathrm{II})_{\mathrm{sc}}=61.41$ cm^{3}mol^{-1}] which was calculated from Equation (1),[10] where V_{m1a} is the molar volume of the rubbery amorphous polymer at 298.15 K ($V_{\mathrm{m1a}}=65.24$ cm^{3}mol^{-1}) and c is the degree of crystallinity ($0<c\leq 1$). The degree of crystallinity c for Form I is 0.62.[3] The molar volumes for the hydrocarbons (n-hexadecane, 1-heptene, 1-heptyne, cyclopentane, cyclohexane, cycloheptane, cyclooctane, benzene and propylbenzene) are presented in Table 3.

Table 2. Physical constants[a] for iPBu-1 (Form I) per polymer unit.[3]

$T_{\mathrm{fus,1}}(\mathrm{I})$ [K]	$\Delta_{\mathrm{fus}}H_1(\mathrm{I})$ [J mol^{-1}]	$V_{\mathrm{m1}}(\mathrm{I})_{\mathrm{sc}}$[b] [cm^{3}mol^{-1}]
376.83	4348.78	49.13

[a] $T_{\mathrm{fus,1}}(\mathrm{I})$, melting temperature; $\Delta_{\mathrm{fus}}H_1(\mathrm{I})$, enthalpy of fusion; $V_{\mathrm{m1}}(\mathrm{I})_{\mathrm{sc}}^{298.15}$, molar volume for 62% crystallinity. [b] At 298.15 K. The unit mol refers to the monomer.

Table 3. Molar volumes of solvents, $V_{\mathrm{m}}^{298.15}$.[11a]

Solvent	$V_{\mathrm{m}}^{298.15}$ [cm^{3}mol^{-1}]	Solvent	$V_{\mathrm{m}}^{298.15}$ [cm^{3}mol^{-1}]
n-hexadecane	294.11[11b]	cycloheptane	121.70[11c]
1-heptene	141.76	cyclooctane	134.83[11d]
1-heptyne	132.05[11b]	benzene	89.41
cyclopentane	94.72	propylbenzene	140.41[11e]
cyclohexane	108.75		

$$V_{\mathrm{m1a}}/V_{\mathrm{m1sc}} = 1(1-0.0103c) \tag{1}$$

(Solid+liquid) equilibria: Dynamic experiments were performed over a large concentration range at 291–398 K in order to construct phase diagrams for the (iPBu-1+hydrocarbon) system. The experimental data correspond to the crystalline form (Form I) of iPBu-1. The melting temperature of Form I (376.83 K) of pure iPBu-1 was measured after the fifth heating cycle. The results of the solubility measurements, the equilibrium temperatures, T_1, and the corresponding activity coefficients, γ_1, at specific mole fractions of the crystallographic modification of iPBu-1 (Form I) x_1, are presented in Table 4. The solid–liquid equilibria diagrams of iPBu-1 (1)+n-hexadecane, n-octadecane,[3] and cyclooctane (2) are shown as examples in Figure 3 for the concentration range measured.

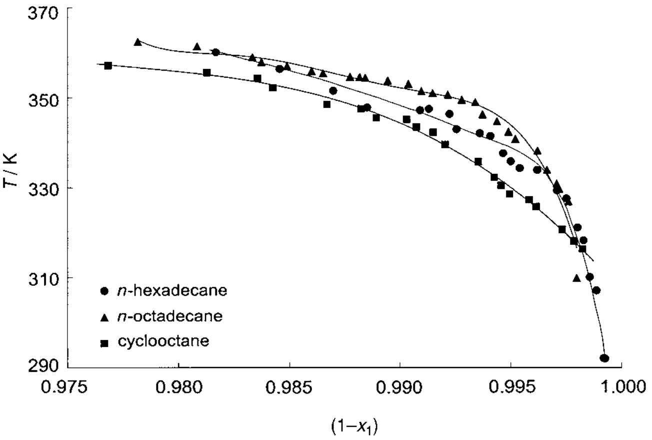

Figure 3. The solubilities of iPBu-1 in three hydrocarbons (n-hexadecane, n-octadecane,[3] and cyclooctane). The solid lines are derived from polynomial correlations.

Table 4. Experimental solid–liquid equilibrium temperatures, T, and the experimental activity coefficients, γ_1, for the polymer in [iPBu-1[a] (1)+hydrocarbon (2)] systems.

