



Thermodynamics of poly(benzyl methacrylate)–probe interactions at different temperatures by using inverse gas chromatography



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ARTICLE INFO

Article history:

Received 6 December 2013

Received in revised form 3 April 2014

Accepted 6 April 2014

Available online 28 April 2014

Keywords:

Poly(benzyl methacrylate)
Inverse gas chromatography
Thermodynamic properties

ABSTRACT

In this study, some thermodynamic properties of poly(benzyl methacrylate) (PBzMA) were studied by using the inverse gas chromatography (IGC) technique. The retention times (t_r) of probes were determined from the interactions with PBzMA of four groups of solvents with different chemical natures and polarities. Then, specific volume (V_g^0) values were determined for each probe molecules. The glass transition temperature (T_g) of PBzMA was found as 323 K from inverse gas chromatography measurements. Under the glass transition temperatures adsorption heat (ΔH_a) and above the glass transition molar heat (ΔH_1^S), free energies (ΔG_1^S) and entropies (ΔS_1^S) belonging to sorption for every probe were calculated from inverse gas chromatography measurements. The partial molar heat (ΔH_1^∞), partial molar free energy (ΔG_1^∞), Flory–Huggins interaction parameter (χ_{12}^∞) and weight fraction activity coefficient (a_1/w_1)[∞], values for infinite dilute solutions were calculated for polymer–probe systems. The solubility parameter (δ_2) of the polymer was obtained from the slope and intercepts of Flory–Huggins interaction parameter (χ_{12}^∞) graphs with solubility parameters (δ_1) of probes.

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1. Introduction

The methacrylate polymers are widely used for a variety of applications such as prostheses, contact lenses, adhesives, and coating [1]. 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 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 [2]. As molecular weights of polymeric substances are very high and polymeric substances are non-volatile, the inverse gas chromatography (IGC) method has been used extensively to investigate properties of those substances instead of normal gas chromatography. IGC was developed by Smidrod and Guillet [3] and has been applied to many polymeric systems.

The few methods that exist to investigate polymer–solvent interactions such as vapor sorption and membrane osmometry are difficult and time-consuming experiments [4]. In addition, the amount of polymer used in the inverse gas chromatography technique is less compared to other methods as the formulas are derived from traces of solvent. For that reason, quantitative results about thermodynamic interactions of polymer–solvent systems can be obtained as soon as possible, by using a small amount of polymer [5]. Despite this, inverse gas chromatography is a fast, reliable, accurate, simple and commonly-used technique [6].

IGC is widely used for the measurement of thermodynamic properties of various materials, over a wide temperature range [7–14]. The basic tenet of IGC is that the stationary phase of the chromatographic column is the object of investigation while probes of known physicochemical properties are injected [7]. IGC provides insight into the thermodynamic properties of both traditional and novel materials like green solvents [15] and dendritic polymers [16,17].

Some thermodynamic quantities such as adsorption heat (ΔH_a), sorption enthalpy (ΔH_1^S), sorption free energy (ΔG_1^S) and entropy (ΔS_1^S), the partial molar heat of mixing (ΔH_1^∞), the partial molar free energy of mixing (ΔG_1^∞), Flory–Huggins interaction

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parameter (χ_{12}^∞) and weight fraction activity coefficient (a_1/w_1) $^\infty$ can be obtained with the IGC method.

The probe specific retention volumes, V_g^0 , corrected to 0 °C were calculated from the standard chromatographic relationship

$$V_g^0 = \left[\frac{(\Delta t F 273.2)}{(w T_r)} \right] 3/2 \left[\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \right] \quad (1)$$

where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe, t_p , and the retention times of the substances that stay in mobile phase while moving along the column and do not pass to stationary phase, so the retention times (t_g) of inert gas, F is the flow rate of the carrier gas measured at room temperature (T_r), w is the mass of the polymeric stationary phase and P_i and P_0 are the inlet and outlet pressures, respectively. The molar heat (enthalpy) (ΔH_1^S) and the molar free energy (ΔG_1^S) of sorption of the probe absorbed by the polymer are given by the following equations [18–21].

$$\Delta H_1^S = -R \left[\frac{\partial \ln(V_g^0)}{\partial(1/T)} \right] \quad (2)$$

$$\Delta G_1^S = -RT \ln \left[\frac{(M_1 V_g^0)}{(273.2 R)} \right] \quad (3)$$

where R is the ideal gas constant and M_1 is molecular weight of solvent. We calculate the entropy of sorption of solutes by incorporating Eqs. (2) and (3) as follows:

$$\Delta S_1^S = \frac{(\Delta H_1^S - \Delta G_1^S)}{T} \quad (4)$$

The adsorption enthalpy of probes adsorbed by the PBzMA, ΔH_a , is given by the following equation [9].

