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Physical and Thermodynamic Properties of Poly(2-phenyl-1,3-dioxolane-4-yl-methyl-methacrylate-co-ethylmethacrylate) Polymer with Inverse Gas Chromatography

M. HAMDI KARAGÖZ*, HASAN ERGE and ZÜLFIYE ILTER†
Department of Chemistry, Faculty of Science and Arts, Yüzüncü Yil University, Van, Turkey
E-mail: hamdikaragoz@hotmail.com

In this study, the physical and thermodynamic properties of poly(2-phenyl-1,3-dioxolane-4-yl-methyl-methacrylate-co-ethylmethacrylate) (PDMMA-EM) were investigated by using inverse gas chromatography. Two groups of alcohols and alkanes with different chemical natures and polarities were used to obtain some properties of (PDMMA-EM-solvent) systems. The specific retention volume, V_g^0, glass transition temperature, Tg, the sorption enthalpy, ΔH_1^S, sorption free energy, ΔG_1^S, sorption entropy, ΔS_1^S, the weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞ and Flory-Huggins interaction parameters, χ_{12}^∞, between polymer and solvents were determined in the temperature range of 333-473 K. The solubility parameters of PDMMA-EM at infinite dilution was also found by plotting the graph of $[\delta_1^2 - (\Delta G_1^\infty/V_1)]$ *versus* solubility parameters, δ_1, of probes.

Key Words: Poly(2-phenyl-1,3-dioxolane-4-yl-methyl-methacrylate-co-ethylmethacrylate), Thermodynamic properties, Inverse gas chromatography.

INTRODUCTION

Inverse gas chromatography (IGC) is a useful method for the study of some of the thermodynamic and physical properties of (polymer-solute) systems. Inverse gas chromatography has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials and to investigate polymer-polymer miscibility[1-5]. It is also a reliable method for the characterization of amorphous and semi crystalline polymers. The method is simple, fast, economical and provides valuable thermodynamic information for the characterization of polymeric substances.

Inverse gas chromatography was developed by Smidsord and Guillet[6] and has been applied to many polymeric systems. It has been shown that IGC yields information on polymer-solvent and polymer-polymer systems such as solubility parameters, interaction parameters, diffusion constants, enthalpies of mixing, surface energies and areas, adsorption isotherms, glass transition temperatures, melting point temperatures and degrees of crystallinity. Furthermore, IGC is capable of obtaining physicochemical properties, the structure and chemical interactions of macromolecules[7-14].

†Department of Chemistry, Faculty of Science and Arts, Firat University, Elazig, Turkey.

Dipaola-Baranyi and Guillet[15] have shown that IGC, using a polymer as the stationary phase, can be a simple method for estimating solubility parameters of polymers. In this study, the polymer-solvent interaction parameters and the solubility parameters of poly(2-phenyl-1,3-dioxolane-4-yl-methyl-methacrylate-co-styrene) (PDMMA-EM) by using IGC in the temperature range 60-200 ºC were examined.

Data reduction: The probe specific retention volumes, V_g^0, are calculated from the standard chromatographic relation[16]:

$$V_g^0 = (F \times 273.2 \times t_r) / W \times T \times 3/2 \times [[(P_i/P_0)^2 - 1] / [(P_i/P_0)^3 - 1] \quad (1)$$

where t_r is the retention times of probe, F is the flow rate of the carrier gas measured at room temperature, W is the mass of the polymeric stationary phase, T is the column temperature, P_i and P_0 are 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, is given by the following equation[17]:

$$\Delta H_1^S = - R\partial V_g^0/\partial(1/T) \quad (2)$$

$$\Delta G_1^S = -RT \ln (M_1 V_g^0/273.2R) \quad (3)$$

By incorporating eqns. 2 and 3, we calculated the entropy of sorption of solutes as follows:

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

where V_g^0 is the probes specific retention volume, T is the column temperature (K), M_1 is the molecular weight of probe and R is the gas constant. The adsorption enthalpy of probes adsorbed by the polymer, ΔH_a, is given by the following equation[18]:

