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Some thermodynamic quantities were obtained for the interactions of poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] with alcohols, ketones, acetates, aromatics and alkanes by inverse gas chromatography in the temperature range 160-200 °C. The specific retention volumes, V_g°, weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞, Flory-Huggins thermodynamic interaction parameters, χ_{12}^∞ between polymer and solvents were determined. The partial molar free energy, $\Delta\bar{G}_1^\infty$, the partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ at infinite dilution and the solubility parameters of the polymer, δ_2 were calculated.

Key words: Poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate], inverse gas chromatography, polymer-solvent interactions.

Introduction

DiPalo-Baranyi and Guillet[1] have recently shown that inverse gas chromatography, using a polymer as the stationary phase, can be a simple method for estimating the solubility parameters of polymers. In principle, the technique of gas-liquid chromatography should be ideally suited for determining solubility parameters directly for polymer substrates, since the method yields energies of mixing of polymer-solute systems. Moreover, the method is not restricted to the study of polymer-solvent systems but can also be used to investigate interactions between polymers and non-solvents. In addition, the system is amenable to high as well as to low temperatures[2−6]. For some acrylate polymers [poly (methyl methacrylate), poly (ethyl methacrylate), poly (isobutyl methacrylate) and poly (-tert-butyl methacrylate)]-solvents systems[5] have been studied by the IGC method. For these polymers some thermodynamic parameters such as, $\Omega_1^\infty, \chi_{12}^\infty, \Delta\bar{G}_1^\infty$ and $\Delta\bar{H}_1^\infty$ have been determined by Kaya and Özdemir[5].

In this study, we examined the interactions of Poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] (PMCHEMA) with alcohols, ketones, acetates, aromatics and alkanes as solute probes by the IGC method. As solute probes, methanol, ethanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetae, benzene, toluene, o-xylene, n-octane, n-nonane, n-decane, n-undecane and n-dodecane were chosen. Ketones, acetates and aromatics (except o-xylene) are good solvents but alkanes and o-xylene are non-solvents for PMCHEMA. The polymer-solvent interaction parameters and the solubility parameter of the polymer were determined.

Data Reduction

The specific retention volumes of the probes, V_g°, corrected to O°C were calculated from the standard chromatographic relation:

$$V_g^0 = \Delta t F 273.2/wT_r 3/2[(P_i/P_0)^2 - 1/(P_i/P_0)^3 - 1] \quad (1)$$

where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe, t_p, and the methane, t_g, 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[7–12].

The weight fraction activity coefficient, Ω_1^∞, the average partial molar enthalpy $\Delta\bar{H}_1^\infty$ and the partial molar free energy, $\Delta\bar{G}_1^\infty$ at infinite dilution of the organic solvents were calculated according to the following equations[4].

$$\Omega_1^\infty = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/RT] \quad (2)$$

$$\Delta\bar{H}_1^\infty = R\partial \ln(\Omega_1^\infty)/\partial(1/T) \quad (3)$$

$$\Delta\bar{G}_1^\infty = RT \ln \Omega_1^\infty \quad (4)$$

where B_{11} is the second virial coefficient of the organic solute in the gaseous state and P_1^0 is the vapour pressure of the probes at temperature $T(K)$.P_1^0 and B_{11} were calculated as in the literature[13].
The molar volume of the solute V_1 was calculated from the following relation[15]:

$$V_1 = V_c/\rho_r \quad (5)$$

where V_c is the critical molar volume and ρ_r is he reduced density of the solute given as:

$$\rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)^{0.8Z_c + 0.31} \quad (6)$$

where z_c is the critical compressibility factor.

The Flory-Huggins parameters, χ_{12}^∞ characterizing the interactions of the vapour-phase probe with polymer were determined from the following equation:

$$\chi_{12}^\infty = Ln(273.2Rv_2/V_g^0 V_1 P_1^0) - 1 - P_1^0/RT(B_{11} - V_1) \quad (7)$$

where R is the gas constant, v_2 is the specific volume of the polymer. The solubility parameter of the probe was calculated from the relation[15–18]:

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \quad (8)$$

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

$$[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \quad (9)$$

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. The solubility parameter of the polymer δ_2 can be determined from both the slope and intercept of the straight line[1].