x_1	T_I [K]	γ_1	x_1	T_I [K]	γ_1	x_1	T_I [K]	γ_1
				n-hexadecane				
0.0007	292.0	2.55×10^{-49}	0.0038	334.0	1.18×10^{-22}	0.0087	347.5	5.47×10^{-15}
0.0008	292.1	2.68×10^{-49}	0.0046	334.4	1.71×10^{-22}	0.0091	347.2	7.81×10^{-15}
0.0011	307.2	3.66×10^{-39}	0.0050	335.9	1.27×10^{-21}	0.0115	347.8	4.00×10^{-14}
0.0014	310.1	2.73×10^{-37}	0.0053	337.7	1.40×10^{-20}	0.0130	351.6	8.09×10^{-13}
0.0017	318.3	4.62×10^{-32}	0.0059	341.5	2.39×10^{-18}	0.0155	356.4	3.82×10^{-10}
0.0020	321.2	2.63×10^{-30}	0.0064	342.1	5.01×10^{-18}	0.0183	360.0	3.47×10^{-08}
0.0025	327.6	2.29×10^{-26}	0.0074	343.0	1.46×10^{-17}	1.0000	376.8[b]	1.00
0.0029	329.4	2.49×10^{-25}	0.0078	346.4	1.36×10^{-15}			
				1-heptene				
0.0011	280.5	1.03×10^{-57}	0.0013	310.4	4.73×10^{-37}	0.0016	321.0	2.31×10^{-30}
0.0011	295.2	3.17×10^{-47}	0.0013	313.0	2.08×10^{-35}	0.0018	329.2	3.08×10^{-25}
0.0011	296.6	2.77×10^{-46}	0.0014	315.0	4.40×10^{-34}	0.0019	330.9	2.99×10^{-24}
0.0012	300.6	1.34×10^{-43}	0.0014	316.7	5.20×10^{-33}	1.0000	376.8[b]	1.00
0.0013	304.3	3.85×10^{-41}	0.0015	318.7	9.04×10^{-32}			
				1-heptyne				
0.0008	291.5	1.15×10^{-49}	0.0013	318.4	6.53×10^{-32}	0.0021	331.4	5.18×10^{-24}
0.0009	298.5	7.31×10^{-45}	0.0013	320.1	8.12×10^{-31}	0.0023	332.7	2.92×10^{-23}
0.0009	299.5	3.11×10^{-44}	0.0016	322.4	1.92×10^{-29}	0.0024	335.6	3.19×10^{-21}
0.0011	303.5	1.39×10^{-41}	0.0016	324.8	6.32×10^{-28}	0.0026	336.0	2.91×10^{-21}
0.0011	308.8	5.03×10^{-38}	0.0017	325.3	2.32×10^{-27}	0.0026	337.0	1.08×10^{-20}
0.0011	310.0	2.91×10^{-37}	0.0019	328.8	1.53×10^{-25}	1.0000	376.8[b]	1.00
0.0012	316.1	2.28×10^{-33}	0.0020	329.6	4.21×10^{-25}			
				cyclopentane				
0.0010	298.7	9.05×10^{-45}	0.0010	300.7	2.08×10^{-43}	0.0017	305.0	8.93×10^{-41}
0.0010	299.4	2.59×10^{-44}	0.0013	302.8	3.87×10^{-42}	1.0000	376.8[b]	1.00
				cyclohexane				
0.0010	304.2	4.39×10^{-41}	0.0019	311.6	1.74×10^{-36}	0.0026	317.7	1.25×10^{-32}
0.0013	306.3	9.45×10^{-40}	0.0021	312.9	1.11×10^{-35}	0.0027	318.6	4.23×10^{-32}
0.0016	310.5	4.59×10^{-37}	0.0023	315.2	3.44×10^{-34}	1.0000	376.8[b]	1.00
				cycloheptane				
0.0014	306.5	8.62×10^{-47}	0.0042	326.0	1.26×10^{-27}	0.0077	340.5	4.45×10^{-19}
0.0016	307.6	5.02×10^{-39}	0.0049	328.0	1.89×10^{-26}	0.0086	340.9	7.55×10^{-19}
0.0017	313.0	1.67×10^{-35}	0.0051	330.2	4.48×10^{-25}	0.0089	342.0	2.97×10^{-18}
0.0021	314.7	1.68×10^{-34}	0.0053	330.4	5.06×10^{-25}	0.0109	344.4	6.55×10^{-17}
0.0023	316.4	1.91×10^{-33}	0.0058	334.5	1.53×10^{-22}	0.0128	353.6	1.25×10^{-11}
0.0028	319.5	1.58×10^{-31}	0.0059	335.4	5.34×10^{-22}	1.0000	376.8[b]	1.00
0.0034	320.4	5.00×10^{-31}	0.0076	339.3	8.82×10^{-20}			
				cyclooctane				
0.0018	316.4	2.68×10^{-33}	0.0057	332.3	6.95×10^{-24}	0.0118	347.6	4.32×10^{-15}
0.0021	318.2	2.96×10^{-32}	0.0065	335.8	8.67×10^{-22}	0.0133	348.5	1.36×10^{-14}
0.0027	320.7	9.97×10^{-31}	0.0080	339.6	1.32×10^{-19}	0.0158	352.2	1.60×10^{-12}
0.0039	325.8	1.03×10^{-27}	0.0085	342.3	5.22×10^{-18}	0.0165	354.4	2.66×10^{-11}
0.0042	327.3	8.66×10^{-27}	0.0092	343.5	2.34×10^{-16}	0.0187	355.6	1.09×10^{-10}
0.0050	328.7	4.88×10^{-26}	0.0097	345.2	2.23×10^{-16}	0.0232	357.1	6.59×10^{-10}
0.0054	330.5	6.24×10^{-25}	0.0111	345.5	3.00×10^{-16}	1.0000	376.8[b]	1.00
				benzene				
0.0012	320.1	8.84×10^{-31}	0.0020	327.3	1.77×10^{-26}	0.0032	335.8	1.61×10^{-21}
0.0012	322.5	2.70×10^{-29}	0.0028	334.3	2.41×10^{-22}	1.0000	376.8[b]	1.00
				propylbenzene				
0.0001	321.2	8.21×10^{-29}	0.0022	325.5	1.26×10^{-27}	0.0072	328.7	3.61×10^{-26}
0.0006	322.9	1.04×10^{-28}	0.0033	327.3	1.06×10^{-26}	1.0000	376.8[b]	1.00
0.0009	323.6	1.96×10^{-28}	0.0050	328.4	3.15×10^{-26}			
0.0017	324.7	4.83×10^{-28}	0.0057	328.5	3.54×10^{-26}			

[a] The crystallographic phase of iPBu-1, Form I. [b] DSC measurements.

The experimental phase diagrams of the SLE that have been investigated in this work are mainly characterised by the following:

1. Negative deviations from ideality were found for all of the mixtures. Thus, the solubility was higher than the ideal one and the activity coefficients were much less than one, $\gamma_1 \ll 1$ (see Table 4).
2. Generally, the solubility of iPBu-1 decreases as the number of carbon atoms in the solvent increases (see Figure 3 and Figure 4); the polymer was observed to have the highest solubility in cyclopentane (Table 4) in the measured mole fraction range.
3. iPBu-1 is more soluble in cycloheptane than in 1-heptene or 1-heptyne (Figure 5), especially at higher concentrations. This may be explained by the fact that a poly-

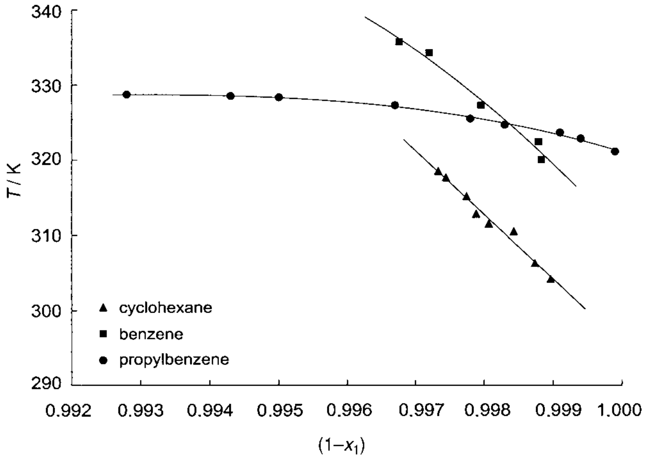

Figure 4. The solubilities of iPBu-1 in three hydrocarbons (cyclohexane, benzene and propylbenzene). The solid lines are derived from polynomial correlations.

