Synthesis, Characterization, and Thermodynamic Properties of Poly(3-mesityl-2-hydroxypropyl methacrylate)

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ABSTRACT: Poly(3-mesityl-2-hydroxypropyl methacrylate) (PMHPMA) was synthesized in a 1,4-dioxane solution with 2,2′-azobisisobutyronitrile as the initiator at 60°C. The homopolymer and its monomer were characterized with ^{1}H- and ^{13}C-NMR, Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, size exclusion chromatography, and elemental analysis techniques. According to size exclusion chromatography analysis, the number-average molecular weight, weight-average molecular weight, and polydispersity index of PMHPMA were 65,864 g/mol, 215,375 g/mol, and 3.275, respectively. According to thermogravimetric analysis, the carbonaceous residue value of PMHPMA was 14% at 500°C. The values of the specific retention volume, adsorption enthalpy, sorption enthalpy, sorption free energy, sorption entropy, partial molar free energy, partial molar heat of mixing, weight fraction activity coefficient of solute probes at infinite dilution (Ω_1^∞), and Flory–Huggins interaction parameter (χ_{12}^∞) were calculated for the interactions of PMHPMA with selected alcohols and alkanes by the inverse gas chromatography method at various temperatures. According to Ω_1^∞ and χ_{12}^∞, selected alcohols and alkanes were nonsolvents for PMHPMA at 423–453 K. Also, the solubility parameter of PMHPMA (δ_2) was found to be 24.24 and 26.33 $(J/cm^3)^{0.5}$ from the slope and intercept of $(\delta_1^2/RT) - \chi_{12}^\infty/V_1 = (2\delta_2/RT)\delta_1 - \delta_2^2/RT$ at 443 K, respectively [where δ_1 is the solubility parameter of the probe, V_1 is the molar volume of the solute, T is the column temperature (K), and R is the universal gas constant]. The glass-transition temperature of PMHPMA was found to be 386 and 385 K by inverse gas chromatography and differential scanning calorimetry techniques, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 101–109, 2006

Key words: chromatography; synthesis; thermodynamics; thermal properties

INTRODUCTION

Poly(2-hydroxyethyl methacrylate) is an important commercial polymer with a wide range of biomedical applications. For this reason, it is important to study the thermodynamic properties of these types of polymers. Poly(3-mesityl-2-hydroxypropyl methacrylate) (PMHPMA) has received much attention because of its useful properties and biological applications, such as the binding of drugs and biomolecules, negative electron-beam resists, and good resistance to dry etching.[1,2] Because of these properties, it is very important to investigate the polymer–solute interactions of methacrylate polymers by inverse gas chromatography (IGC). The method was developed by Smidsrod and Guillet[3] and has been applied to many polymer–solvent and polymer–nonsolvent systems. The physicochemical properties that can be obtained for polymeric systems include the interaction parameters of polymer–solvent, polymer–nonsolvent, and polymer–polymer systems, solubility parameters, and weight fraction coefficients, the molar heat and free energy of mixing and sorption, the degree of crystallinity of semicrystalline polymers, the glass-transition and melting points of polymers, the decomposition temperatures of polymers, and the surface energy of polymers. The IGC method has been used extensively to study the structures of polymers, the interactions of various liquids and gases with polymeric materials, and polymer–polymer miscibility. The method is simple, fast, and economical and provides valuable thermodynamic information for the characterization of polymeric materials.[4–14]

In this study, we synthesized PMHPMA in a 1,4-dioxane solution with 2,2′-azobisisobutyronitrile (AIBN) as the initiator at 60°C, and PMHPMA was characterized with ^{1}H-NMR, ^{13}C-NMR, Fourier transform infrared (FTIR), differential scanning calorimetry, size exclusion chromatography (SEC), and elemental analysis techniques. Then, we examined the interactions of PMHPMA with alcohols and alkanes with the IGC method in the temperature range of 323–453 K. We also determined the solubility parameter of PMHPMA (δ_2), and we determined the thermal

degradation of PMHPMA with thermogravimetric analysis.

IGC METHODOLOGY

The specific retention volume at 0°C (V_g^0) was determined experimentally with the following relationship:[11]

$$V_g^0 = \Delta t \frac{F(273.15)}{wT} J \tag{1}$$

$$J = \frac{3}{2}\left[\frac{(P_1/P_o)^2 - 1}{(P_1/P_o)^3 - 1}\right] \tag{2}$$

where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe (t_p) and methane (t_g); F is the flow rate of the carrier gas measured at room temperature; T is the column temperature (K); w is the mass of the polymeric stationary phase; J is the pressure correction coefficient; and P_i and P_o are the inlet and outlet pressures, respectively.

The adsorption enthalpy (ΔH_a) of the probes adsorbed by PMHPMA was given by eq. (3):

$$\partial \ln V_g^0 / \partial(1/T) = -\Delta H_a/R \tag{3}$$

where R is the universal gas constant.

The molar volume of the solute (V_1) was calculated with the following relation:[15,16]

$$V_1 = V_c/\rho_r \tag{4}$$

where V_c is the critical molar volume and ρ_r is the reduced density of the solute. This is given as

$$\rho_r = 1.20 + (5.565 - 11.03_{z_c})(1 - T/T_c)^{(0.8Z_c + 0.31)} \tag{5}$$

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

The molar enthalpy of sorption (ΔH_1^s) and molar free energy of sorption (ΔG_1^s) of the probe absorbed by PMHPMA were determined with the following equations:

$$\Delta H_1^s = -R\delta \ln\left(\frac{V_g^0}{\delta(1/T)}\right) \tag{6}$$

$$\Delta G_1^s = -RT \ln\left(\frac{M_1 V_g^0}{273.15R}\right) \tag{7}$$

By incorporating eqs. (6) and (7), we calculated the entropy of sorption of solutes (ΔS_1^s) as follows:

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \tag{8}$$

The weight fraction activity coefficient (Ω_1^∞), partial molar free energy (ΔG_1^∞), and average partial molar enthalpy (ΔH_1^∞) at infinite dilution of the organic solvents were calculated according to the following equations:[5]

$$\Omega_1^\infty = \frac{273.15R}{V_g^0 P_1^0 M_1}\exp\left(-\frac{P_1^0(B_{11} - V_1)}{RT}\right) \tag{9}$$

P_1^0 is the vapor pressure of the probe at T, B_{11} is the second virial coefficient of the organic solute in the gaseous state, and M_1 is the molecular weight of the probe:

$$\Delta G_1^\infty = RT \ln\Omega_1^\infty \tag{10}$$

$$\Delta H_1^\infty = R\delta \ln\left(\frac{\Omega_1^\infty}{\delta(1/T)}\right) \tag{11}$$

The values of P_1^0 and B_{11} were calculated as in the literature.[16]

The Flory–Huggins parameter (χ_{12}^∞), characterizing the interactions of a vapor-phase probe with a polymer, were determined with the following equation:

$$\chi_{12}^\infty = \ln(273.2Rv_2/\bar{V}_g^0 V_1 P_1^0) - 1 - P_1^0/RT (B_{11} - V_1) \tag{12}$$

where v_2 is the specific volume of the polymer. The solubility parameter of the probe (δ_1) was calculated with the following relation:[17–20]

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \tag{13}$$

δ_2 was calculated with the following relation:

$$[(\delta_1^2/RT) - \chi_{12}^\infty/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \tag{14}$$

where ΔH_v is the molar evaporation enthalpy. 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. δ_2 can be determined from both the slope and intercept of the straight line.[12]

EXPERIMENTAL

Materials

Methanol (MeOH), ethanol (EtOH), 1-propanol, 1-butanol, 1-pentanol, hexane, heptane, octane, and decane were supplied by Merck Chemical Co. (Germany) (chromatographic-grade). Methacrylic acid, pyridine, toluene, mesitylene, AIBN, anhydrous MgSO₄, diethyl ether, KOH, NaOH, epichlorohydrin, anhydrous

AlCl$_3$, and 1,4-dioxane were supplied by Merck Chemical. 3-Mesityl-2-hydroxypropyl methyl methacrylate was synthesized as follows. Hydroquinone was added as an inhibitor for the polymerization of 3-mesityl-2-hydroxypropyl methacrylate (MHPMA). Chromosorb W (80–100 mesh) was supplied by Sigma Chemical Co. (St. Louis, MO).

Synthesis of 3-mesityl-2-hydroxypropyl chloride

Mesitylene (1.25 mol, 166 g) and AlCl$_3$ were placed in a 500-mL, four-necked flask fitted with a condenser, a thermometer, a stirrer, and an addition funnel containing 95 mL of 1-chloro-2,3-epoxy propane (1.2 mol, 11.2 g). 1-Chloro-2,3-epoxy propane was added dropwise over the solution between 0 and 5°C for 5–6 h. The reaction mixture was stirred at 30°C for 1 h, and then the mixture was added to an HCl and freezing water solution. The organic phase was extracted several times with diethyl ether and dried over anhydrous MgSO$_4$. Diethyl ether was removed with a vacuum evaporator. Unreacted mesitylene was removed by vacuum distillation. The product was distilled in vacuo (5 mmHg, 90°C).[21]

Synthesis of 3-mesityl-1,2-epoxy propane

Diethyl ether (350 mL) and KOH (1.5 mol, 84 g) were placed in a 500-mL, four-necked flask fitted with a condenser, a thermometer, a stirrer, and an addition funnel containing 106 mL (0.7 mol) of epichlorohydrin. The chlorohydrin was added dropwise over the solution, and the mixture was heated between 30 and 35°C for 8–9 h. The organic phase was extracted several times with diethyl ether, washed with water (50 mL × 3), and dried over anhydrous MgSO$_4$. Diethyl ether was removed with a vacuum evaporator. The product was distilled in vacuo (5 mmHg, 95°C). The product was characterized with FTIR, ^{1}H-NMR, and ^{13}C-NMR techniques.

FTIR (KBr, cm^{-1}, ν): 3100–3000 (C—H aryl), 2918–2860 (C—H aliphatic), 1635 (C=C), 1095 (C—O), 3100–3000 (epoxy C—H). ^{1}H-NMR (CDCl$_3$, δ ppm): 1.80–2.40 (s, 9H, aryl CH$_3$), 2.63 (d, 2H,—CH$_2$), 2.92 (d, 2H, oxirane CH$_2$), 3.80 (m, 1H, oxirane CH), 6.60–7.00 (s, 2H, aromatic). ^{13}C-NMR (CDCl$_3$, δ ppm): 20–21.30 (s, 3C, aryl CH$_3$), 46.70 (s, 1C, —CH$_2$), 31.80 (s, 1C, oxirane CH$_2$), 51.60 (s, 1C, oxirane CH), 129.60 (s, 2C, aromatic CH), 131.20 (s, 1C, aromatic, —C—, ipso carbon), 135.90 (s, 1C, aromatic, —C—, ipso carbon), 137.30 (s, 2C, aromatic C, ipso carbon).

Synthesis of MHPMA

3-Mesityl-1,2-epoxy propane (15 g), methacrylic acid (18 g), toluene (150 mL), and pyridine (3 mL; used as a catalyst) were placed in a 250-mL, single-necked flask. Hydroquinone was added as a solid over the mixture for unpolymerization. The mixture was heated between 85 and 90°C for 30 h. The organic phase was extracted several times with diethyl ether and 5% NaOH added, and the crude product was washed with water (50 mL × 3) and dried over anhydrous MgSO$_4$. Toluene and diethyl ether were removed with a vacuum evaporator. The product was distilled in vacuo (5 mmHg, 135–140°C). The product was characterized with FTIR, ^{1}H-NMR, and ^{13}C-NMR techniques.