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

The weight fraction activity coefficient, Ω_1^∞, of the solute probe at infinite dilution is calculated according to the following equation[19]:

$$\Omega_1^\infty = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/RT] \quad (6)$$

(PDMMA-ST-solute) interaction parameters, χ_{12}^∞, at infinite dilution of different solutes used in this work are defined by the following equation[6]:

$$\chi_{12}^\infty = \ln [(273.2 \times R \times V_2)/(V_g^0 \times V_1 \times P_1^0)] - 1 - P_1^0/RT(B_{11} - V_1) \quad (7)$$

where R is the gas constant, V_2 is the specific volume of the polymer, V_1 is the molar volume of the solute, P_1^0 is the vapour pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. V_1, P_1^0 and B_{11} were calculated at the column temperature.

Second virial coefficients, B_{11}, were computed using the following equation[15]:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (8)$$

where V_c and T_c are the critical molar volume and the critical temperature of the solute, respectively and n is the number of carbon atoms in the solute.

The solubility parameters of polymers, δ_2, can be determined by using the following relation[10]:

$$\delta_1^2 - \Delta G_1^\infty/V_1 = 2\,\delta_1\delta_2 - \delta_2^2 \quad (9)$$

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

If the left-hand side of this equation is plotted against δ_1, then a straight line with a slope of $(2\delta_1\delta_2)$ and an intercept of $-\delta_2^2$ is obtained. Solubility parameters of polymer, δ_2, can be calculated from both the slope and intercept of straight line[15,20,21].

EXPERIMENTAL

Molecular probes such as ethyl alcohol (C_2), 1-propyl alcohol (C_3), 1-butyl alcohol (C_4), *n*-hexane (C_6), *n*-heptane (C_7), *n*-octane (C_8) used were supplied from Merck Chemical Co. as chromatographic grade. Poly(2-phenyl-1,3-dioxolane-4-yl-methyl-methacrylate-co-styrene) was supplied from the Chemistry Department of Firat University, Elazig, Turkey and Chromosorb W (80-100 mesh) was supplied from Sigma Chemical Co.

Instrumentation and Procedure: The number average molecular weight (M_n) and mass average molecular weight (M_w) of (PDMMA-EM) are 365361 g/mol and 1215483 g/mol, respectively. The amount of polymer in charging material consists of 10 % of the whole material. The glass transition temperature, T_g, of (PDMMA-EM) was found to be about 363 K.

A Shimadzu GC-14A model gas chromatograph equipped with a dual flame ionization detector (FID) was used in this analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Pressures (mm-Hg) at the inlet and outlet of the column, read from mercury manometer, were used to compute corrected retention volumes by standard procedure. The flow rate was measured at the end of the column with a soap bubble flow meter. A flow rate of about 20 mL min^{-1} was used throughout in present experiment. The column consisted of a 1 m copper pipe with 3.2 mm ID. The copper column was washed with distilled water and benzene and then was dried. A column packing material was prepared by coating 80-100 mesh size Chromosorb W with DMMA: Polymer was dissolved in 100 mL benzene (Merck) and the solid supporting material was then added to this solution and stirred. The prepared material was packed into the copper column (3.2 mm IDx1 m). The column was conditioned at 200 ºC with a fast carrier gas flow rate for 48 h prior to use. Probes were injected into the column with 1 µL Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume of 0.3 µL was selected. The retention times of the probes were measured by using chromatopac CR6A (Shimadzu).