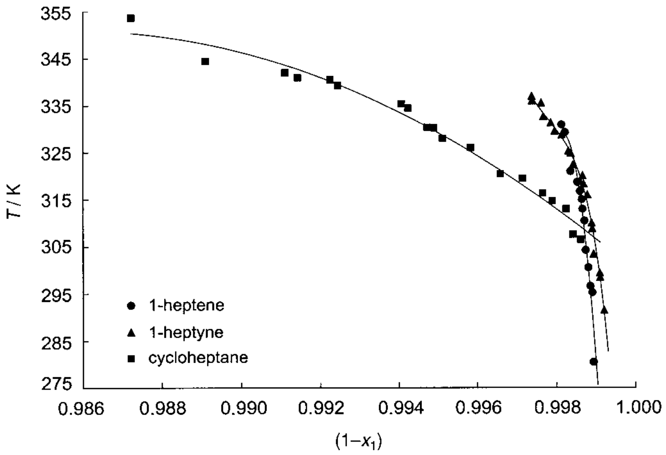

Figure 5. The solubilities of iPBu-1 in three hydrocarbons (1-heptene, 1-heptyne and cycloheptane). The solid lines are derived from polynomial correlations.

mer is a macromolecule built from chains that are swollen when the solvent concentration in the mixture is low. Cycloheptane is an example of a cyclic solvent that penetrates into the macromolecule's chains. The chains straighten as the solvent content in the mixture increases and a macromolecule is more soluble in a linear solvent even with double or triple carbon–carbon bonds (see Figure 5).

4. iPBu-1 is more soluble in cyclohexane than in benzene or propylbenzene (see Figure 4).
5. Generally, the differences in the solubilities of iPBu-1 in the various hydrocarbons in the measured mole fraction range are noticeable but very small.

The solubility measurements of crystalline polymers are usually presented as the temperature, T, as a function of the weight fraction of the polymer, which is more appropriate for high-molecular-weight compounds. The solubilities of iPBu-1 in three different hydrocarbons (an alkane, a cycloalkane and an aromatic solvent) are compared in Figure 6 together with a correlation of the liquidus curves.

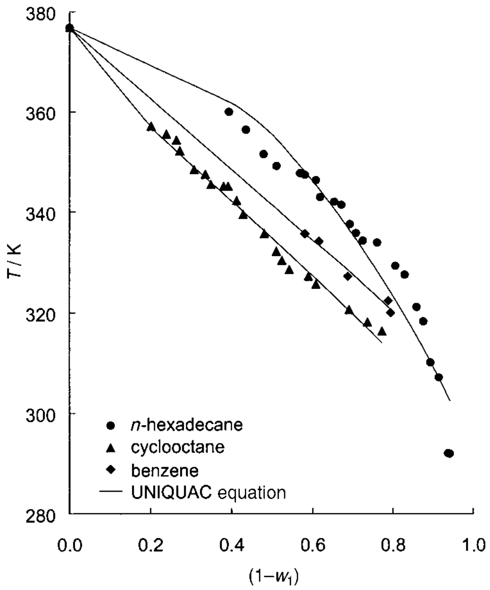

Figure 6. The solubilities of iPBu-1 in three hydrocarbons (n-hexadecane, cyclooctane or benzene) presented as the temperature versus weight fraction of iPBu-1. The solid lines are derived from the correlation with the UNIQUAC equation.

Correlation of solid–liquid equilibria: From the equality of the fugacities of the polymer in the crystalline (S) and solution (L) phases we have Equation (2), where x_1 is the mole fraction of the polymer, γ_1 is the activity coefficient of the polymer in solution, f^S is 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.

$$f^S = x_1\gamma_1 f^L \tag{2}$$

The solubility of a polymer (1) in a liquid that undergoes a solid–solid phase transition before fusion may be expressed in a very general manner by Equation (3). The solubility equation at temperatures below that of the phase transition must include the effect of the transition.[12] The result for the first-order transition is given in Equation (3), where x_1, γ_1, $\Delta_{fus}H_1$, $\Delta_{fus}C_{p1}$, $T_{fus,1}$ and T represent the mole fraction, activity coefficient, enthalpy of fusion (100 % crystallinity), the difference between the heat capacity of the polymer in the solid and liquid states at the melting temperature, the melting temperature of the solute (1) and the equilibrium temperature, respectively. $\Delta_{tr}H_1$ (100 % crystallinity) and $T_{tr,1}$ represent the enthalpy of the solid–solid transition and the transition temperature of the polymer, respectively. Equation (3) is valid for simple eutectic mixtures with complete immiscibility in the solid phase and full miscibility in the liquid phase. In this work the eutectic point for all the measured systems was at very low temperatures, that is, below the melting point of the solvent, and at very low polymer concentrations (close to zero). Physical data for 62% crystalline iPBu-1 per unit and for the hydrocarbon solvents are presented in Table 2 and Table 3, respectively. The molar volume of the crystalline, twinned Form I was assumed to be 20% lower than that of Form II, as was discussed previously. $\Delta_{fus}C_{p1}$ for the crystallographic form (I) is the difference between the solid and liquid state heat capacities at the melting temperature. The values of the solid and liquid heat capacities at 298.15 K were calculated by a group-contribution method and were extrapolated to the melting temperature of the polymer. The results are presented in Table 5. The need to use the $\Delta_{fus}C_{p1}$ term in Equation (3) when the solubility is to be evaluated at low temperatures has been discussed previously.[7] For a semicrystalline polymer, Equations (2) and (3) may be presented as Equation (4),[6b,7] where c is the degree of crystallinity of the solid semicrystalline polymer and u is the degree of polymerisation. The degree of polymerisation is given by $u = M_n/M_{mer} = 333.43$. The chemical potential of the polymer and $\ln x_1\gamma_1$ are proportional to the degree of polymerisation, u.