ANAL. Calcd for MHPMA: C, 73.28%; H, 8.40%. Found: C, 73.05%; H, 8.15%. FTIR (KBr, cm^{-1}, ν): 3480–3458 (O—H), 2946–2903 (C—H aryl and alkene C=C), 2827–2816 (C—H aliphatic), 1615 (vinylic C=C), 1735 (C=O), 1274 (C—O—C). ^{1}H-NMR (CDCl$_3$, δ ppm): 1.96 (s, 3H, CH$_3$), 2.00–2.40 (s, 9H, aryl CH$_3$), 2.50–3.10 (d, 2H, —CH$_2$), 4.17 (d, 2H, O—CH$_2$), 3.66 (m, 1H, —CH), 5.58–6.14 (s, 2H, vinylic CH$_2$), 6.90 (s, 2H, aromatic). ^{13}C-NMR (CDCl$_3$, δ ppm): 17.10 (s, 1C, CH$_3$), 19.00–19.80 (s, 3C, aryl CH$_3$), 32.27 (s, 1C, —CH$_2$), 68.68 (s, 1C, O—CH$_2$), 73.60 (s, 1C, —CH), 124.57 (s, 1C, vinylic CH$_2$), 134.40 (s, 1C, aliphatic ipso carbon), 166.00 (s, 1C, C=O), 128.00 (s, 2C, aromatic CH), 132.00 (s, 1C, aromatic, —C—, ipso carbon), 135.80 (s, 1C, aromatic, —C—, ipso carbon), 137.35 (s, 2C, aromatic C, ipso carbon).

Homopolymerization of MHPMA

PMHPMA was prepared by the free-radical polymerization of MHPMA with AIBN (2% of the monomer weight) in 1,4-dioxane in a sealed tube at 60°C for 4 h with 80% conversion (Scheme 1). The polymer was precipitated in excess hexane. After a few reprecipitations from a hexane solution with CH$_2$Cl$_2$, the homopolymer was dried in vacuo at 40°C for 24 h.[21]

ANAL. Calcd for PMHPMA: C, 73.28%; H, 8.40%. Found: C, 72.98%; H, 8.00%. FTIR (KBr, cm^{-1}, ν): 3528–3417 (O—H), 3020–2952 (C—H aryl and alkene), 2917–2862 (C—H aliphatic), 1735 (C=O), 1618 (C=C aromatic), 1256 (C—O—C). ^{1}H-NMR (CDCl$_3$, δ ppm): 0.80–1.60 (s, 5H, CH$_2$ and CH$_3$), 1.80–2.40 (s, 9H, aryl CH$_3$), 2.95 (d, 2H, —CH$_2$), 4.04 (d, 2H, O—CH$_2$), 3.60 (m, 1H, —CH), 4.96 (s, 1H, —OH), 6.60–7.00 (s, 2H, aromatic). ^{13}C-NMR (CDCl$_3$, δ ppm): 19.60 (s, 3C, aryl CH$_3$), 32.13 (s, 1C, —CH$_2$), 68.17 (s, 1C, O—CH$_2$), 44.50 (s, 1C, —CH, ipso carbon), 54.00 (s, 1C, aliphatic ipso carbon), 176.30 (s, 1C, C=O), 129.60 (s, 2C, aromatic CH), 131.20 (s, 1C, aromatic, —C—, ipso carbon), 136.00 (s, 1C, aromatic, —C—, ipso carbon), 137.30 (s, 2C, aromatic C, ipso carbon).

Analysis

PMHPMA and its beginning matters were characterized with a Mattson FTIR-1000 spectrometer (UK) and
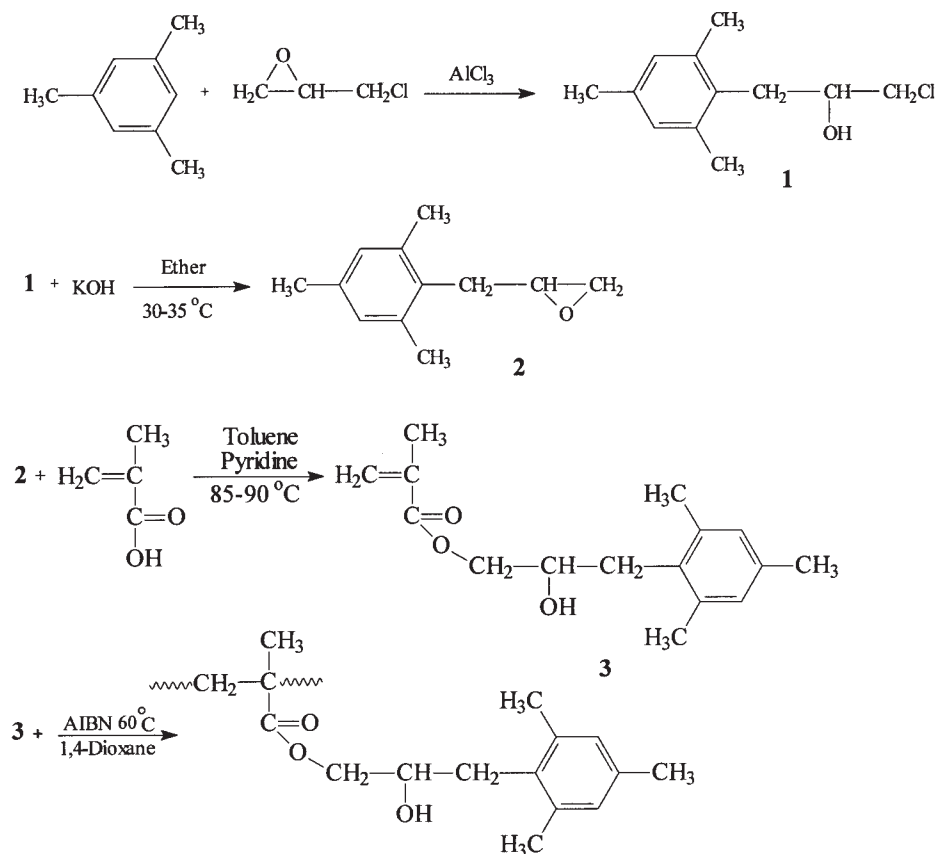
Scheme 1

