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Mehmet Mürşit temüz[a]; Mehmet Coşkun[a]; Aslişah Açikses[a]
[a] Faculty of Science & Arts, Department of Chemistry, University of Fırat, Elazığ, Turkey

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Determination of Some Thermodynamic Parameters of Poly(Styrene-Graft-Ethyl Methacrylate) Using Inverse Gas Chromatography

MEHMET MÜRŞIT TEMÜZ, MEHMET COŞKUN,
AND ASLIŞAH AÇIKSES

Faculty of Science & Arts, Department of Chemistry, University of Fırat,
Elazığ, Turkey

In this study, the specific retention volumes, V_g^o, were determined for poly(styrene-g-ethly methacrylate) obtained from grafting of poly(styrene-co-p-chloromethyl styrene) having a 54% (by mole) chlorine content with ethyl methacrylate and a series of nonsolvent as probe, five n-alkans, five alcohols and carbon tetrachloride, with the aid of inverse gas chromatography, in a temperature range of 333 to 463 K. Some thermodynamic properties, such as the sorption enthalpy, ΔH^s, sorption free energy, ΔG^s, sorption entropy, ΔS^s, in the 373–403 K temperature range, the partial molar free energy, ΔG^∞, and the partial molar heat of mixing, ΔH^∞, in the temperature 413-463 K range, were calculated from the relationships between the specific retention volumes and related properties. The weight fraction activity coefficients of probes as logarithmic value, ln Ω_1^∞, and Flory-Huggins interaction parameters, χ_{12}^∞, between the polymer and probes, were estimated. Also, the glass transition temperature, T_g, and the solubility parameter, δ_2, of the graft copolymer, were found to be about 85°C, and between 5.0–6.8 $(cal/cm^3)^{1/2}$ in the 413–463 temperature range K, respectively, and some extrapolations to room temperature were done and the results were discussed.

Keywords graft copolymer, poly(ethyl methacrylate), thermodynamic properties, inverse gas chromatography

Introduction

Inverse gas chromatography (IGC) has been used in the study of physicochemical properties of polymers such as interaction of polymeric materials with organic liquids and vapors, sorption properties, polymer-polymer miscibility (1–4). The method providing valuable information for the properties of polymers is simple, relatively rapid, with good accuracy, low cost and available equipment.

In IGC measurements, a known amount of a polymer is dissolved in a volatile solvent and coated on an inert support by gently evaporating the solvent. During the operation in an IGC apparatus, a carrier gas is continuously passed through the column. At the desired

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Address correspondence to Mehmet Coşkun, Faculty of Science & Arts, Department of Chemistry, University of Fırat, Elazığ, Turkey. Tel.: 0424 237 00 00; Fax: 0424 233 00 62; E-mail: mcoskun_firat@hotmail.com or mcoskun@firat.edu.tr

temperature, a probe is injected into the column flows with a carrier gas. In IGC experiments the inlet and outlet pressure and flow rate of the carrier gas, mass of the polymer, net retention time of the probe, and column temperature are commonly obtained. The reduced specific retention volume, V_g^o, is defined as (4).

$$V_g^o = \frac{\Delta t.F.273,2}{w.T_r} \times \frac{3}{2}\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] \tag{1}$$

where $\Delta t = t_p - t_m$ is the difference between retention time of the probe t_p and of the marker t_m (methane); F is the flow rate of the carrier gas at room temperature; w is the mass of the polymeric stationary phase; p_i and p_o are the inlet and the outlet pressure of the carrier gas, respectively.

The molar enthalpy, ΔH_1^s, the molar free enthalpy, ΔG_1^s, and the molar entropy, ΔS_1^s, of sorption of probes absorbed by the polymer are given by the following equations (2, 5):

$$\Delta H_1^s = -R\frac{\partial \ln V_g^o}{\partial(1/T)} \tag{2}$$

$$\Delta G_1^s = -RT\ln(M_1 V_g^o/273.2R) \tag{3}$$

$$\Delta S_1^s = (\Delta H_1^s - \Delta G_1^s)/T \tag{4}$$

Where M_1 is the molecular weight of the probe, and R is the gas constant.