Table 5. Heat capacities [J mol^{-1} K^{-1}] at 298.15 K and at the melting temperature.[a]

C_{pl}^{S}(298.15 K)[b]	C_{pl}^{L}(298.15 K)[b]	$C_{pl}^{S}[T_{m1}(I)]$[c]	$C_{pl}^{L}[T_{m1}(I)]$[c]	$\Delta_{fus}C_{pl}(I)$[d]
97.2	118.65	120.91	131.72	10.81

[a] C_{pl}^{S}, in the solid phase; C_{pl}^{L}, in the liquid phase; $\Delta_{fus}C_{pl}$, difference between the solid and liquid heat capacities of the polymer at the melting temperature per unit of polymer. [b] Calculated by the group-contribution method.[10] [c] Calculated from the polynomial.[10] [d] Calculated at the melting temperature.[10]

$$\begin{aligned}-\ln x_1\gamma_1 &= \frac{\Delta_{fus}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{fus,1}}\right)\\&+\frac{\Delta_{tr}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{tr,1}}\right)-\frac{\Delta_{fus}C_{p1}}{R}\left(\ln\frac{T}{T_{fus,1}}+\frac{T_{fus,1}}{T}-1\right)\end{aligned} \tag{3}$$

$$\ln\frac{f^S}{f^L} = \ln x_1\gamma_1 = c\cdot \mathrm{u}\left(\ln\frac{f^S}{f^L}\right)_{cryst.unit} \tag{4}$$

In this study three correlating equations were used to describe the Gibbs excess energy, G^E: the Wilson,[13a] UNIQUAC[13b] and NRTL[13c] models. The exact mathematical forms of these equations were presented in our previous paper.[13d] The pure component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC equation were obtained by means of the following simple relationships [Eq. (5) and Eq. (6)],[13e] where V_{mi} is the molar volume of the pure component i at 298.15 K (Form I), Z is the coordination number, assumed to be equal to 10, and l_i is the bulk factor; it was assumed that $l_i = 0$ for chain-like molecules and $l_i = 1$ for cyclohydrocarbons. Model parameters were found by minimisation of the objective function Ω using Marquardt's algorithm [Eq. (7)],[14] where n is the number of experimental points and T^{exp}_i and T^{cal}_i denote, respectively, the experimental and calculated equilibrium temperatures corresponding to the concentration x_{1i}. P_1 and P_2 are the model parameters that result from the minimisation procedure. The root-mean-square deviation of temperature was defined by Equation (8).

$$r_i = 0.029281 V_{mi} \tag{5}$$

$$q_i = \frac{(Z-2)r_i}{Z}+\frac{2(1-l_i)}{Z} \tag{6}$$

$$\Omega = \sum_{i=1}^{n}\left[T_i^{exp}-T_i^{cal}(x_{1i},P_1,P_2)\right]^2 \tag{7}$$

$$\sigma_T = \left(\sum_{i=1}^{n}\frac{(T_i^{exp}-T_i^{cal})^2}{n-2}\right)^{0.5} \tag{8}$$

The calculations were carried out by using the molar volumes for the polymer and hydrocarbons presented in Table 2 and Table 3, respectively. Each equation that was used has two adjustable parameters per binary mixture except for the NRTL equation in which an additional parameter, α_{12}, a constant of proportionality similar to the nonrandomness constant, was set to $\alpha_{12} = \alpha_{21} = 0.8$, 0.95 or 0.5.

Equation (3) was used for the correlation of the experimental points on the assumption that the mixtures under study exhibit a single eutectic; this was confirmed in our previous work in which the solubilities of iPBu-1 in n-alkanes were measured by the DSC method.[3] In particular the eutectic point for the (iPBu-1+n-tricosane) system was described in detail.[3]

Table 6 shows the results of the correlation of the solubility data obtained by using the Wilson, UNIQUAC and NRTL equations. The values of the model parameters are shown together with the corresponding root-mean-square deviations, σ_T. For the cyclic and aromatic hydrocarbons, an acceptable description of the (solid+liquid) equilibrium was obtained with all three equations and the average standard deviation, σ_T, was 2.5 K. Note, however, that for most of the systems tested the best mathematical description was obtained by using the UNIQUAC model.

The SLE data for solutions with high concentrations of polymer are very difficult to measure experimentally. Thus the results of the correlations may be used to estimate the solubility of such solutions. In fact, this is the easiest way to estimate the solubility of the polymer at higher concentrations. The results obtained with the UNIQUAC and Wilson equations are presented in Table 7. For example, for benzene mole fractions $x_1 = 0.5$ and $x_1 = 0.8$ the transition temperatures are 376.0 and 376.6 K, respectively.

As expected, the lower the temperature, the lower the solubility and, as can be seen from Equation (3), the lower the f^S/f^L ratio. Figure 7, Figure 8 and Figure 9 show the variation of the logarithm of the activity of the solid polymer per structural unit (for crystalline Form I) versus T_{fus}/T, as expressed by Equation (3), which represents a measure of the

Table 6. Correlation of the solubility data, the SLE, of [iPBu-1 (1)+hydrocarbon (2)] by means of the Wilson, UNIQUAC and NRTL equations: values of parameters and measures of the standard deviations.

Solvent	Parameters [J mol^{-1}]			Deviations [K]		
	Wilson	UNIQUAC	NRTL[a]	Wilson	UNIQUAC	NRTL[a]
	$g_{12}-g_{11}$	Δu_{12}	Δg_{12}	σ_T[b]	σ_T[b]	σ_T[b]
	$g_{12}-g_{22}$	Δu_{21}	Δg_{21}			
hexadecane	1440.66	4613.33	−10172.70	9.5	5.2	8.1
	−1294.27	−2450.41	9687.95			
1-heptene	−333.22	–	−10198.36	13.0	–	9.1
	297.86		10968.58			
1-heptyne	−1019.86	–	−8893.27[c]	12.0	–	9.3[c]
	927.28		9678.53[c]			
cyclopentane	−1089.93	1557.02	−14150.70[d]	0.84	0.60	0.58[d]
	965.80	−834.82	−15185.11[d]			
cyclohexane	−1063.39	2416.83	−10055.50	2.2	0.78	0.96
	953.60	−1335.43	−5221.71			
cycloheptane	−915.71	3080.42	−10240.72	6.1	2.9	4.7
	823.79	−1708.97	9113.04			
cyclooctane	−1035.94	2493.73	−10087.75	3.6	1.6	3.9
	943.61	−1502.22	8086.90			
benzene	−2690.94	3523.25	−9905.44	4.4	1.0	3.8
	2490.80	−1348.31	8902.73			
propylbenzene	–	−1006.66	–	–	2.5	–
		1566.68				

[a] Calculated with the third nonrandomness parameter $\alpha = 0.8$. [b] According to Equation (3) in the text. [c] Calculated with the third nonrandomness parameter $\alpha = 0.95$. [d] Calculated with the third nonrandomness parameter $\alpha = 0.5$.