a Varian XL200 ^{1}H- and ^{13}C-NMR spectrometer (200 MHz) at 25°C with CDCl$_3$ as the solvent. Tetramethylsilane was used as the internal standard. Elemental analysis was carried out with a Carlo Erba 1106 (Italy). The FTIR spectra were recorded with KBr discs (4000–400 cm^{-1}). Gel permeation chromatography (GPC) analyses were performed at 30°C with THF as the eluent at a flow rate of 1.0 mL/min. A refractive-index detector was used as a detector. The instrument, a Hewlett–Packard GPC–SEC system, was calibrated with a mixture of polystyrene standards with GPC software for the determination of the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the polymer sample. The glass-transition temperature (T_g) of PMHPMA was found to be about 385 K with a Shimadzu DSC-50 (Japan). Thermal data were obtained with a Shimadzu TG-50H thermal analyzer. Thermogravimetric analysis measurements were taken between 20 and 500°C (in air at 10°C/min). The density was measured by the determination of the weight of a volume-calibrated pycnometer filled with a liquid of known density with a certain quantity of the polymer sample.[22] The density of PMHPMA was found to be 1.040 g/cm^3 by pycnometric measurements at 25°C.

Instrumentation and procedure

A Packard 430 model gas chromatograph (Italy) 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 noninteracting marker to correct for the dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and the probe molecule at each temperature. Pressures at the inlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap-bubble flow meter. A flow rate of about 15 cm^3/min was used throughout our experiments. The copper tubing (3.2-mm i.d. × 1 m) was washed with dichloromethane and was annealed before use. A column packing material was prepared by the coating of 80–100-mesh Chromosorb W treated with PMHPMA. PMHPMA (0.300 g) was dissolved in 50 mL of 1,4-dioxane, and 3.000 g of the solid supporting materials was then added to this solution, which was stirred. The solvent was removed by continuous stirring and slow evaporation under a partial vacuum in a rotary evaporator. The prepared material was packed into spiral glass tubing. The column was conditioned at temper-
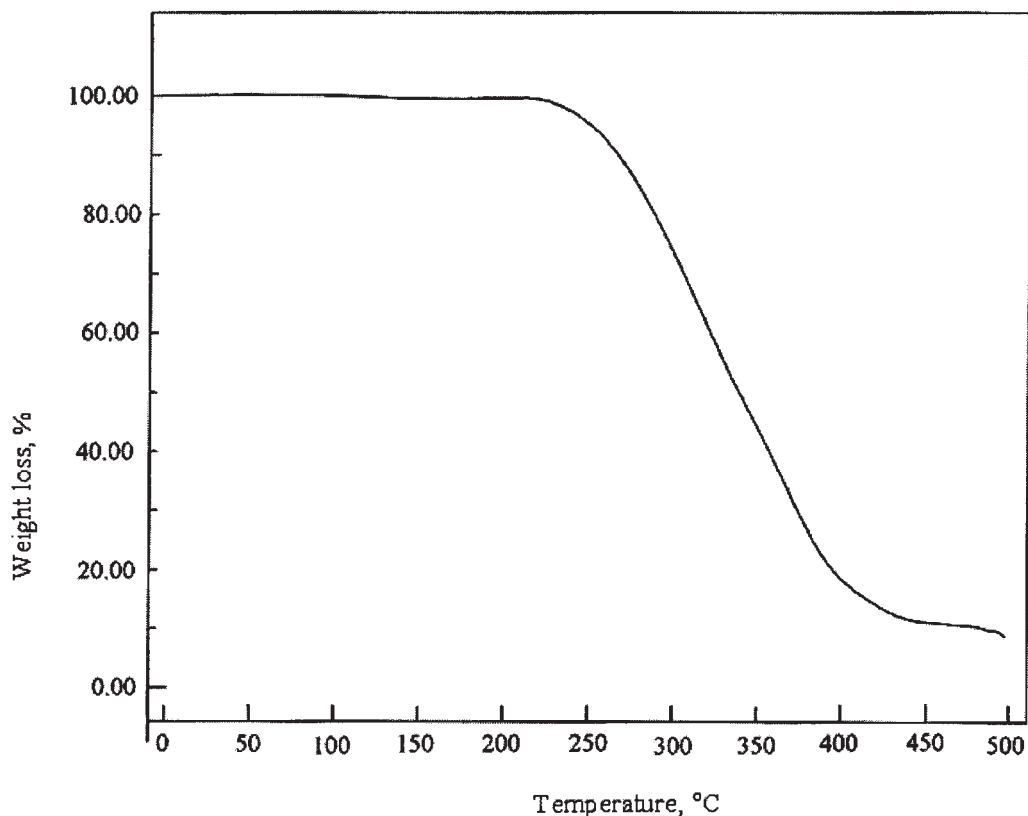
Figure 1 Thermogravimetric curve of PMHPMA.

atures above T_g and at a fast carrier gas (N$_2$) flow rate for 24 h before use. The probes were injected into the column with Hamilton 1-μL syringes (New York, NY). Three consecutive injections were made for each probe at each set of measurements. An injection volume of 0.2 μL was selected. The retention times of the probes were measured with a Shimadzu CR2A Chromatopac model integrator. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide.[23]

RESULTS AND DISCUSSION

Structure of PMHPMA

According to the molecular weight distribution, the M_n, M_w, and PDI values of PMHPMA were 65,864