The weight fraction activity coefficient, Ω_1^∞, partial molar free enthalpy, ΔG_1^∞, and the partial molar enthalpy, ΔH_1^∞, at infinite dilution of the probes, are calculated from the following equations (6):

$$\Omega_1^\infty = (273.2R/V_g^o P_1^o M_1)\exp[-P_1^o(B_{11} - V_1)/RT] \tag{5}$$

$$\Delta G_1^\infty = RT\ln\Omega_1^\infty \tag{6}$$

$$\Delta H_1^\infty = R\frac{\partial(\ln\Omega_1^\infty)}{\partial(1/T)} \tag{7}$$

Where B_{11}, V_1 and P_1^o are the second virial coefficient, the molar volume and the vapor pressure of the probes at temperature, T K, respectively, and they are obtained from the critical values as in the literature (7).

To calculate the interaction parameter, $\chi_{1,2}^\infty$, of polymer-probe system, is utilized the following equation (8):

$$\chi_{1,2}^\infty = \ln(273.2Rv_2/V_g^o V_1 P_1^o) - P_1^o/RT(B_{11} - V_1) - 1 \tag{8}$$

Where v_2 is the specific volume of the polymer. The solubility parameter is defined as the square root of cohesive energy density and for volatile substance it may be calculated as follows (9):

$$\delta_1 = \sqrt{(\Delta H_v - RT)/V_1} \tag{9}$$

Where ΔH_v is the molar vaporization enthalpy of the probes. For the polymers, some authors use a graphical approach to estimate Hildebrand solubility parameters from IGC data. According this method, the solubility parameter of the polymer being stationary phase in IGC is obtained from the following equation (10):

$$[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1)] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \tag{10}$$

δ_2 is determined from both the slope and the intercept of a plot of the left hand side of this equation vs. δ_1 for a series of probes.

This study describes the determination of some physicochemical properties of poly (S-*g*-EMA) by inverse gas chromatography.

Experimental

Materials

Thirteen different organic solvents were used as the probes. These probes are composed of five normal alkanes (n-hexane, n-heptane, n-octane, n-nonane and n-decane), five alcohols (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and carbon tetrachloride. Chromosorb W (80−100 mesh) used as a inert solid support and all the probes are purchased from Aldrich Chemical Co. and are chromatographic grade and used without further purification. Poly(styrene-*g*-ethly methacrylate), poly(S-*g*-EMA) prepared from grafting of poly(styrene-*co*-p-chloromethyl styrene) having a 54% (by mole) chlorine content with ethyl methacrylate, in previous study (11), was used as a stationary phase.

Procedure and Instrumentation

A chromatographic column was made in the laboratory from copper tubing (3.2 mm inner diameter and 1 m long) purchased locally, and it was washed with hexane and methanol and then dried prior to use. 10% wt/wt of poly(S-*g*-EMA) was coated onto 3.000 g of Chromosorb W. The polymer was dissolved in 50 ml methylene chloride and the Chromosorb W was added to this solution. Then, the polymer was deposited onto the inert support by gently evaporating the solvent in a rotary evaporator. After drying, the prepared material was packed into the copper column by aid of mechanical vibrator (12), and the column was attached as spiral to a Packard 430 model gas chromatograph equipped with a dual flame ionization detector. The column was conditioned in the gas chromatography chamber for 2 days at 200°C under carrier gas (dry N_2) flow prior to use. Pressures at the inlet and outlet of the column were read from a mercury manometer. Methane was used as a non-interacting marker to correct for dead volume in the column, and it was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide (13). The flow rate of the carrier gas was measured from the end of the column with a soap bubble flow meter. 0.2 μL of the probe was injected onto the column with a 1 μL Hamilton syringe. Three consecutive injections were made for each probe at each temperature. The retention times of the probes were measured by using a Shimadzu CR2A Chromatopac model integrator.