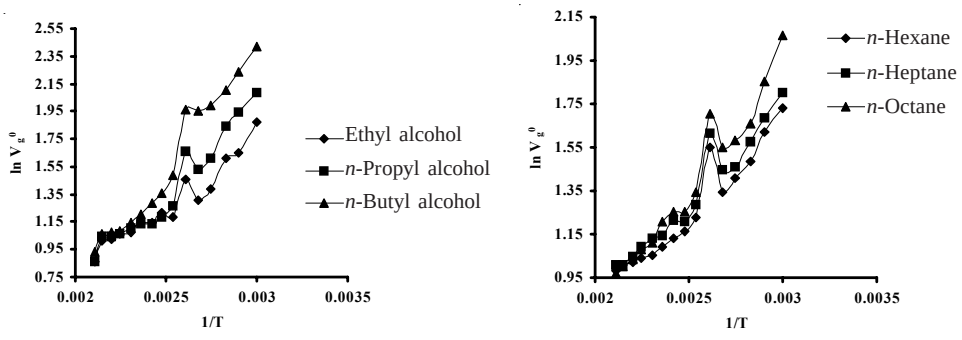
RESULTS AND DISCUSSION

The specific retention volumes, V_g^0, of probes were obtained by using one loading of polymer and at a series of temperatures. The V_g^0 values of these probes were calculated according to the eqn. 1. The retention volume was confirmed to be independent of solute sample size in all cases studied[22]. The specific retention volume data are essential in the determination of physico-chemical or thermodynamic properties

of a polymer by IGC. In order to obtain these data, it is necessary to know the amount of the polymer that has been coated onto the support, gas flow rate, column pressures and temperature. The specific retention volumes, V_g^0, are given in Table-1. As can be seen from this table, the specific retention volumes of probes on PDMMA-EM varied for each probes with temperature and decreased with increasing temperature. The glass transition temperature, T_g, of (PDMMA-EM) are given in Fig. 1. As can be seen from Fig. 1, the glass transition temperature, T_g, of (PDMMA-EM) was found to be about 363 K.

TABLE-1
VARIATION IN SPECIFIC RETENTION VOLUMES, V_g^0 (mL g), OF ALCOHOLS AND ALKANES WITH TEMPERATURE USING PDMMA-EM AS STATIONARY PHASE

T (K)	Ethyl alcohol	1-Propyl alcohol	1-Butyl alcohol	*n*-Hexane	*n*-Heptane	*n*-Octane
333	6.4743	8.0552	11.179	5.6459	6.0599	7.9043
343	5.2235	7.0002	9.3456	5.0459	5.4012	6.3962
353	4.9774	6.2803	8.1843	4.4095	4.8438	5.2446
363	3.9887	5.0252	7.3807	4.0829	4.3028	4.8681
373	3.6775	4.6044	7.086	3.8379	4.2456	4.724
383	4.2920	5.2362	7.1533	4.7190	5.0294	5.4951
393	3.2689	3.5368	4.421	3.4028	3.6172	3.8315
403	3.3571	3.2554	3.8658	3.2045	3.3571	3.5097
413	3.1498	3.1006	3.6173	3.1006	3.3713	3.4943
423	3.1442	3.0976	3.3305	2.9812	3.1442	3.3539
433	2.9365	3.0248	3.1352	2.8703	3.091	3.0468



(a) (b)

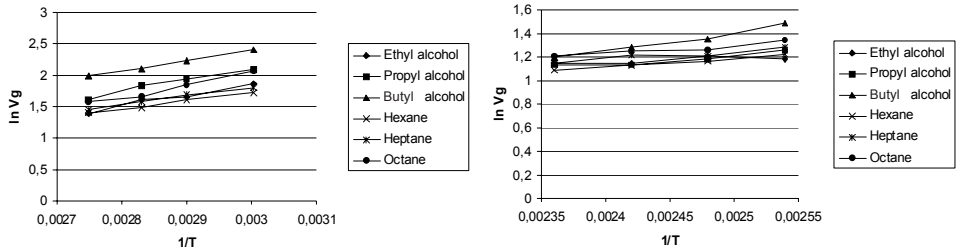
Fig. 1a and b. Variation of logarithm of specific retention volumes, V_{g0} (mL g) with reciprocal of absolute column temperature and he glass transition temperature, T_g, for PDMMA-EM, (a): for alcohols, (b): for alkanes