TABLE I
Variation of V_g^0 (cm^3/g) of Selected Alcohols and Alkanes with Temperature with PMHPMA as the Stationary Phase

| Temperature (K)	Probe								
	Hexane	Heptane	Octane	Decane	MeOH	EtOH	1-Propanol	1-Butanol	1-Pentanol
323	4.440	4.836	5.782	12.940	6.781	5.818	6.127	7.709	13.188
333	4.062	4.364	4.951	9.047	5.757	5.186	5.304	6.261	8.359
343	3.830	4.018	4.366	6.738	5.030	4.619	4.635	5.299	6.279
353	3.612	3.731	3.999	5.492	4.507	4.187	4.208	4.581	5.323
363	3.470	3.537	3.707	4.655	4.117	3.976	3.947	4.174	4.711
373	3.203	3.284	3.417	4.101	3.779	3.632	3.685	3.873	4.476
383	3.010	3.082	3.196	3.676	3.449	3.411	3.474	3.701	4.207
393	2.882	2.930	3.038	3.409	3.253	3.229	3.161	3.248	3.732
403	2.967	3.035	3.127	3.539	3.265	3.299	3.173	3.425	3.940
413	2.879	2.945	3.021	3.381	3.119	3.130	3.261	3.534	3.992
423	2.765	2.827	2.921	3.222	2.973	2.983	3.098	3.326	3.742
433	2.631	2.711	2.771	3.062	2.831	2.821	2.942	3.139	3.444
443	2.541	2.598	2.666	2.915	2.666	2.666	2.761	2.934	3.203
453	2.396	2.469	2.514	2.725	2.514	2.542	2.606	2.752	2.962
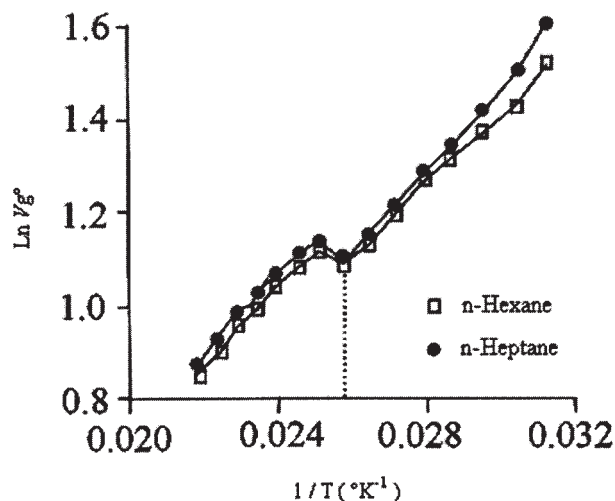
Figure 2 Changes in V_g^0 of selected alcohols and alkanes as a function of the inverse of the temperature.

g/mol, 215,375 g/mol, and 3.275, respectively. The FTIR spectra of MHPMA and its homopolymer had similar bands. In the polymer and monomer, the vibration band of the OH groups gave intense and wide bands at 3528–3417 and 3480–3458 cm^{-1}, respectively. The vibration bands of the C=O and vinylic C=C groups of the polymer and monomer were observed at 1735 and 1618 cm^{-1} and 1735 and 1615 cm^{-1}, respectively. According to ^{1}H- and ^{13}C-NMR spectra, the signals at 6.60–7.00 and 129.60–137.30 ppm, respectively, were assigned to the aromatic protons for the polymer. The signals at 1.80–2.40 ppm were due to methyl protons of the aromatic ring. The absence of vinyl protons in the region of 5.75–6.10 ppm indicated the polymerization of MHPMA. The ^{1}H- and ^{13}C-NMR and FTIR results showed the formation of macromolecules from MHPMA by the 1,4-dioxane solution with AIBN as the initiator at 60°C.

Thermal behavior

A thermogravimetric trace of PMHPMA is shown in Figure 1. PMHPMA was demonstrated to have rela-

tive thermal stability. The initial decomposition starting temperature, the 20% weight loss, 50% weight loss, and final decomposition temperatures, the temperature of the maximum rate of weight loss, and the carbonaceous residue value of PMHPMA were found to be 225°C, 296°C, 345°C, 445°C, 330°C, and 13.97%, respectively.

Thermodynamic properties

The V_g^0 values of selected alcohols and alkanes were obtained with one loading of PMHPMA (ca. 10 wt %) between 323 and 453 K. The V_g^0 values of these organic solvents were calculated according to eq. (1) and are given in Table I. The V_g^0 values changed for each group of solvents with the temperature. V_g^0 of the probes decreased with increasing temperature. V_g^0 of hexane and heptane is shown in Figure 2. T_g of PMHPMA was found to be about 386 K by IGC. El-Naggar and Turkey[24] studied the effect of coatings of various poly(ethylene glycol)s (molecular weight = 600, 2000, or 4000) on Chromosorb for the separation of saturated hydrocarbons, aromatic hydrocarbons, and alcohols. The polarity and selectivity of the prepared packing columns and their thermodynamic parameters were determined via IGC. The dependence of the V_g^0, enthalpy, and entropy values on the loading of the polymer on the support was studied. In all the investigated polymers, the mass of the polymer was about 5 or 10% to deactivate the support surface.

ΔH_a [eq. (3)] and ΔH_1^s [eq. (6)] values of the PMHPMA–probe systems were calculated by the plotting of ln V_g^0 against the reciprocal of the absolute column temperature [$1/T$ (K^{-1})]. Table II shows the experimentally obtained ΔH_a and ΔH_1^s values in the temperature ranges of 323–363 and 393–413 K, respectively. The ΔG_1^s [eq. (7)] and ΔS_1^s [eq. (8)] values of the PMHPMA–probe systems were calculated as in the literature[25] and are given in Table II. The ΔH_1^s and ΔS_1^s values (see Table II) and ΔH_1^∞ values [eq. (11); shown later in Table IV] were negative and positive, respectively.