Table 7. Predicted solid–liquid equilibrium temperatures, T_I (crystallographic phase, Form I), for [iPBu-1 (1)+hydrocarbon (2)] systems.

x_1	T_I [K]	x_1	T_I [K]
	n-hexadecane		
0.035	371.8	0.500	376.1
0.100	374.9	0.700	376.3
0.300	375.5		
	1-heptene		
0.038	360.0	0.500	376.1
0.100	370.2	0.700	376.5
0.300	375.0		
	1-heptyne		
0.043	362.2	0.500	376.0
0.100	370.4	0.700	376.3
0.300	375.0		
	cyclopentane		
0.020	346.2	0.500	376.0
0.049	363.6	0.700	376.5
0.200	373.7		
	cyclohexane		
0.021	349.0	0.500	376.0
0.050	365.0	0.700	376.5
0.200	373.8		
	cycloheptane		
0.100	370.8	0.500	376.0
0.300	375.1	0.800	376.6
	cyclooctane		
0.100	370.6	0.500	376.0
0.300	375.1	0.700	376.5
	benzene		
0.020	354.6	0.500	376.0
0.063	367.8	0.800	376.6
0.200	373.7		
	propylbenzene		
0.020	348.5	0.500	376.0
0.073	368.0	0.800	376.6
0.300	374.9		

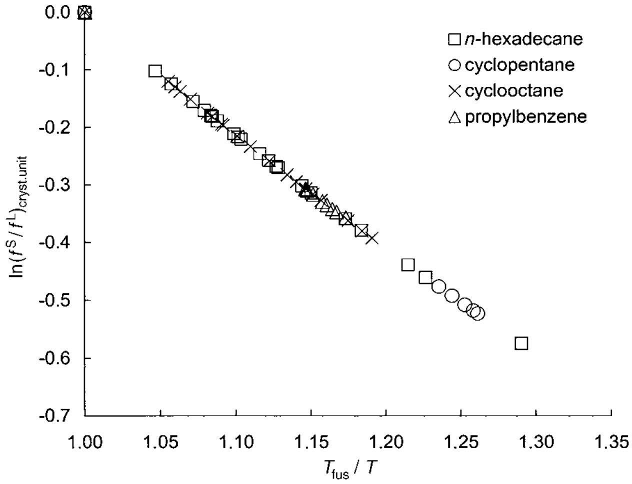

Figure 7. The logarithm of the activity of the solid polymer in saturated solutions of *n*-hexadecane, cyclopentane, cyclooctane and propylbenzene per structural unit versus T_{fus}/T. The degree of crystallinity is 62%.

polymer subcooling. These curves exhibit minimal concave character similar to the results obtained with the total solubility equation (without the term for the solid–solid phase transition) by Harismiadis and co-workers.[7] The logarithm of iPBu-1 activity per structural unit, $\ln(f^S/f^L)_{\mathrm{cryst.unit}}$, in all hydrocarbons decreases monotonically with decreasing mole fraction of the polymer (see Figure 7, Figure 8 and Figure 9).

The infinite dilution activity coefficients could also be obtained by extrapolating values of the correlation of the experimental data. By using two equations, UNIQUAC and

Wilson, the “experimental” activity coefficients at infinite dilution of polymer, $\gamma_{1\mathrm{exp}}^{\infty}$, and solvent, $\gamma_{2\mathrm{exp}}^{\infty}$, were calculated for $x_1 = 0$ and $x_2 = 0$, respectively.

Many combinatorial-free-volume expressions have been proposed for polymer solutions in the last 10 years. The UNIFAC-FV model was used in this work to predict the solvent activity coefficients, $\gamma_{2\mathrm{exp}}^{\infty}$, at infinite dilution.[5a,b] For comparison, the molecular Monte Carlo simulation (MS) method was also used to study the polymer–solvent systems following a method proposed by Sheng et al.[15] for bead-spring polymers dissolved in a monomeric solvent as a function of the number of beads in the polymer. The chain-increment method was used for chain lengths up to 60. The simple expression for $\gamma_{2\mathrm{pred}}^{\infty}$, the activity coefficient of a solvent in polymer, according to Sheng et al. is shown in the footnotes to Table 8. The solvent weight-fraction activity coefficients, $\Omega_{2\mathrm{exp}}^{\infty}$ and $\Omega_{2\mathrm{pred}}^{\infty}$, were calculated and are presented in Table 8 together with other values discussed above. However, only the activity coefficients at infinite dilution obtained by using the Wilson equation are given because the other values differ from the predicted one (for the solvent) about 90 % of the time. For example, in cyclopentane $\gamma_{2\mathrm{exp}}^{\infty} = 4.51$ (UNIQUAC model) whilst the predicted value, $\gamma_{2\mathrm{pred}}^{\infty}$, is 0.0127. Wilson’s equation appears to provide a good representation of the excess Gibbs energies for a variety of miscible mixtures and is particularly useful for solutions with nonpolar solvents. One can assume that the best description would be obtained from a correlation of the experimental data by using the local composition model with a free volume term (LCM FV), however the results given by the Wilson model are acceptable.

The values of the polymer activity coefficients, presented in Table 8 as $\ln\gamma_{1\mathrm{exp}}^{\infty}$, are very small and range from −62 to −111. Values of the experimental solvent activity coefficients, $\gamma_{2\mathrm{exp}}^{\infty}$, are comparable with solutions of other polymers, for example, 0.0287 for iPBu-1/*n*-hexadecane and 0.0262 for iPBu-1/cyclohexane, whilst values of 0.0882 and 0.0095 are given for polyethylene(PE: 7400)/*n*-dodecane[17a] and PE(35 000)/cyclohexane, respectively.[17a] The experimental solvent weight-fraction activity coefficients at

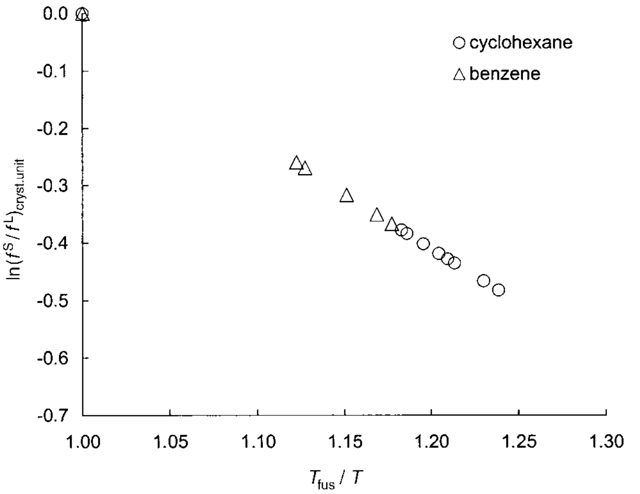

Figure 8. The logarithm of the activity of the solid polymer in saturated solutions of cyclohexane and benzene per structural unit versus T_{fus}/T. The degree of crystallinity is 62 %.