Experimental

Materials

Fourteen polar and non-polar probes were used in this study. They were selected to provide several groups of chemically different nature and polarity. N-Octane, n-nonane, n-decane, n-undecane and n-dodecane were supplied from the Aldrich Chemical Co. and methanol, ethanol, acetone, ethyl methyl ketone, (EMK), methyl acetate, ethyl acetate, benzene, toluene and o-xylene were supplied from the Merck Chemical Co. as chromatographic grade. Chromosorb-W (60-80 mesh) was supplied from the Sigma Chemical Co. 1,4-Doxane and n-hexane (Aldrich) were dried over anhydrous $MgSO_4$ before use. Mesitylene (Aldrich) was dried over sodium and freshly distilled before use. KOH (Aldrich) was used as received. 1-chloro-2,3-epoxy-5-methyl-5-hexene was received from the Institute of Polymeric Materials in the Academy of Science of Azerbaijan and freshly distilled before use. The monomer [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] was synthesized by the method given for the epoxy-carboxy reactions[19–23].

Polymerization of the monomer

The monomer [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] was freed from the inhibitor by washing with dilute KOH solution followed by reacting with distilled water and drying over anhydrous $MgSO_4$. Appropriate amounts of 2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate and 1,4-dioxane and benzoyl peroxide (0.2 % of the weight of the monomer) were placed in a reaction tube and purged with Ar for about 10 min. The sealed tube was kept at 60 °C for 15 h. PMCHEMA was purified by reprecipitation in n-hexane from 1,4-dioxane solution and finally dried under vacuum. The yield was about 75 % for PMCHEMA.

Analysis

Molecular weight of PMCHEMA was determined by gel permeation chromatography using polystyrene and tetrahydrofurane as standard and solvent, respectively, Weight average molecular weight of PMCHEMA was found to be 200000 g/mol (polydispersity: 2.38) for PMCHEMA[23]. The glass transition temperature of PMCHEMA was to be about 137 °C with a Shimadzu differential scanning calorimeter (DSC) DSC-50 model. The monomer and homopolymer were characterized by using Mattson FT-IR-1000 and Varian the ^{1}H-and ^{13}C-NMR spectra (200 MHz) at 25 °C $CDCl_3$ as solvent[23].

Density was measured by determining the weight of a volume-calibrated pycnometer filled with a liquid of known density containing a certain quantity of the polymer sample[24]. The density of PMCHEMA was found to be 1.042 g/cm^3 by pycnometric measurement.

Instrumentation and procedure

For gas chromatography a Shimadzu GC-14B model equipped with dual flame ionization detectors (FID) was used. A dried nitrogen gas (research grade) was used as a crarier gas. Methane was used as a nonointeracting marker to correct for dead volume in the column. The net retention time was determined from the positions of the peak maxima for the methane and for the probe molecule at each column temperature. Pressures at the inlet of the column, read from a mercury manometer as mmHg were used to compute corrected retention volumes by the usual procedures. The flow rates were measured from the end of the column with a soap bubble flow meter. A flow rate of about 20 mL/min^{-1} was used throughout our experiment. Spiral glass tubing (3.2 mm I.D.x1.1m.) was washed with methylene chloride and was annealed prior to use. Column packing material was prepared by coating 60-80 mesh size Chromosorb-W with PMCHEMA. Then, 0.2430 g of PMCHEMA was dissolved in 25 mL of tetrahydrofurane and 2.9000 g of the solid supporting material was then added to this solution and stirred. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a rotary evaporator. The prepared material was packed into the spiral glass tubing[15]. The column was conditioned at a temperature above the glass transition temperature, Tg and fast carrier gas (N_2) flow rate for 24 h prior to use. The probes were injected onto the column with 1μL Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume of 0.2μL was selected. The retention times of the probes were measured by using a Shimadzu CR6A Chromatopac model integrator. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide[25].

Results and Discussion

The specific retention volumes, V_g^0 of 14 probes were obtained by using one loading PMCHEMA at a series of temperatures (160, 170, 180, 190 and 200 °C). The probes with different chemical natures and polarities were selected for this study. The V_g^0 values of these probes were calculated according to equation (1) and are given in Table 1. The specific retention volumes, V_g^0 of the probes decreased with increasing column temperature.

The Ω_1^∞ and χ_{12}^∞ values obtained from equations (2) and (7), respectively, are shown in Table 2. Our Ω_1^∞ values for n-alkanes, o-xylene, ketones, methanol and acetates at 160 °C are also in good agreement with the values given by Kaya and Özdemir[15] for poly (methyl methacrylate) at 160 °C (Table 2). As mentioned above, according to Ω_1^∞, n-alkanes and o-xylene are non-solvents but acetates, ketones, benzene, toluene and alcohols (at high temperature) are good solvents for PMCHEMA. In all the series, the values of Ω_1^∞ decreased with increasing temperature. The largest weight fraction activity coefficients, Ω_1^∞ were found for the n-alkanes. Similar trends were observed for the calculated χ_{12}^∞ parameters (Table 2).