TABLE II
ΔG_1^s, ΔH_1^s, ΔH_a, and ΔS_1^s of PMHPMA with Selected Alcohol and Alkane Systems

Probe	ΔG_1^s (kJ/mol)			ΔH_1^s (kJ/mol) at 393–413 K	ΔH_a (kJ/mol) at 323–363 K	ΔS_1^s (J/mol)		
	393 K	403 K	413 K			393 K	403 K	413 K
MeOH	17.53	17.96	18.56	−5.63	−25.41	−58.93	−58.54	−58.57
EtOH	16.36	16.71	17.30	−4.23	−31.48	−52.39	−51.96	−52.13
1-Propanol	15.56	15.95	16.25	−4.37	−33.27	−50.71	−50.42	−49.93
1-Butanol	14.79	14.99	15.25	−3.49	−33.82	−46.51	−45.86	−45.38
1-Pentanol	13.77	13.94	14.25	−3.93	−28.88	−45.04	−44.34	−44.02
Hexane	14.69	14.97	16.50	−2.98	−23.19	−44.96	−44.54	−47.17
Heptane	14.15	14.39	16.01	−3.05	−26.46	−43.77	−43.28	−46.15
Octane	13.60	13.85	15.55	−3.48	−27.92	−43.46	−43.00	−46.08
Decane	12.51	12.70	14.19	−5.51	−24.12	−45.85	−45.19	−47.70

TABLE III
Ω_1^∞ and χ_{12}^∞ of PMHPMA with Selected Alcohol and Alkane Systems

Probe	Ω_1^∞				χ_{12}^∞			
	423 K	433 K	443 K	453 K	423 K	433 K	443 K	453 K
MeOH	17.04	14.16	12.04	10.33	1.39	1.19	1.03	0.87
EtOH	16.29	13.35	11.09	9.24	1.38	1.18	0.99	0.82
1-Propanol	22.53	18.27	15.19	12.74	1.71	1.50	1.31	1.14
1-Butanol	32.27	25.79	21.15	17.55	2.09	1.86	1.66	1.47
1-Pentanol	46.67	37.93	31.04	25.95	2.47	2.26	2.26	1.87
Hexane	12.79	11.14	9.65	8.64	1.05	0.91	0.77	0.34
Heptane	21.62	18.26	15.59	13.57	1.58	1.41	1.25	1.12
Octane	35.88	29.89	24.87	21.35	2.09	1.91	1.72	1.57
Decane	94.65	75.02	60.29	50.05	3.07	2.83	2.61	2.42

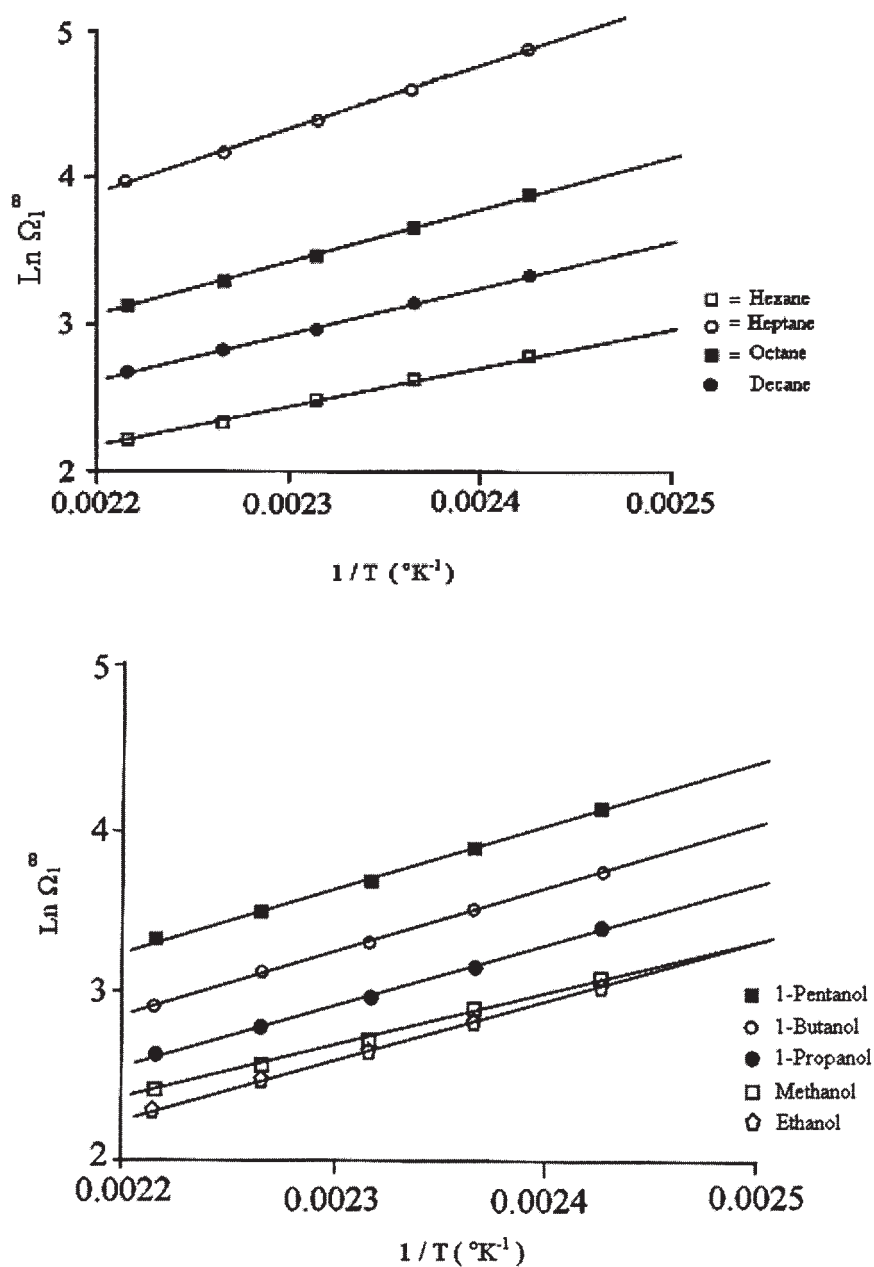**Figure 3** Variation of the logarithm of $OHgr_1^\infty$ with $1/T$ (K^{-1}) for selected alcohols and alkanes on PMHPMA.