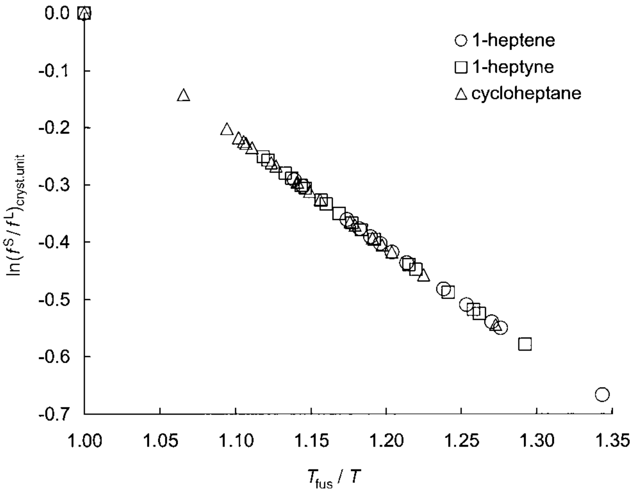

Figure 9. The logarithm of the activity of the solid polymer in saturated solutions of 1-heptene, 1-heptyne and cycloheptane per structural unit versus T_{fus}/T. The degree of crystallinity is 62 %.

Table 8. Activity coefficients for iPBu-1 solutions with hydrocarbons at infinite dilution.[a]

Solvent	$\mathrm{Ln}\,\gamma_{1\mathrm{exp}}^{\infty}$ [b]	$\gamma_{2\mathrm{exp}}^{\infty}$ [b]	$\gamma_{2\mathrm{pred}}^{\infty}$ [c]/AD [%]	$\gamma_{2\mathrm{pred}}^{\infty}$ [d]/AD [%]	$\Omega_{2\mathrm{exp}}^{\infty}$ [e]	$\Omega_{2\mathrm{pred}}^{\infty}$ [f]
n-hexadecane	−88.3	0.0287	–	0.0532/85.5	2.37	–
1-heptene	−96.9	0.0263	0.0214/18.6	0.0230/12.2	5.00	4.09
1-heptyne	−79.9	0.0315	–	0.0226/28.3	6.12	–
cyclopentane	−111	0.0230	0.0127/44.8	0.0165/28.4	6.13	3.39
cyclohexane	−96.9	0.0262	0.0139/46.9	0.0198/24.7	5.83	3.09
cycloheptane	−91.0	0.0279	–	0.0230/17.3	5.31	–
cyclooctane	−77.6	0.0323	–	0.0263/18.5	5.39	–
benzene	−61.9	0.0399	0.0184/53.9	0.0183/54.0	9.55	4.40

[a] $\mathrm{Ln}\,\gamma_{1\mathrm{exp}}^{\infty}$, logarithm of the experimental polymer activity coefficients; $\gamma_{2\mathrm{exp}}^{\infty}$, experimental, and $\gamma_{2\mathrm{pred}}^{\infty}$, predicted (with the UNIFAC-FV model or by using the molecular-simulation-based equation) solvent activity coefficients; AD, absolute percentage deviation between experimental and predicted values; $\Omega_{2\mathrm{exp}}^{\infty}$, experimental, and $\Omega_{2\mathrm{pred}}^{\infty}$, predicted (with the UNIFAC-FV model) weight-fraction activity coefficients. [b] Calculated from the correlation with the Wilson equation. [c] Calculated according to the formula $\gamma_{2\mathrm{pred}}^{\infty} = \Omega_{2\mathrm{pred}}^{\infty}\frac{M_2}{M_1}$, assuming the solvent weight fraction is equal to zero; $\Omega_{2\mathrm{pred}}^{\infty}$ was predicted by using the UNIFAC FV model at room temperature (298.15 K).[16] [d] Predicted according to the molecular-simulation-based equation $\gamma_{2\mathrm{pred}}^{\infty} = 4.391/n$,[15] where n is the ratio between the polymer and the solvent molecular weights. [e] Calculated according to the formula $\Omega_{2\mathrm{exp}}^{\infty} = \gamma_{2\mathrm{exp}}^{\infty}\frac{M_2}{M_1}$, assuming the solvent weight fraction is equal to zero.[16] [f] Values predicted by the UNIFAC FV model at room temperature (298.15 K).[16]

298.15 K, $\Omega_{2\mathrm{exp}}^{\infty}$, presented in Table 8 are, for example, 5.83 for iPBu-1/cyclohexane and 9.55 for iPBu-1/benzene. These data are comparable to the literature values for polyisobutylene (PIB) at 323.2 K: 4.56 for PIB(53000)/cyclohexane[17b] and 5.90 PIB(53000)/benzene.[17c] Recently it was stated[17a] that the infinite dilution solvent weight-fraction-based activity coefficients, $\Omega_{2\mathrm{pred}}^{\infty}$, of a polyolefin could be assumed to be constant (4.39), independent of the system, the polymer molecular weight and temperature. This is valid for polymers like PE and PIB with normal and cycloalkanes.[17a] Our values range from 2.37 (*n*-hexadecane) to 6.13 (cyclopentane). Both models, UNIFAC FV and MS, underestimate the infinite dilution solvent activity coefficients measured in the experimental procedure (correlated values) with the exception of *n*-hexadecane (MS method).

Conclusion

Isotactic low-molecular-weight poly(1-butene) was obtained by using a metallocene catalyst. The characteristics of the polymer were established by GPC, ^{13}C NMR spectroscopy and DSC. The temperature and enthalpy of fusion of the crystallographic form (I) of the polymer were determined. Polymer iPBu-1 was used directly to study the mutual influence of different hydrocarbons on the macromolecule in binary mixtures using the dynamic method presented in our previous work.[3] From the thermodynamic point of view Form I has to be accepted as the stable form relative to Forms II and I′ (metastable forms).[3] On the basis of the dynamic method, the main conclusion found was that the solubility of iPBu-1 in different hydrocarbons increases as the solvent molecular weight decreases. No miscibility gap in the liquid phase was observed for iPBu-1 in nine different hydrocarbons in the range of the experiment. It has been shown that the correlation of the SLE in polymer solutions with activity coefficient models can be obtained with reasonable accuracy although the results were much worse than those obtained for typical organic mixtures. High negative deviations from ideality were observed, which are typical of polymer solutions. Figure 10 shows as an example the complete calculated liquidus curve of iPBu-1 in cyclooctane together with experimental points and calculated ideal solubility.