$$\frac{\partial \ln(V_g^0)}{\partial(1/T)} = \frac{-\Delta H_a}{R} \quad (5)$$

where ΔH_a is the adsorption enthalpy. The weight fraction activity coefficient (a_1/w_1) $^\infty$, the partial molar free energy (ΔG_1^∞) and the average partial molar enthalpy (ΔH_1^∞) at infinite dilution of the organic solvents were calculated according to the following equations. Heats of vaporization (ΔH_v) for the probes were obtained from the heat of solution and heat of mixing by using the following relationship [22–30]:

$$\left(\frac{a_1}{w_1} \right)^\infty = \ln \left[\frac{(273.2R)}{(P_1^0 V_g^0 M_1)} \right] - P_1^0 \left[\frac{(B_{11} - V_1)}{(RT)} \right] \quad (6)$$

$$\Delta G_1^\infty = RT \left(\frac{a_1}{w_1} \right)^\infty \quad (7)$$

$$\Delta H_1^\infty = R \left[\frac{\partial \ln(a_1/(w_1))^\infty}{\partial(1/T)} \right] \quad (8)$$

$$\Delta H_v = \Delta H_1^\infty - \Delta H_1^S \quad (9)$$

where B_{11} is the second virial coefficient of the organic solute in the gaseous state and P_1^0 is the vapor pressure of the probes at temperature, T (K) and M_1 is the molecular weight of the probe. The values of P_1^0 and B_{11} have been calculated in the literature [23]. The molar volume of the solute, V_1 , was calculated by using the following relationship [24].

$$V_1 = \frac{V_c}{q_r} \quad (10)$$

where V_c is the critical molar volume and q_r is the reduced density of the solute given as

$$q_r = 1.20 + (5.565 - 11.03z_c) \left(1 - \frac{T}{T_c} \right)^{(0.8z_c + 0.31)} \quad (11)$$

where z_c is the critical compressibility factor and T_c is critical temperature.

The Flory–Huggins parameter (χ_{12}^∞) characterizing the interaction of a vapor-phase probe with a polymer is determined by the following equation.

$$\chi_{12}^\infty = \ln \left[\frac{(273.2 R v_2)}{(P_1^0 V_g^0 V_1)} \right] - P_1^0 \left[\frac{(B_{11} - V_1)}{(RT)} \right] - 1 \quad (12)$$

where R is the gas constant, v_2 is the specific volume of the polymer. The solubility parameter of the probe is calculated from the relationship [25]

$$\delta_1 = \left[\frac{(\Delta H_v - RT)}{V_1} \right]^{1/2} \quad (13)$$

where ΔH_v is the molar enthalpy of vaporization for the probe at temperature T .

The solubility parameter of the polymer (δ_2) can be calculated by using the following relation:

$$\left[\left(\frac{\delta_1^2}{RT} \right) - \left(\frac{\chi_{12}^\infty}{V_1} \right) \right] = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \frac{\delta_2^2}{RT} \quad (14)$$

If the left hand side of this equation is plotted against δ_1 , a straight line with a slope of $2\delta_2/(RT)$ and an intercept of $(-\delta_2^2/(RT))$ is obtained. Then δ_2 can be determined from both the slope and intercept of the straight line [20].

In this paper, we examined the interactions of poly(benzyl methacrylate) with solute probes of alcohols, *n*-alkanes, ketones and aromatics by using IGC in the temperature range 313–413 K. Also, we determined the solubility parameter (δ_2) of the polymer of PBzMA by using IGC techniques. The glass transition temperature (T_g) of PBzMA was found to be 323 and 329 K from IGC and DSC measurements, respectively.

2. Experimental

2.1. Materials

Fourteen polar and non-polar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. Methanol, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, ethanol, 2-propanol, *n*-butanol, acetone, ethyl-methylketone, benzene, toluene and *o*-xylene were supplied from Sigma-Aldrich Chemical Co. (Istanbul, Turkey) and used without further purification. Poly(benzyl methacrylate) was supplied by Acros Organics in powder form and its CAS number was 25085-83-0 (Belgium). The weight molecular mass of poly(benzyl methacrylate) was 70.000 g/mol. Chromosorb W (45–60 mesh) was supplied by Sigma Chemical Co. (Germany).

2.2. Instrumentation and procedure of thermodynamic studies

A Shimadzu GC-2010 model gas chromatograph equipped with a dual flame ionization detector was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a non-interacting marker to correct for dead volume in the column [24]. The net retention time was determined from the positions of the peak maxima for methane and for the probe solvents at each temperature. Pressures at the inlet of the column, read from IGC, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured with a soap bubble flow meter at the end of the column. A flow rate of about 15 cm³/min was used throughout our experiments. The glass tubing (3.2 mm i.d. × 2.1 m) was washed with acetone and was annealed prior to use. A column packing material was prepared by coating 45–60 mesh size Chromosorb W treated with polymer. For

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