TABLE IV
ΔG_1^∞ and ΔH_1^∞ of PMHPMA with Selected Alcohol and Alkane Systems

Probe	ΔG_1^∞ (kJ/mol)					ΔH_1^∞ (kJ/mol) at 413–453 K
	413 K	423 K	433 K	443 K	453 K	
MeOH	10.40	9.96	9.53	9.15	8.78	27.54
EtOH	10.32	9.80	9.32	8.85	8.36	31.19
1-Propanol	11.46	10.94	10.45	10.01	9.57	31.51
1-Butanol	12.73	12.20	11.68	11.22	10.78	33.43
1-Pentanol	14.02	13.50	13.07	12.64	12.25	32.81
Hexane	9.78	8.95	8.67	8.34	8.11	21.97
Heptane	11.16	10.80	10.45	10.10	9.81	25.80
Octane	13.01	12.57	12.22	11.82	11.52	29.30
Decane	16.47	15.98	15.53	15.08	14.72	35.66

Chen and Al-Saigh[26] used three loading of PEMA (3–12 wt %) and determined ΔH_1^s, ΔG_1^s, and ΔS_1^s values for alkanes, acetates, and alcohols with PEMA. The ΔH_1^s and ΔS_1^s values and ΔG_1^s values of the alkanes, acetates, and alcohols were negative and positive, respectively, for PEMA at 458 K.[26] The values of Ω_1^∞ [eq. (9)] and χ_{12}^∞ [eq. (12)] were calculated and also are collected in Table III. Selected alcohols and alkanes showed an exothermic heat of sorption and negative entropy of sorption, which was responsible for the endothermic free energy of sorption. The enthalpy change of the sorption process was dependent on the interaction between the probe and PMHPMA. Because the chemical nature and number of carbons of each probe were different, the heat of sorption became more exothermic as more CH_2 groups were added to the two families of probes. This was an indication that the individual CH_2 group, regardless of the chemical nature of the probe, had a significant interaction with PMHPMA. The alcohols showed more exothermic values than the alkanes. Although the alcohols made two contributions to the sorption process interaction with PMHPMA via OH and via CH_2, the alkanes made only one contribution, which was the interaction of CH_2 groups with PMHPMA. Our interpretation is that alcohols form stronger attraction forces with PMHPMA than alkanes. The attraction forces between PMHPMA and alcohols are actually a combination of two types. The first is dispersive forces between the CH_2 groups of the alcohols and the 3-mesityl-2-hydroxypropyl group of PMHPMA, and the second is the dipole–dipole interaction of the OH group of the alcohols with the C=O group of PMHPMA.

The values of ΔH_1^∞ of the probes were determined from the slopes of ln Ω_1^∞ versus $1/T$ (K^{-1}; Fig. 3). According to the literature, ΔG_1^∞ [eq. (10)] and ΔH_1^∞ of the solutes were calculated and are collected in Table IV. The ΔH_1^∞ values of the alcohols and alkanes changed from 27.54 to 33.43 kJ/mol and from 21.97 to 35.66 kJ/mol, respectively, as shown in Table IV.

It has been proposed that values of Ω_1^∞ greater than 5 are indicative of poor polymer–solute systems,

whereas lower values characterize good solubility for such systems.[27] The values of χ_{12}^∞ greater than 0.5 represent unfavorable polymer–solvent interactions, whereas the values lower than 0.5 indicate favorable interactions in dilute polymer solutions.[28] According to the values of Ω_1^∞ and χ_{12}^∞ (shown in Table III), selected alcohols and alkanes were nonsolvent for PMHPMA. The values increased with an increasing number of carbons in the alcohols and alkanes. That is, the solubility of PMHPMA decreased in alcohols and alkanes at these temperatures. The χ_{12}^∞, ΔG_1^∞, Ω_1^∞, and ΔH_1^∞ values showed a dependence on the change in the number of carbons in the series. That is, these values (χ_{12}^∞, Ω_1^∞, ΔG_1^∞, and ΔH_1^∞) increased with an increasing number of carbons in the series. The χ_{12}^∞, Ω_1^∞, and ΔG_1^∞ values decreased with an increase in the column temperature for the PMHPMA–probe system. According to Kaya et al.,[25] propylamine, butylamine, benzene, hexane, heptane, EtOH, and 1-propanol are good solvents but octane, decane, 1-butanol, and 1-pentanol are nonsolvents for poly[(2-phenyl-1,3-dioxolane-4-yl)-methylmethacrylate] between 443 and 453 K.
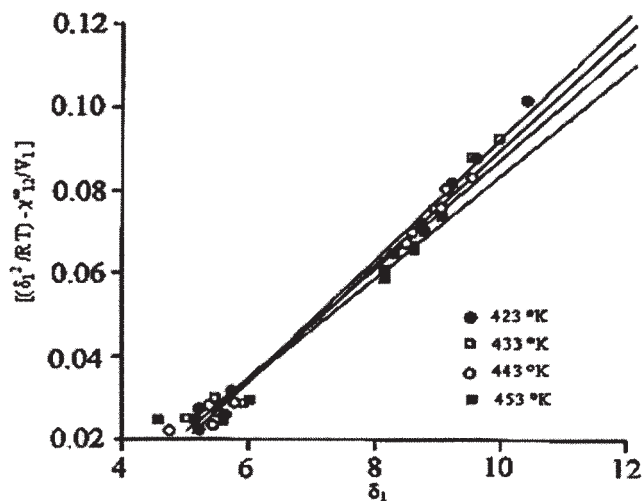

Figure 4 Variation of the term $(\delta_1^2/RT) - \chi_{12}^\infty/V_1$ with δ_1 [(J/cm^3)$^{0.5}$] at different temperatures.