In most reports in the literature the effects of the heat capacities at the melting point were neglected. It has been shown herein that it is possible to extrapolate $\Delta_{\mathrm{fus}}C_{p1}$ to the melting temperature and perform the calculations more properly. Qualitative predictions of polymer–-solution solubility at higher temperatures and concentrations have also been presented. The accuracy of the predictions depended, as expected, on the model used to describe the nonideality of the liquid phase (here Wilson and UNIQUAC work quite well) and also on the solid polymer data. The predicted solubilities were very similar in the different solvents, which are considered to be model components of gasoline. The solubility data of gasoline additives should result in improved physical properties of gasoline and motor oil; this will be the subject of further investigations on such systems.

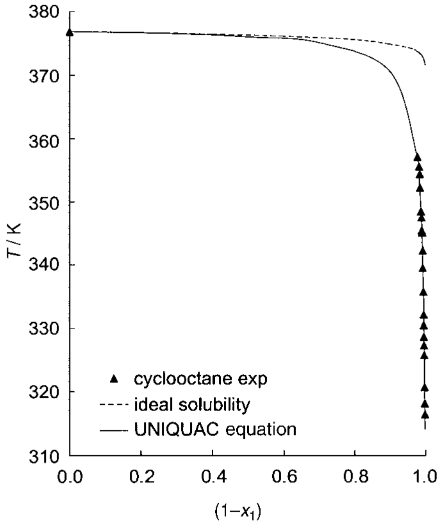

Figure 10. Schematic diagram of the (solid+liquid) equilibrium for the [iPBu-1(1)+cyclooctane (2)] binary mixture. The solid line is derived from the correlation by the UNIQUAC equation. The dotted line represents ideal solubility.

Experimental Section

Materials: 1-Butene (99+ %, *106-98-9*), toluene (99.5+ %, *108-88-3*), *n*-hexadecane (99 %, *544-76-3*), 1-heptene (97 %, *592-76-7*), 1-heptyne (98 %, *628-71-7*), cycloheptane (99 %, *291-64-5*), benzene (99 %, *71-43-2*) and propylbenzene (98 %, *103-65-1*) were purchased from Aldrich Chemical Company. Cyclopentane (99.8 %, *287-92-3*) was purchased from Merck & Co., Inc. and cyclohexane (99 %, *110-82-7*) from Int. Enzymes Limited. Cyclooctane (>99 %, *292-64-8*) was purchased from Janssen Pharmaceutica Products, L.P. 1,2-Ethylenebis(5-indenyl)zirconium dichloride (catalyst) and methylaluminoxane (MAO), 30 wt. % solution in toluene (Al 5100/30T, pure, *120144-90-3*), were purchased from WITCO Eurocen. All the solvents were fractionally distilled over different drying reagents to a mass-fraction purity better than 0.998 and 0.999. Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide).

Synthesis of poly(1-butene): Low-molecular-weight isotactic poly(1-butene) was synthesised as follows: the reaction was carried out under conditions free of water and oxygen. An autoclave (600 mL) equipped with stirrer, thermocouple, heating jacket, manometer and pressure gauges was filled with dry 1-butene (2 atm), solvent (toluene, 300 mL) and MAO (2.0×10^{-2} mol) and after 10 min of mixing a catalyst (2.0×10^{-5} mol) was added. The reaction was carried out for 1, 1.5, 2 or 24 h at 303.15 K.[3] The reaction was completed by the addition of methanol and then the mixture was washed with 5 % HCl/methanol solution to remove any residual catalyst. The differences in the molecular-mass distribution after the different reaction times were not significant. In this paper the final form of the polymer obtained after 24 h of reaction was used.

Gel-permeation chromatography: The molecular-mass distribution of iPBu-1 obtained after 24 h is presented in Table 1. GPC was performed at 408.15 K with a Waters GPC 150CV chromatograph equipped with a Styragel HT4 MS column by using atactic polystyrene as the standard and 1,2,4-trichlorobenzene as the eluent.

^{13}C NMR spectroscopy: The high-temperature ^{13}C NMR spectrum was obtained on a VARIAN GEMINI-200BB spectrometer at 413.15 K using

4 mm o.d. tubes inset in 5 mm o.d. tubes. In the thinner one was pure iPBu-1 and in the thicker one was dimethyl sulfoxide (DMSO) used as the internal reference. Also the low-temperature ^{13}C NMR spectrum was obtained on the same apparatus using 5 mm tubes with deuteriated benzene as the solvent and TMS as the internal reference. The sample concentrations were approximately 50 mg/2.5 mL.

Differential scanning calorimetry: The thermal properties of iPBu-1 were studied by using a Differential Scanning Microcalorimeter Perkin-Elmer Pyris 1 calibrated against an indium sample with 99.9999 mol% purity. Five scans were performed from room temperature to 393.15 K and the samples then cooled with air. All heating cycles were performed at a rate of 2 K min^{-1}. The calorimetric accuracy was ±1% and the calorimetric precision was 0.5%.

Dynamic method: Solid+liquid equilibrium temperatures were determined by using a dynamic method which has been described in detail previously.[18] The samples (the mixtures of iPBu-1 and a solvent) placed in a thermostatted, Pyrex glass cell were first heated quickly to achieve dissolution and then after crystallisation in the solvent the samples were heated again very slowly (at less than 2 K h^{-1} near the equilibrium temperature) with continuous stirring. The temperature at which the crystal disappeared during the second or third heating cycle was detected visually and measured with an electronic thermometer P 500 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostatted liquid. The accuracy of the temperature measurements was ±0.01 K. The error in the mole fraction did not exceed $\delta_{x1} = 0.0005$.

Acknowledgement

This work was financially supported by the Warsaw University of Technology.