Results and Discussion

The net retention times of 11 probes, which are five alcohols, five hydrocarbons and carbon tetrachloride, were obtained on 10% poly(S-*g*-EMA) at 413–463 K. The specific retention volumes were calculated according to Equation (1) and are given in Table 1.

Table 1

The variation of V_g^o values of five alcohols, five hydrocarbon and carbon tetrachloride with temperature using poly(S-*g*-EMA) as stationary phase

Probe/T(K)	333	343	353	363	373	383	393	403	413	423	433	443	453	463
Methanol	3.63	3.36	3.09	2.52	2.77	2.31	2.15	1.97	1.82	1.67	1.63	1.47	1.41	1.27
Etanol	3.34	3.75	3.13	2.59	2.81	2.35	2.18	1.99	1.85	1.69	1.63	1.49	1.43	1.29
1-Propanol	4.02	3.67	3.39	2.74	3.00	2.49	2.25	2.09	1.94	1.73	1.69	1.54	1.46	1.32
1-Butanol	4.34	4.13	3.74	2.89	3.24	2.74	2.56	2.22	2.06	1.84	1.79	1.59	1.53	1.37
1-Pentanol	5.49	4.76	4.52	3.61	3.99	3.09	2.82	2.51	2.29	2.03	1.94	1.72	1.69	1.49
n-Hexane	3.45	3.22	2.96	2.43	2.78	2.31	2.08	1.94	1.79	1.61	1.55	1.42	1.38	1.25
n-Heptane	3.51	3.27	3.09	2.52	2.73	2.35	2.18	2.03	1.88	1.67	1.58	1.44	1.41	1.27
n-Octane	3.59	3.31	3.13	2.63	2.81	2.45	2.23	2.09	1.94	1.72	1.66	1.52	1.46	1.29
n-Nonane	3.93	3.67	3.39	2.82	3.00	2.59	2.32	2.16	1.99	1.81	1.77	1.59	1.51	1.37
n-Decane	4.59	4.04	3.83	3.39	3.12	2.81	2.59	2.38	2.21	1.95	1.91	1.69	1.58	1.44
Carbon tetrachloride	3.59	3.31	3.09	2.56	2.77	2.41	2.25	1.99	1.85	1.69	1.68	1.54	1.46	1.32

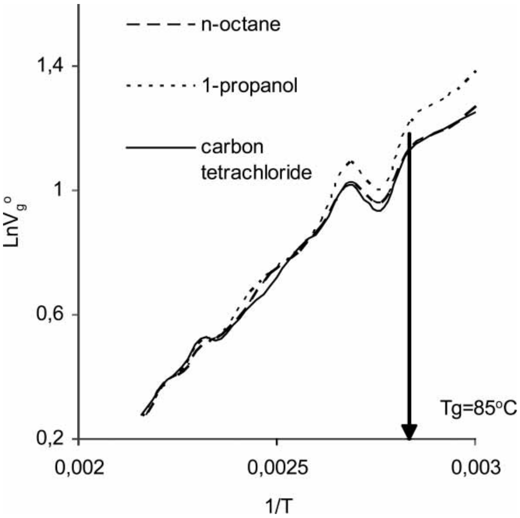

Figure 1. Plot of $\ln V_g^o$ against 1/T for three probes as an example over the temperature range 373–463 K.

As is shown in Table 1, V_g^o values of each group solvents decrease generally with increasing temperature, but they deviate from this tendency at around glass transition temperature. In this temperature region below glass transition temperature of the polymer, penetration of the solute molecules into the bulk of the polymer phase is precluded. For whole temperature range (333–463 K), plots of $\ln V_g^o$ vs. 1/T for n-octane, 1-propanol and carbon tetrachloride are shown in Figure 1. The glass transition temperature was defined as the temperature that deviate from the linearity at low temperature region of the curve (14), and this temperature of poly(S-*g*-EMA) was estimated to be about 85°C by IGC (see Figure 1). The DSC curve gives also the same value for the glass transition temperature. This result for the glass transition temperature is about 20°C greater than values given in the literature for poly(EMA) (15, 16). Since one end of the poly(S-*g*-EMA) chains are bounded to phenyl groups in poly(styrene), the motion of one end of poly(EMA) chains in the graft copolymer is restricted, and this phenomenon causes decreasing of free volume in poly(S-*g*-EMA) and increasing of glass transition temperature.