TABLE V
δ_2 of PMHPMA Between 423 and 453 K

Temperature (K)	Slope	Intercept	δ_2 [(J/cm^3)$^{0.5}$] Calculated from the slope	Calculated from the intercept	r
423	0.0149	−0.0558	26.33	28.42	1.00
433	0.0141	−0.0511	25.49	28.01	0.99
443	0.0132	−0.0450	24.24	26.33	0.99
453	0.0122	−0.0380	22.99	24.66	0.98

r, correlation constant.

δ_2 could be determined with eq. (14).[29] δ_2 was determined from either the slope or intercept of a straight line obtained by the plotting of the left-hand side of eq. (14) versus δ_1. δ_2 was evaluated from either the slope or intercept of Figure 4 to be 24.24 or 26.33 (J/cm^3)$^{0.5}$ at 443 K, respectively. δ_2 decreased with increasing temperature (see Table V). Also, δ_2 of PMHPMA was calculated to be 42.64 (J/cm^3)$^{0.5}$ at 25°C with the swelling coefficient method.[30]

CONCLUSIONS

The technique is simple, fast, and economical and provides valuable thermodynamic and physical chemistry information for the characterization of polymeric materials. This technique was successfully applied to determine polymer–solvent and polymer–nonsolvent interactions. The IGC technique was successfully applied to determine some thermodynamic properties of PMHPMA, such as ΔH_a, ΔH_1^s, ΔG_1^s, ΔS_1^s, χ_{12}^∞, ΔG_1^∞, Ω_1^∞, δ_2, and ΔH_1^∞. Alcohols showed a stronger interaction than alkanes for PMHPMA. The contributions of the two functional groups, OH and CH$_2$, to the sorption functions were obtained. The hydroxyl group showed more interactions than the methyl group with PMHPMA. According to χ_{12}^∞ and Ω_1^∞, selected alcohols and alkanes were nonsolvents for the PMHPMA system. Also, from the IGC results, δ_2 could be determined from either the slope or intercept of a straight line obtained by the plotting of the left-hand side of eq. (14) versus the solubility parameter of the organic solvents.

References

1. Mori, H.; Wakisaka, O.; Himo, A.; Nakahama, S. Macromol Chem Phys 1994, 195, 3213.
2. Montheard, J. P.; Catzopoulos, M.; Chappard, D. J Macromol Sci Rev Macromol Chem Phys 1992, 32, 1.
3. Smidsrod, O.; Guillet, J. E. Macromolecules 1969, 2, 272.
4. Al-Saigh, Z. Y. Polymer 1999, 40, 3479.
5. Price, G. J.; Guillet, J. E.; Purnell, J. H. J Chromatogr A 1986, 369, 273.
6. Exteberria, A.; Alfageme, J.; Uriarte, C.; Iruin, J. J. J Chromatogr A 1992, 607, 227.
7. Kaya, İ.; Demirelli, K. J Polym Eng 2001, 21, 1.
8. Munk, P.; Al-Saigh, Z. Y.; Card, T. W. Macromolecules 1985, 18, 2196.
9. Sanetra, R.; Kolarz, B. N.; Wlochowicz, A. Polymer 1987, 28, 1753.
10. Al-Saigh, Z. Y. Polym Commun 1991, 32, 459.
11. Smidsrod, O.; Guillet, J. E. Macromolecules 1976, 2, 272.
12. Braun, J. M.; Guillet, J. E. Macromolecules 1977, 10, 101.
13. DiPaola-Baranyi, G.; Guillet, J. E. Macromolecules 1978, 11, 228.
14. Galin, M.; Maslinco, L. Macromolecules 1985, 18, 2192.
15. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. The Properties of Gases and Liquids; McGraw-Hill: New York, 1977.
16. Reid, R. C.; Sherwood, T. K. The Properties of Gases and Liquids, 2nd ed.; McGraw-Hill: New York, 1966.
17. Kaya, İ.; İlter, Z.; Şenol, D. Polymer 2002, 43, 6455.
18. Desgupta, A.; Santee, Y. R.; Harwood, H. J. J Macromol Sci Chem 1986, 23, 97.
19. Kaya, İ.; Demirelli, K.; Coşkun, M. Polymer 2001, 42, 5181.
20. Kaya, İ.; Demirelli, K. Polymer 2000, 41, 2855.
21. Erol, İ.; İlter, Z.; Coşkun, M.; Ahmedzade, M. J Polym Sci Part A: Polym Chem 2001, 39, 4167.
22. Rabek, J. F. Experimental Methods in Polymer Chemistry; Wiley: Sweden, 1980; p 520.
23. Kaya, İ. Ph.D. Thesis, Study of Physical and Thermodynamic Properties of Alkyl Methacrylates, Fırat University, Elaziğ, Turkey. 1995.
24. El-Naggar, A. Y.; Turkey, G. M. J Appl Polym Sci 2001, 82, 1709.
25. İlter, Z.; Kaya, İ.; Açıkses, A. J Polym Eng 2002, 22, 45.
26. Chen, C. T.; Al-Saigh, Z. Y. Polymer 1990, 31, 1170.
27. Guillet, J. E.; Purnel, J. H. Advances in Analytical Chemistry and Instrumentation; Wiley: New York, 1973.
28. Klein, J.; Jeberien, H. E. Macromol Chem 1980, 181, 1237.
29. Kaya, İ.; Özdemir, E. Polymer 1999, 40, 2405.
30. Choudhary, M. S.; Varma, I. K. J Polym Sci Part A: Polym Chem 1985, 23, 1917.