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Thermodynamic interactions and characterisation of poly[(glycidyl methacrylate-*co*-methyl, ethyl, butyl) methacrylate] by inverse gas chromatography

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Abstract

Poly(glycidyl methacrylate-*co*-methyl methacrylate) poly(GMA-*co*-MMA), poly(glycidyl methacrylate-*co*-ethyl methacrylate) poly(GMA-*co*-EMA) and poly(glycidyl methacrylate-*co*-butyl methacrylate) poly(GMA-*co*-BMA) were synthesized in 1,4-dioxane solution using 2,2′-azobisisobutyronitrile (AIBN) as initiator at 60 °C. The copolymer compositions were determined by ^{1}H NMR analysis. The FT-IR and ^{13}C NMR spectra of the copolymers have been discussed. According to TG, carbonaceous residue values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were found to be 3.00, 4.00 and 4.20%, respectively, at 500 °C. Some thermodynamic quantities such as the sorption enthalpy, $\Delta \mathrm{H}_1^{\mathrm{s}}$, the sorption entropy, $T\Delta S_1^{\mathrm{s}}$, the sorption free energy, ΔG_1^{s}, the partial molar free energy, ΔG_1^{∞}, the partial molar heat of mixing, ΔH_1^{∞}, at infinite dilution were obtained for the interactions of poly[(glycidyl methacrylate-*co*-methyl, ethyl, butyl) methacrylate] with *n*-alkanes, aromatics, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane by inverse gas chromatography method in the temperature range of 363–453 K. The specific retention volumes, V_{g}^0, the weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^{∞}, Flory–Huggins thermodynamic interaction parameters, χ_{12}^{∞} between polymers and solvents were determined. Also, the solubility parameters, δ_2, of the poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) was found to be 30.85, 25.83, 25.00 $(\mathrm{J\ cm^{-3}})^{0.5}$ and 31.94, 26.59, 25.71 $(\mathrm{J\ cm^{-3}})^{0.5}$ from slope and intercept of $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT$ equation, at 433, 423 and 393 K, respectively. The glass transition temperature, T_{g}, of the poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) was found to be 373, 355 and 334 K, respectively, by DSC and inverse gas chromatography. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly[(glycidyl methacrylate-*co*-methyl, ethyl, butyl) methacrylate]; Inverse gas chromatography; Polymer–solvent interactions

1. Introduction

Copolymers based on GMA have applications in biology for the binding of drugs and bio molecules and in electronics industries as negative electron-beam resists [1,2]. The inverse gas chromatography (IGC) method 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. The method is simple, fast, economical and provides valuable thermodynamic information for characterisation of polymeric materials [3–8].

In this study, poly(glycidyl methacrylate-*co*-methyl methacrylate) poly(GMA-*co*-MMA), poly(glycidyl methacrylate-*co*-ethyl methacrylate) poly(GMA-*co*-EMA) and poly(glycidyl methacrylate-*co*-butyl methacrylate) poly(GMA-*co*-BMA) were characterised by using FT-IR, ^{1}H and ^{13}C NMR, element analysis, thermogravimetric analysis (TGA) and high pressure liquid chromatography (HPLC) techniques. Also, we examined the interactions of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) with solvents by using IGC in the temperature range 333–443 K. Therefore, the solubility parameters, δ_2, of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were determined between 433–443, 423–433 and 393–403 K, respectively.

The probe specific retention volumes, V_{g}^0, corrected to 0 °C were calculated from the standard chromatographic

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relation

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

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_o 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, is given by the following equation [9–12].

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

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

By incorporating Eqs. (2) and (3) we calculated the entropy of sorption of solutes as follows:

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

The weight fraction activity coefficient, Ω_1^∞, 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 [5]

$$\Omega_1^\infty = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/RT] \quad (5)$$

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \quad (6)$$

$$\Delta H_1^\infty = R\,\partial \ln(\Omega_1^\infty)/\partial(1/T) \quad (7)$$

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) and M_1 is the molecular weight of the probe. The values of P_1^0 and B_{11} have been calculated as in the literature [13].