ΔH_a and ΔH_1^S values of PDMMA-EM-probe systems were calculated by plotting $\ln V_g^0$ against $1/T(K^{-1})$ using eqns. 5 and 2, respectively. Table-2 shows experimentally obtained sorption heats, ΔH_1^S and adsorption heats ΔH_a, in the temperature range of

373-423 K and 333-363 K, respectively. ΔH_a and ΔH_1^S values of probes found from the slope of straight lines in Fig. 2a and b. ΔH_a values were found to be positive[23]. At the temperatures below T_g temperature, positive ΔH_a values indicate that polymer do not interact with probes. As can be seen in Table-2, ΔH_a of alcohols decrease as the carbon number increases, but ΔH_a of alkanes show an increase as the carbon number of alkanes increases. ΔG_1^S and ΔS_1^S values of (PDMMA-EM-probe) systems were calculated from eqns. 3 and 4, respectively and given in Table-2.

TABLE-2
ADSORPTION ENTHALPY, ΔH_a (cal/mol), PARTIAL MOLAR ENTHALPY, ΔH_1^S (cal/mol), PARTIAL MOLAR FREE ENERGY OF MIXING, ΔG_1^S (cal/mol) AND PARTIAL MOLAR ENTROPY, ΔS_1^S (cal/mol), OF (PDMMA-EM) WITH ALCOHOLS AND ALKANES

Probe / T (K)	ΔH_a (cal/mol)	ΔH_1^S (cal/mol)	ΔG_1^S (cal/mol)		ΔS_1^S (cal/mol)	
	333-363	393-423	393	403	393	403
Ethyl alcohol	934.86	-3614.9	3905.7	3983.7	-19.13	-9.81
1-Propyl alcohol	1642.50	-3620.3	3636.6	3795.5	-18.47	-9.81
1-Buthyl alcohol	2678.60	-3309.3	3298.5	3489.9	-16.81	-12.82
n-Hexane	820.40	-2638.1	3385.2	3519.5	-15.33	-7.63
n-Heptane	1343.90	-2706.1	3219.8	3361.5	-15.08	-6.97
n-Octane	911.40	-3967.2	3072.5	3221.0	-17.91	-6.85



(a) (b)

Fig. 2a and b. Variation of logarithm of specific retention volumes, V_g^0 (mL g), of alcohols and alkanes with reciprocal of absolute column temperature, for PDMMA-EM, (a): for ΔH_a (cal/mol), (b): for ΔH_1^S (cal/mol)

The values of Ω_1^∞ and χ_{12}^∞ obtained using eqns. 6 and 7, respectively are also collected in Table-3.

It has been proposed that Ω_1^∞ values more than 5 are indicative of poor polymer-solute systems while lower values characterize good solubility for such systems. The following rules have been formulated by Guillet[24]:

$\Omega_1^\infty < 5$: good solvents
$5 < \Omega_1^\infty < 10$: moderate solvents
$\Omega_1^\infty > 10$: bad solvents

TABLE-3
WEIGHT FRACTION ACTIVITY COEFFICIENTS, Ω_1^{∞} AND INTERACTION PARAMETERS, χ_{12}^{∞}, OF PDMMA-EM WITH ALCOHOLS AND ALKANES SYSTEMS

Probe / T (K)	Ω_1^{∞}			χ_{12}^{∞}		
	413	423	433	413	423	433
Ethyl alcohol	3.0052	2.7384	2.5518	1.5996	1.3295	1.1417
1-Propyl alcohol	3.3916	3.1151	2.8772	1.9952	1.7138	1.4723
1-Buthyl alcohol	3.6899	3.4728	3.2512	2.3088	2.0864	1.8609
n-Hexane	2.6319	2.4732	2.3235	1.1289	0.9707	0.8218
n-Heptane	3.1205	2.9674	2.7735	1.6294	1.7451	1.2807
n-Octane	3.6494	3.4419	3.3028	2.1648	1.9544	1.8132