For a temperature range beginning from above 15 K of the glass transition temperature, the molar heats of sorption, ΔH_1^s, of the probes into poly(S-*g*-EMA) were found from the slopes of the straight lines of $\ln V_g^o$ vs. 1/T (Figure 2). Table 2 shows the ΔH_1^s values in temperature range 373–403 K. It is seen that the sorption heats of all the probes indicate exothermic values and are not very different from each other. For only the alcohol series, as the number of CH_2 groups increases, the sorption heats become slightly more exothermic. This indicates that the probe molecule interacts better with the polymer in the case of the longer CH_2 in the molecule. A similar tendency was also observed for sorption enthalpy of some n-alkanes on poly(vinyl methyl ketone) (17). The sorption entropy, ΔS_1^s, calculated using Equation (4) from ΔH_1^s in Table 2, and ΔG_1^s obtained from Equation (3), are given in Table 3. All the ΔS_1^s values are negative in all classes, suggesting that the probe molecules in the sorbed state are in a more regular state than those of the gas state.

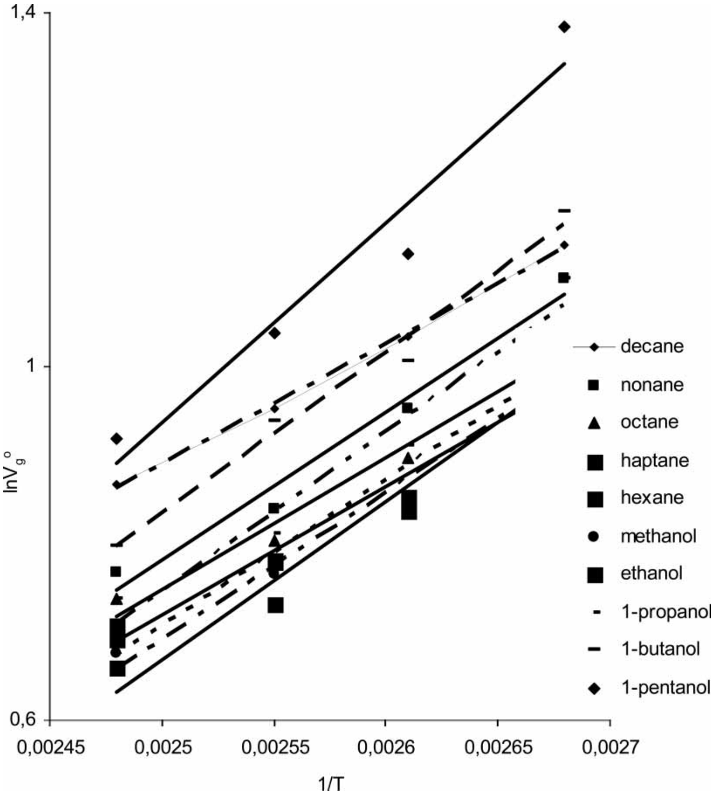

Figure 2. The linear dependence of $\ln V_g^o$ to $1/T$ in the temperature range 373–403 K.

Over the 413–463 K temperature range, the weight fraction activity coefficient as logarithmic, $\ln \Omega_1^\infty$, and the interaction parameter, $\chi_{1,2}^\infty$, of the polymer-probe system, at infinite dilution conditions, are given in Table 4. For the hydrocarbons and alcohols, $\ln \Omega_1^\infty$ and $\chi_{1,2}^\infty$ values increased with decreasing temperature and increasing carbon

Table 2

Molar heat of sorption, ΔH_1^s, at temperatures between 373–403 K

Probes	ΔH_1^s(kcal/mol)
Hexane	−3.58
Heptane	−3.08
Octane	−2.96
Nonane	−3.33
Decane	−2.69
Methanol	−3.31
Ethanol	−3.29
1-Propanol	−3.57
1-Butanol	−3.63
1-Pentanol	−4.50
Carbon tetrachloride	−3.09