It has been proposed that Ω_1^∞ values greater than 5 are indicative of poor polymer solute systems while lower values characterize good solubility for such a system[26].

Values of χ_{12}^∞ greater than 0.5 represent unfavourable polymer-solvent interactions while values lower than 0.5 indicate favourable interactions in dilute polymer solutions[27]. It can be seen from these values (in Table 2) that acetates, aromatics (except o-xylene), alcohols (at high temperature) and ketones are good solvents but alkanes and o-xylene are non-solvents for PMCHEMA. The interaction parameters, χ_{12}^∞, the partial molar free energy of mixing, $\Delta\bar{G}_1^\infty$ and the weight fraction activity coefficients, Ω_1^∞ were found to be dependent on the number of carbons in the series (except alcohols). That is these values increased with increasing number of carbons in the series. Moreover, these values decreased with increasing column

temperature in all the series.

Table 1. Changes in specific retention volumes V_g^0 (mL/g) of some alcohols, ketones, acetates, aromatics and alkanes at 160-200 °C using poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] as stationary phase

Probe/T(°C)	160	170	180	190	200
Methanol	5.13	4.91	5.02	4.99	4.67
Ethanol	5.40	5.95	5.26	5.23	4.90
Acetone	5.80	5.44	5.68	5.40	5.08
Ethyl methyl ketone	7.67	7.22	6.90	6.17	5.98
Methyl acetate	5.56	5.37	5.51	5.23	5.01
Ethyl acetate	6.60	6.34	6.27	5.89	5.59
Benzene	8.47	7.54	7.10	6.52	6.20
Toluene	10.63	9.79	8.89	8.40	7.77
o-Xylene	17.45	14.87	13.84	11.38	9.68
n-Octane	7.08	6.65	6.61	6.22	5.75
n-Nonane	9.41	8.61	7.79	7.41	6.94
n-Decane	14.08	11.50	10.95	9.45	7.84
n-Undecane	18.65	18.11	13.77	12.20	10.02
n-Dodecane	27.97	24.33	20.01	14.90	13.54

Table 2. Poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate]-solute interaction parameters, χ_{12}^{∞} and weight fraction activity coefficient, Ω_1^{∞}, of some alcohols, ketones, acetates, aromatics and alkanes in the range of 160-200 °C

	Ω_{12}^{∞}						χ_{12}^{∞}					
Probe/T(°C)	160	170	180	190	200	160*	160	170	180	190	200	160*
Methanol	7.96	6.72	5.33	4.45	3.98	7.85	0.783	0.718	0.466	0.258	0.117	0.644
Ethanol	7.12	5.69	3.91	3.51	2.91	-	0.633	0.518	0.114	-0.024	-0.252	-
Acetone	5.04	4.54	3.73	3.36	3.13	5.99	0.477	0.351	0.124	-0.010	-0123	0.254
EMK	5.54	5.08	4.11	4.04	3.57	4.58	0.535	0.436	0.204	0.175	0.030	0.037
Methyl acetate	4.24	3.75	3.15	2.88	2.63	5.76	0.403	0.257	0.051	-0.072	-0.209	0.261
Ethyl acetate	4.89	4.26	3.65	3.29	3.01	6.83	0.518	0.362	0.178	0.061	-0.060	0.463
Benzene	6.27	5.74	4.98	4.48	3.94	-	0.748	0.651	0.498	0.379	0.235	-
Toluene	6.88	6.02	5.35	4.54	3.97	-	0.853	0.713	0.586	0.418	0.258	-
o-Xylene	8.20	7.68	6.56	6.49	6.26	10.03	0.995	0.920	0.758	0.740	0.698	1.001
n-Octane	11.78	10.09	8.28	7.24	6.52	12.98	1.152	0.991	0.780	0.645	0.531	1.170
n-Nonane	14.75	12.71	11.19	9.47	8.23	19.91	1.389	1.233	1.099	0.927	0.780	1.668
n-Decane	16.33	15.43	12.52	11.43	10.96	25.00	1.538	1.475	1.211	1.163	1.117	1.919
n-Undecane	20.41	15.75	15.82	13.78	13.09	40.08	1.791	1.524	1.520	1.378	1.321	2.447
n-Dodecane	22.52	19.00	17.39	17.12	14.75	49.32	1.905	1.727	1.616	1.580	1.454	2.676

