

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

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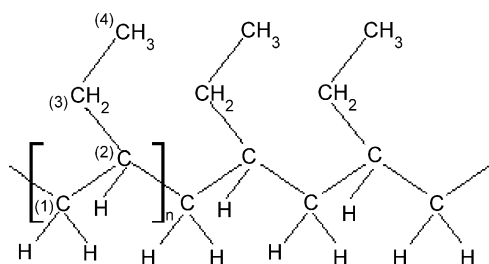


Fig. 1. The chemical structure of the isotactic poly(1-butene).

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 $T_{fus,1}(II)$ (K) [1], solid–solid transition temperature (Form II \rightarrow I) $T_{tr,1}$ (K) [1], molar volume of Form II per unit $V_{m1}(II)^{298.15K}$ (cm³ mol⁻¹) [1], molar volume of Form II per unit (this work) $V_{m1}(II)^{293.15K}$ (cm³ mol⁻¹), melting temperature of Form I $T_{fus,1}(I)$ (K) [1], molar volume of Form I per unit $V_{m1}(I)^{298.15K}$ (cm³ mol⁻¹) [1]

\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$	u	$T_{fus,1}(II)$	$T_{tr,1}$	$V_{m1}(II)^a$	$V_{m1}(II)^b$	$T_{fus,1}(I)$	$V_{m1}(I)^a$
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.

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