Table 3
The sorption entropies, ΔS_1^s, for temperaturesbetween 373–403 K

	ΔS_1^s(cal/mol · K)			
Probes	373 K	383 K	393 K	403 K
Hexane	−19.1	−19.0	−18.9	−18.9
Heptane	−16.9	−16.9	−16.8	−16.8
Octane	−16.7	−16.7	−16.6	−16.6
Nonane	−17.1	−17.2	−17.2	−17.1
Decane	−15.3	−15.3	−15.3	−15.3
Methanol	−19.7	−19.8	−19.8	−19.7
Ethanol	−18.9	−19.0	−19.0	−18.9
1-Propanol	−19.0	−19.1	−19.1	−19.0
1-Butanol	−18.5	−18.6	−18.5	−18.6
1-Pentanol	−20.1	−20.3	−20.2	−20.1
Carbon tetrachloride	−16.2	−16.2	−16.1	−16.2

number in the probes. Flory-Huggins interaction parameter, $\chi_{1,2}^{\infty}$, exhibits high values when the probes are poor solvents for tested polymer, while low values reflect good solubility capacities. According to a measure given in the literature, that is, values of Ω_1^{∞} higher than 5(10) (or for ln Ω_1^{∞} higher than 1.609) and values of $\chi_{1,2}^{\infty}$ greater than 0.5(18), represent unfavorable polymer-solvent interaction while values lower than these limit values indicate that these interactions are favorable for solvent dissolution, for the values obtained for ln Ω_1^{∞} and $\chi_{1,2}^{\infty}$ indicate that all the probes tested are poor solvents (or nonsolvent) for poly(S-*g*-EMA) between 413–463 K. Decreasing with

Table 4
ln Ω_1^{∞}, $\chi_{1,2}^{\infty}$ values of poly(S-*g*-EMA)-the probe system between 413–463 K

	ln Ω_1^{∞}						$\chi_{1,2}^{\infty}$					
Probes/T K	413	423	433	443	453	463	413	423	433	443	453	463
Hexane	3.18	3.09	2.94	2.85	2.71	2.65	1.68	1.59	1.44	1.35	1.21	1.15
Heptane	3.71	3.60	3.45	3.34	3.17	3.09	2.22	2.11	1.95	1.85	1.68	1.59
Octane	4.24	4.11	3.91	3.78	3.61	3.52	2.76	2.62	2.42	2.28	2.11	2.03
Nonane	4.77	4.59	4.36	4.21	4.04	3.92	3.29	3.12	2.87	2.72	2.55	2.43
Decane	5.23	5.04	4.79	4.64	4.46	4.31	3.76	3.57	3.30	3.15	2.96	2.81
Methanol	3.57	3.42	3.20	3.08	2.92	2.81	2.13	1.96	1.75	1.63	1.45	1.35
Ethanol	3.54	3.36	3.14	2.98	2.79	2.67	2.14	1.95	1.73	1.56	1.39	1.28
1-Propanol	3.86	3.70	3.45	3.30	3.12	3.01	2.46	2.29	2.05	1.89	1.72	1.59
1-Butanol	4.26	4.06	3.80	3.66	3.45	3.32	2.87	2.68	2.42	2.26	2.06	1.94
1-Pentanol	4.64	4.36	4.21	4.06	3.82	3.71	3.27	3.08	2.83	2.67	2.43	2.31
Carbon tetrachloride	2.56	2.46	2.30	2.23	2.13	2.08	1.77	1.67	1.51	1.43	1.34	1.29

Table 5

ΔH_1^∞ and ΔG_1^∞ values of the probes on the polymer between 413–463 K

	ΔH_1^∞ (kcal/mol)	ΔG_1^∞ (kcal/mol)	
Probes	(413–463 K)	413 K $\rightarrow$	463 K
Hexane	4.36	2.61	2.44
Heptane	4.89	3.04	2.84
Octane	5.69	3.48	3.24
Nonane	6.66	3.92	3.61
Decane	7.17	4.29	3.97
Methanol	5.96	2.93	2.59
Ethanol	6.84	2.90	2.46
1-Propanol	6.75	3.17	2.76
1-Butanol	7.34	3.49	3.06
1-Pentanol	7.39	3.81	3.41
Carbon tetrachloride	3.81	2.10	1.91

increasing temperature of the polymer-solute interaction parameter exhibit that there may be an upper critical solution temperature for each probe, and such as temperatures may be estimated by aid of the relation between $\chi_{1,2}^\infty$ and reciprocal of the absolute column temperature (19) (these procedures were not done in this study).