The values of χ_{12}^{∞} greater than 0.5 represent unfavourable polymer-solvent interactions while the values lower than 0.5 indicate favourable interactions in dilute polymer solutions[25]. It will be seen that these values (Table-3) according to Ω_1^{∞} and χ_{12}^{∞}, ethanol, *n*-hexane, *n*-heptane are good solvents, but propanol, butanol and *n*-octane are non-solvents for PDMMA-EM. It is observed from Table-3 that the values increased with increasing in the number of carbon in the alcohols and alkanes. At these temperatures the solubility of (PDMMA-EM) was decreased in the alcohols. The interaction parameters, χ_{12}^{∞} and the weight coefficients, Ω_1^{∞} did show dependence with change in the number of carbons in the series. But in all series, Ω_1^{∞} and χ_{12}^{∞} values decreased with increasing of the column temperature[26].

The solubility parameter of a polymer δ_2, can be determined by using eqn. 9[9-15]. The solubility parameter of a polymer δ_2, is determined from either slope or intercept of a straight line obtained by plotting the left-hand side of eqn. 9 *versus* δ_1. The values are shown in Table-4. The solubility parameter of PDMMA-EM was evaluated from either slope or intercepts of Fig. 3a and b as 5.16 $(cal/cm^3)^{0.5}$, 6.33 $(cal/cm^3)^{0.5}$ at 423 K, respectively. In comparing the solubility values of PDMMA-EM at different temperatures, it can be seen that the solubility parameters decrease with increasing temperature[27].

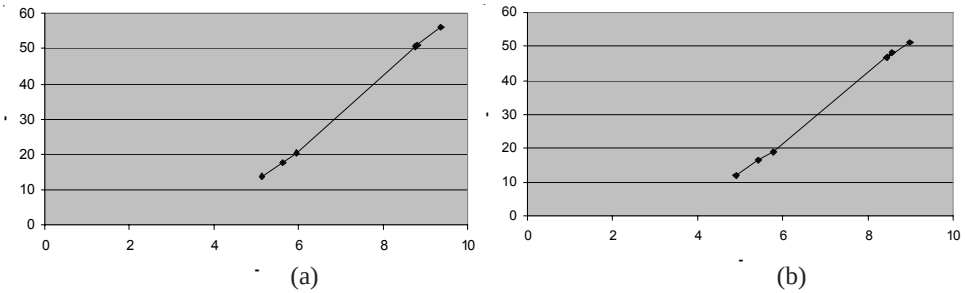


Fig. 3a and b. Variation of term $[\delta_1^2-\Delta G_1^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at temperatures (a): 423 K (b): 433 K for PDMMA-EM

TABLE-4
SOLUBILITY PARAMETER, δ_2 $(cal/cm^3)^{0.5}$, OF PDMMA-EM AT 423 AND 433 K

T (K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
423	10.3190	40.115	5.16	6.33	0.99
433	9.9711	37.593	4.98	6.13	0.99

Conclusion

Inverse gas chromatography (IGC) technique is simple, fast and economical and provides valuable thermodynamic information for characterization of polymeric materials. In this study this technique was successfully applied to determine some thermodynamic properties of PDMMA-EM such as the sorption enthalpy, ΔH_1^S, sorption free energy, ΔG_1^S, sorption entropy, ΔS_1^S, the weight fraction activity coefficients, Ω_1^∞, partial molar free energy of mixing, ΔG_1^∞, partial molar heat of mixing, ΔH_1^∞ and Flory-Huggins interaction parameters, χ_{12}^∞, at infinite dilution. According to Flory-Huggins interaction parameters, χ_{12}^∞ and the weight fraction activity coefficients, Ω_1^∞, it was seen that ethanol, *n*-hexane and *n*-heptane are good solvents, but propanol, butanol and *n*-octane are non-solvents for (PDMMA-EM). The solubility parameter values of (PDMMA-EM), δ_2, were also determined as 5.16 $(cal/cm^3)^{0.5}$, 6.33 $(cal/cm^3)^{0.5}$, respectively at 423 K from both slope and intercept of the straight line obtained by plotting the left-hand side of eqn. 9 *versus* δ_1 values of probes.

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