[1] a) R. L. Miller, V. F. Holland, *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 519–521; b) G. C. Alfonso, F. Azzurri, M. Castellano, *J. Therm. Anal. Calorim.* **2001**, *66*, 197–207; c) A. K. Winkel, M. J. Miles, *Polymer* **2000**, *41*, 2313–2317; d) Y.-T. Shieh, M.-S. Lee, S.-A. Chen, *Polymer* **2001**, *42*, 4439–4448; e) G. Natta, P. Corradini, I. W. Bassi, *Atti Accad. Naz. Lincei* **1955**, *19*, 404–409; f) G. Natta, P. Corradini, I. W. Bassi, *Makromol. Chem.* **1956**, *21*, 240–244; g) R. Zannetti, P. Manaresi, G. C. Buzzoni, *Chim. Ind.* **1961**, *43*, 735–740; h) V. F. Holland, R. L. Miller, *J. Appl. Phys.* **1964**, *35*, 3241–3248; i) C. Armeniades, E. Baer, *J. Macromol. Sci. Phys.* **1967**, *B1*, 309–334; j) J. Foglia, *Appl. Polym. Symp.* **1969**, *11*, 1–18; k) C. Nakafuku, T. Miyaki, *Polymer* **1983**, *24*, 141–148; l) S. Kopp, J. C. Wittmann, B. Lotz, *Polymer* **1994**, *35*, 916–924.

[2] a) I. D. Rubin, *Poly(1-Butene)* (Ed.: H. Morawitz), Gordon and Breach Science Publisher Ltd., London, **1968**, p. VII; b) P. Parrini, G. Crespi in *Encyclopedia of Polymer Science and Technology, Vol. 13* (Eds.: H. F. Mark, N. G. Gaylord, N. M. Bikales), Wiley, New York, **1970**, p. 117; c) M. Azuma, R. Aoki, I. Suzuki, Y. Oishi, *Furukawa Denko Jiho* **1971**, *49*, 13–18.

[3] U. Domańska, M. K. Kozłowska, M. Rogalski, W. Skupiński, unpublished results.

[4] a) R. M. Hikmet, S. Callister, A. Keller, *Polymer* **1988**, *29*, 1378–1388; b) F. J. Tsai, J. M. Torkelson, *Macromolecules* **1989**, *23*, 775–784; c) S. S. Kim, D. R. Lloyd, *Polymer* **1992**, *33*, 1047–1057.

[5] a) J. Arnauts, H. Berghmans, *Polymer* **1987**, *28*, 66–68; b) P. Vandeweerdt, H. Berghmans, Y. Tervoort, *Macromolecules* **1991**, *24*, 3547–3552; c) J. Arnauts, R. De Cooman, P. Vandeweerdt, R. Koningsveld, H. Berghmans, *Thermochim. Acta* **1994**, *238*, 1–16; d) J. Arnauts, H. Berghmans, R. Koningsveld, *Makromol. Chem.* **1993**, *194*, 77–85.

[6] a) Ch. Pan, M. Radosz, *Ind. Eng. Chem. Res.* **1998**, *37*, 3169–3179 and references therein; b) Ch. Pan, M. Radosz, *Fluid Phase Equilib.* **1999**, *155*, 57–73 and references therein.

[7] a) V. I. Harismiadis, D. P. Tassios, *Ind. Eng. Chem. Res.* **1996**, *35*, 4667–4681; b) A. Saaiva, G. M. Kontogeorgis, V. I. Harismiadis, A. Fredenslund, *Fluid Phase Equilib.* **1996**, *115*, 73–93.

[8] a) T. L. Lindvig, L. L. Hestkjaer, A. F. Hanse, M. L. Michelsen, G. M. Kontogeorgis, *Fluid Phase Equilib.* **2002**, *194–197*, 663–673; b) I. A. Kouskoumvekaki, M. L. Michelsen, G. M. Kontogeorgis, *Fluid Phase Equilib.* **2002**, *202*, 5325–5335.

[9] T. Asanuma, Y. Nishimori, M. Ito, N. Uchikawa, T. Shiomura, *Polym. Bull.* **1991**, *25*, 567–570.

[10] D. W. Van Krevelen, *Properties of Polymers*, Elsevier, New York, **1990**, pp. 84, 86, 87.

[11] a) J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents: Physical Properties, Methods of Purification*, Wiley Interscience, New York, **1986**; b) U. Domańska, J. Łachwa, *J. Chem. Thermodyn.* **2000**, *32*, 857–875; c) P. L. Huyskens, M. C. Haulait-Pirson, *J. Mol. Liquids* **1985**, *31*, 153–176; P. L. Huyskens, M. C. Haulait-Pirson, G. G. Siegel, F. Kapuku, *J. Phys. Chem.* **1988**, *92*, 6841–6847; d) E. F. Mayer, C. A. Holtz, *J. Chem. Eng. Data* **1976**, *21*, 274–281; e) A. F. M. Barton, *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, CRC Press, Boca Raton, **1985**.

[12] P. B. Choi, E. McLaughlin, *AIChE J.* **1983**, *29*, 150–153.

[13] a) G. M. Wilson, *J. Am. Chem. Soc.* **1964**, *86*, 127–130; b) D. S. Abrams, J. M. Prausnitz, *AIChE J.* **1975**, *21*, 116–128; c) H. Renon, J. M. Prausnitz, *AIChE J.* **1968**, *14*, 135–144; d) U. Domańska, *Fluid Phase Equilib.* **1989**, *46*, 223–248; e) T. Hofman, I. Nagata, *Fluid Phase Equilib.* **1986**, *25*, 113–128.

[14] D. Marquardt, *J. Soc. Appl. Math.* **1963**, *11*, 431–441.

[15] Y.-J. Sheng, A. Z. Panagiotopoulos, S. K. Kumar, I. Szleifer, *Macromolecules* **1994**, *27*, 400–421.

[16] R. P. Danner, M. S. High, *Handbook of Polymer Solution Thermodynamics*, Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York, **1993**, pp. 42–48.

[17] a) G. M. Kontogeorgis, E. C. Voutsas, D. P. Tassios, *Chem. Eng. Sci.* **1996**, *51*, 3247–3255; b) G. M. Kontogeorgis, A. Fredenslund, D. P. Tassios, *Ind. Eng. Chem. Res.* **1993**, *32*, 362–372; c) G. M. Kontogeorgis, A. Saaiva, A. Fredenslund, D. P. Tassios, *Ind. Eng. Chem. Res.* **1995**, *34*, 1823–1834.

[18] U. Domańska, *Fluid Phase Equilib.* **1986**, *26*, 201–220.

Received: March 30, 2004
Revised: August 12, 2004