The partial molar free energy of mixing, ΔG_1^∞, and the partial molar heats of mixing, ΔH_1^∞, calculated from Equations (6) and (7), are collected in Table 5. The partial molar heats of mixing, ΔH_1^∞, are positive for all the probes, and reflect that interaction of the probes with the polymer is an endothermic reaction, and they depend slightly on carbon number of each class of the probes. The partial molar free energy of mixing, ΔG_1^∞, increased slightly with increasing carbon number in the hydrocarbons and the alcohols, and decreased slightly with increasing temperature in all the probes. The relatively high values of ΔG_1^∞ indicate that all the probes are immiscible with investigated polymer in temperature range 413–463 K.

The solubility parameter of a polymer, δ_2, can be determined by using Equation (10). If the left-hand side of Equation (10) is plotted against δ_2, a straight line having a slope of $2\delta_2/RT$ and an intercept of $-\delta_2^2/RT$ is obtained, and for three temperatures, this plot is shown in Figure 3. The values obtained from the slope are some lower than those obtained from the intercept. The δ_2 values obtained from intercept for all temperatures in the 413–463 K range was plotted against the temperature, and a linear relationship with $R^2 = 1.00$ (Figure 4) was obtained, and δ_2 was determined as 10.2 $(cal/cm^3)^{1/2}$ by extrapolation of the values of δ_2 obtained according to Equation (10) at column temperatures studied to 298 K. The solubility parameter at room temperature of the polymer was determined as 9.5 $(cal/cm^3)^{1/2}$ from the solubility test. The value of δ_2 obtained from the extrapolation is good agreement with the experimental value. A similar extrapolation of the solubility parameters at high temperatures to room temperature was also done for poly(caprolactone), and an appropriate value was found (20). When the values obtained from the slope were employed in similar calculations, the value at 298 K of δ_2 was determined as 8.6 $(cal/cm^3)^{1/2}$, and this value is somewhat different from the experimental value. The values of $\chi_{1,2}^\infty$ at 298 K were found by extrapolation of the linear plot of $\chi_{1,2}^\infty$ vs. reciprocal of the absolute column temperature to 298 K, and then the left-hand

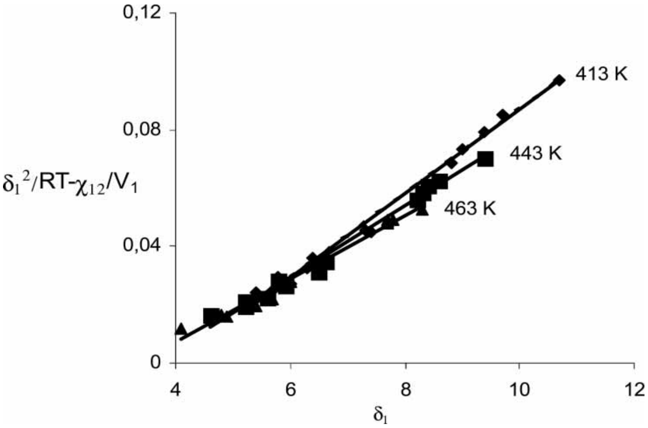

Figure 3. Variation of $[(\delta_1^2/RT) - \chi_{12}^{\infty}\ /V_1]$ with solubility parameters of the probes, δ_1, $(\text{cal/cm}^3)^{1/2}$, for three temperatures, 413, 443 and 463 K.

side of Equation (10) calculated again from $\chi_{1,2}^{\infty}$ and other quantities at 298 K was plotted against the solubility parameters of the probes at 298 K (Figure 5). The values estimated from the slope and intercept for δ_2 at 298 K were 7.1 and 8.6 $(\text{cal/cm}^3)^{1/2}$, respectively. Although the value obtained from the slope is quite different from the experimental value, that obtained from the intercept is acceptable. For the polymer-probe system in this study at least, it may said that the estimation of the values at room temperature of $\chi_{1,2}^{\infty}$ from their the values at higher temperatures is not very reliable, although it gives good established values for some polymer-probe systems (20, 21).