EMK: ethyl methyl ketone, *: Reference:15

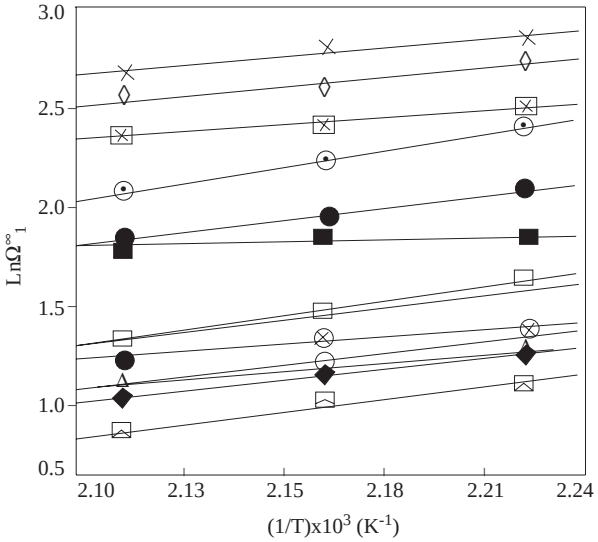

Figure 1. Variation in logarithm of weight fraction activity coefficients, Ω_1^∞ with reciprocal of absolute column temperature, $1/T(K^{-1})$ for poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and some solutes: □: methanol, O: ethanol, Δ: acetone, ⊗: ethyl methyl ketone, ⊠: methyl acetate, ♦: ethyl acetate, ★: benzene, ▽: toluene, ■: o-xylene, •:n-octane, ⊙:n-nonane, ⊠: n-decane, ◊: n-undecane, ×:n-dodecane

The $\Delta\bar{H}_1^\infty$ values of the probes were found from the slope of straight lines in Figure 1 and the partial molar free energy of mixing, $\Delta\bar{G}_1^\infty$ calculated according to equation (4) and are given in Table 3. The $\Delta\bar{H}_1^\infty$ values of n-hydrocarbons and aromatics ranged from 2.78 to 6.16 kcal/mol and from 1.00 to 5.96 kcal/mol, respectively, as seen in Table 3. The $\Delta\bar{H}_1^\infty$ values for methanol and ethanol were found to be 5.76 kcal/mol while the values for methyl acetate, ethyl acetate, acetone and ethyl methyl ketone varied between 2.78 and 4.97 kcal/mol.

Table 3. Partial molar free energies of mixing, $\Delta\bar{G}_1^\infty$ (kcal/mol) and partial molar enthalpy, $\Delta\bar{H}_1^\infty$ (kcal/mol) (range 180-200° C) of poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] with some alcohols, ketones, acetates, aromatics and alkanes

	$\Delta\bar{G}_1^\infty$					$\Delta\bar{H}_1^\infty$
Probe/T(°C)	160	170	180	190	200	180-200° C
Methanol	1.79	1.68	1.51	1.37	1.30	5.76
Ethanol	1.69	1.53	1.23	1.16	1.01	5.76
Acetone	1.39	1.33	1.19	1.12	1.07	3.58
Ethyl methyl ketone	1.47	1.43	1.27	1.29	1.20	2.78
Methyl acetate	1.24	1.16	1.03	1.00	0.91	4.97
Ethyl acetate	1.37	1.28	1.17	1.10	1.04	3.97
Benzene	1.58	1.54	1.45	1.38	1.29	4.77
Tolunene	1.66	1.58	1.51	1.39	1.30	5.96
o-Xylene	1.81	1.79	1.69	1.72	1.72	1.00
n-Octane	2.12	2.04	1.90	1.82	1.76	4.57
n-Nonane	2.32	2.24	2.17	2.07	1.98	6.16
n-Decane	2.40	2.40	2.28	2.24	2.20	2.78
n-Undecane	2.60	2.43	2.49	2.41	2.42	3.78
n-Dodecane	2.68	2.59	2.56	2.63	2.53	3.38