The molar volume of the solute, V_1 was calculated using the following relation [14]

$$V_1 = V_c/\rho_r \quad (8)$$

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

$$\rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)^{(0.8z_c+0.31)} \quad (9)$$

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

The Flory–Huggins parameter, χ_{12}^∞, characterising the interactions of a vapour-phase probe with a polymer are determined by the following equation

$$\chi_{12}^\infty = \ln(273.2Rv_2/V_g^0 V_1 P_1^0) - 1 - P_1^0/RT(B_{11} - V_1) \quad (10)$$

where R is the gas constant, v_2 is the specific volume of the polymer. Solubility parameter of the probe is calculated from the relation [15].

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \quad (11)$$

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

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

If the left hand side of this equation is plotted against δ_1, a straight line having a slope of $2\delta_2/RT$ and an intercept of $(-\delta_2^2/RT)$ is obtained. The solubility parameter of polymer, δ_2 can be determined from both the slope and intercept of the straight line [11].

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA), methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) monomers were washed with 5% NaOH solution and then by distilled water; they were dried over anhydrous magnesium sulphate and distilled under vacuum. 2,2′-Azobisisobutyronitrile (AIBN, Merck) was recrystallised from chloroform–methanol mixture.

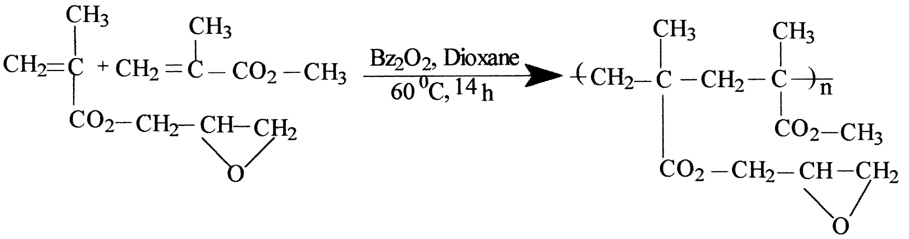
Polar and non-polar probes were used to test the solubility of the copolymers in this study. They were selected to provide several groups of a chemically different nature and polarity. *n*-Pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane were supplied from Aldrich Chemical Co. and benzene, toluene, xylene, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane were supplied from Merck Chemical Co. as chromatographic grade. All probes were used as received. Chromosorb W (60–80 mesh) was supplied from Sigma Chemical Co.

2.2. Copolymerisation

Appropriate quantities of GMA, MMA, EMA and BMA with 1,4-dioxane (monomer/solvent = 2/5 w/v) and AIBN were placed in a standard reaction tube and mixture was flushed with oxygen-free nitrogen for 10 min. In all cases, the initial total monomer concentration was 0.01 mol l^{-1} and the initiator (AIBN) was used as 2% of the total weight of monomers. The tube was then tightly sealed and immersed in a thermostatic oil bath at 60 °C.

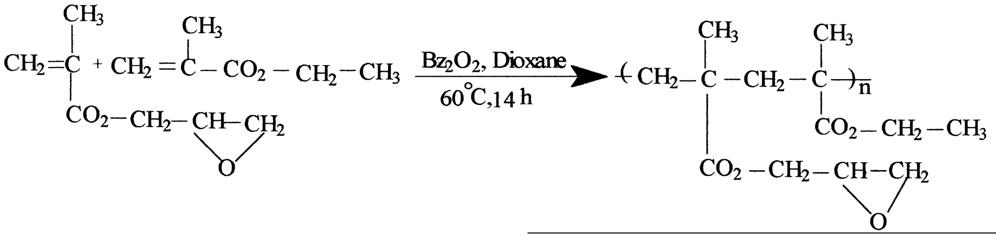
The copolymerisations were restricted to below 15% conversion in order to satisfy the usual copolymerisation equation. Criteria: the copolymers were precipitated in *n*-hexane, and purified by at least two reprecipitations with *n*-hexane from dichloromethane solution. Each copolymer was then dried in a vacuum oven at 40 °C for 24 h.