Conclusions

Some physicochemical properties of poly(S-*g*-EMA)-probe system, such as change of $\ln V_g^o$ with 1/T, T_g, the quantities of sorption, ΔH_1^s, ΔS_1^s, ΔG_1^s, and $\ln \Omega_1^{\infty}$, $\chi_{1,2}^{\infty}$, $\Delta G_1^{\infty}$and ΔH_1^{∞} at infinite dilution conditions, were determined by inverse gas chromatography. T_g from plot of $\ln V_g^o$ vs. 1/T was estimated as 85°C, which is the same value with DSC

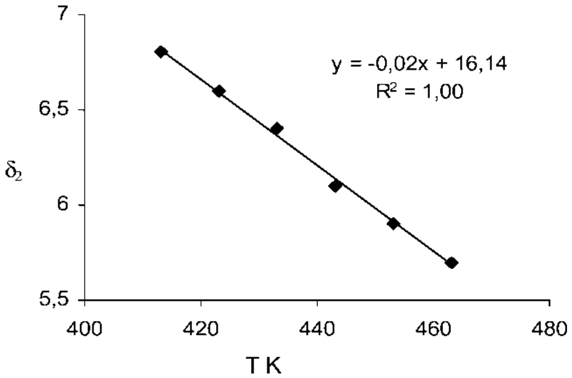

Figure 4. Extrapolation of the solubility parameter of poly(S-*g*-EMA), δ_2, to room temperature.

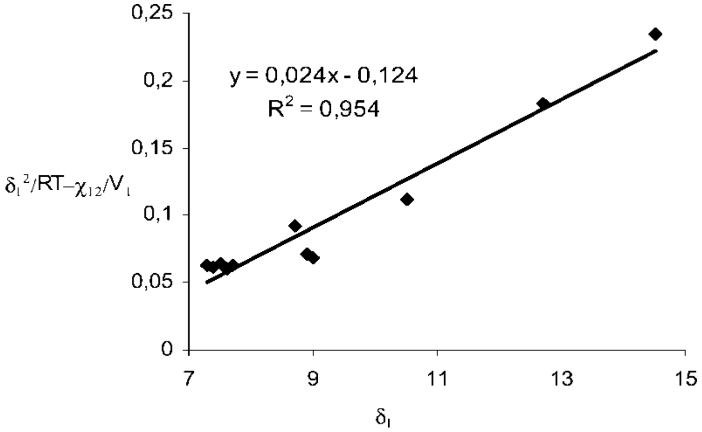

Figure 5. Determination of the solubility parameter of poly(S-*g*-EMA), δ_2, at room temperature (298 K) according to Equation (10).

data. For all the probes, this polymer-probe system indicates negative sorption enthalpy and entropy values slightly depending on the kinds of the probes. The partially molar free energy and partially molar enthalpy of the mixing in infinite dilution conditions indicate positive values for all the probes. The values obtained for the weight fraction activity coefficient as logarithmic, ln Ω_1^{∞}, and the interaction parameter, $\chi_{1,2}^{\infty}$, are greater than the limit values required for polymer-solvent systems. As a result, five alcohols, five hydrocarbons and carbon tetrachloride used as probes are non-solvent for poly(S-*g*-EMA) in the temperature range of 413–463 K. The solubility parameter, δ_2, at room temperature, was estimated as 10.2 $(\text{cal/cm}^3)^{1/2}$, from the values determined at the higher temperatures by extrapolating, and this value is quite close to the value obtained from the solubility test.

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