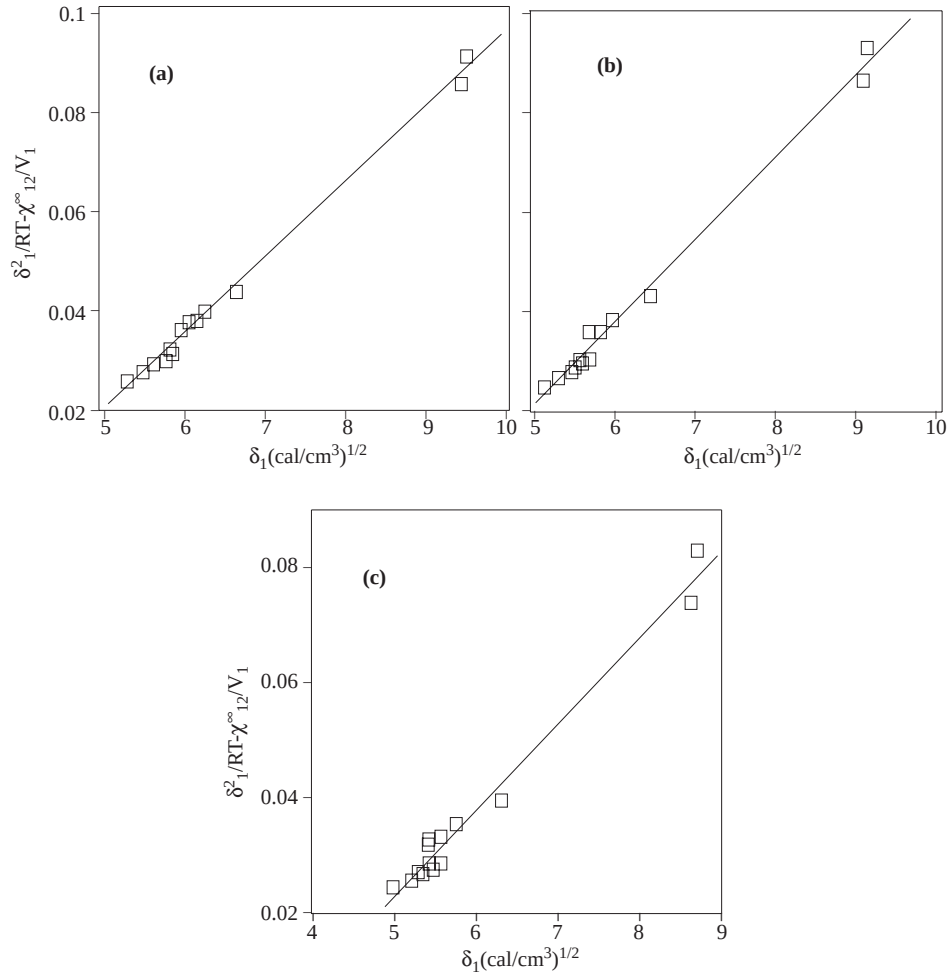

Figure 2. Variation in the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at temperatures (a)=160° C (b)=170° C (c)=180° C

Table 4. Variation in solubility parameters, δ_2 $(cal/cm^3)^{0.5}$ poly [2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] with temperature

T(°C)	slope	intercept	from slope, δ_2	from intercept, δ_2	r
160	0.0150	-0.0561	6.60	6.95	0.998
170	0.0142	-0.0530	6.25	6.83	0.996
180	0.0128	-0.0510	5.76	6.78	0.990

Since the heat of vaporization decreases and the molar volume increases with increasing temperature, the solubility parameters of compounds decrease with increasing temperature. For a polymer one expects the variation of δ_2 to be smaller than for δ_1, because of the relatively small coefficient of thermal expansion of the polymer. The solubility parameter of the polymer, δ_2 is determined from either the slope or the intercept of a straight line obtained by plotting the left-hand side of equation (9) versus δ_1. The solubility parameter of PMCHEMA was evaluated from either the solep or the intercept of Figure 2 to be 6.60 $(cal/cm^3)^{0.5}$ and 6.95 $(cal/cm^3)^{0.5}$ at 160° C, respectively. The values of solubility parameters of PMCHEMA, δ_2 decreased with increasing temperature (see Table 4). DiPaola-Baranyi and Guillet[1], Kaya et al.[11] and Yılmaz et

al.[28] have determined the solubility parameters of polystyrene and poly (methyl acrylate); poly (methyl methacrylate) and poly (ethyl methacrylate); and poly (p-chlorostyrene) to be 7.6 $(cal/cm^3)^{0.5}$ and 8.7 $(cal/cm^3)^{0.5}$; 6.85 $(cal/cm^3)^{0.5}$ 5.99 $(cal/cm^3)^{0.5}$; 7.9 $(cal/cm^3)^{0.5}$ using equation (9) at 193, 100°C and 180°C and 162°C respectively. According to these values, the IGC technique can be successfully applied to determine solubility parameters, δ_2, of polymers at high temperatures. Also the solubility parameters were determined[29] as the mean of the upper limits and lower limits of the solubility parameter using pairs of solvent-nonsolvent and the following solubility parameter, δ_2, was found to be 10.04 $(cal/cm^3)^{0.5}$ for PMCHEMA at 25°C.

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