PGMA-*co*-MMA



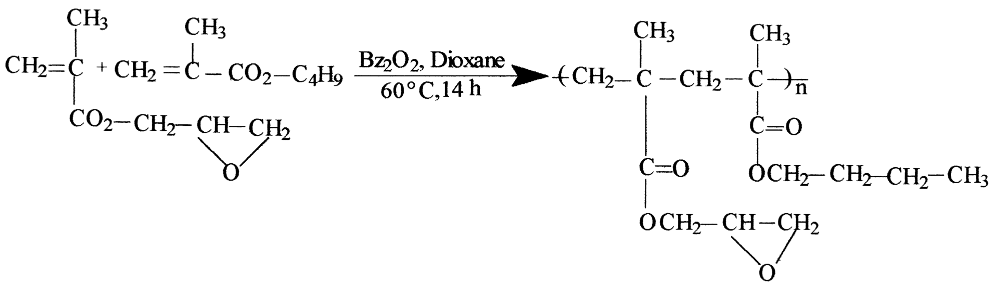
Found: C, 59.05; H, 7.13. Anal. calcd for (1): C, 59.50; H, 7.44; O, 33.06. FT-IR (KBr, cm^{-1}): ν (C–H, bending vibration of epoxide ring) 750, ν (C–H aliphatic) 2997–2951, ν(C=O) 1730, ν(C–O–C) 1250–1049, ν($\underset{\diagdown O \diagup}{-CH-CH_2}$, symmetric ring stretching) 1244. ^{1}H NMR (DMSO): δ ppm, 0.70–1.20 (3H, C*H*$_3$); 1.80–2.20 (2H, C*H*$_2$); 3.50 (3H, OC*H*$_3$); 3.80–4.30 (2H, OC*H*$_2$); 2.50–3.30 (3H, $\underset{\diagdown O \diagup}{-CH-CH_2}$). ^{13}C NMR (DMSO): δ ppm, 17.20, 19.50 (*C*H$_3$); 52.30 (*C*H$_2$); 54.30, 54–60 (–*C*-ipso); 54.80, 54.70 (–O*C*H$_3$); 66.00, 67.50 (-OCH$_2$); 177.30, 178.50 (*C*=O); 45.00, 49.40 ($\underset{\diagdown O \diagup}{-CH-CH_2}$).

PGMA-*co*-EMA



Found: C, 60.50; H, 7.23. Anal. calcd for (1): C, 60.94; H, 7.81; O, 31.25. FT-IR (KBr, cm^{-1}): ν (C–H, bending vibration of epoxide ring) 752, ν (C–H aliphatic) 2990–2950, ν(C=O) 1735, ν(C–O–C) 1255–1044, ν($\underset{\diagdown O \diagup}{-CH-CH_2}$, symmetric ring stretching) 1245. ^{1}H NMR (DMSO): δ ppm, 0.60–1.20 (3H, C*H*$_3$); 1.30 (2H, C*H*$_2$); 3.50–4.50 (2H, OC*H*$_2$); 2.50–3.20 (3H, $\underset{\diagdown O \diagup}{-CH-CH_2}$). ^{13}C NMR (DMSO): δ ppm, 13.80, 16.60 (*C*H$_3$); 16.70, 18.60 (*C*H$_3$); 38.50, 39.70 (*C*H$_2$–*C*H$_3$); 48.80 (–*C*H$_2$); 65.60, 66.60 (–O*C*H$_2$); 60.70 (–*C*-ipso); 176.00, 177.20 (*C*=O); 40.00, 44.80 ($\underset{\diagdown O \diagup}{-CH-CH_2}$).

PGMA-*co*-BMA



Found: C, 63.00; H, 8.20. Anal. calcd for (1): C, 63.38; H, 8.45; O, 28.17. FT-IR (KBr, cm^{-1}): ν (C–H, bending vibration of epoxide ring) 755, ν (C–H aliphatic) 2992–2955, ν(C=O) 1738, ν(C–O–C) 1255–1054, ν($\underset{\diagdown O \diagup}{-CH-CH_2}$, symmetric ring stretching) 1246. ^{1}H NMR (DMSO): δ ppm, 0.50–0.90 (3H, C*H*$_3$); 1.20–2.00 (2H, C*H*$_2$); 3.50–4.20 (2H, OC*H*$_2$); 2.50–3.40 (3H, $\underset{\diagdown O \diagup}{-CH-CH_2}$). ^{13}C NMR (DMSO): δ ppm, 13.70, 16.70 (*C*H$_3$); 18.40, 19.00 (*C*H$_3$); 30.00 (*C*H$_2$); 38.00, 39.00 (–*C*H$_3$); 48.70, 48.80 (–*C*H$_2$); 64.50, 66.70 (–O*C*H$_2$); 53.60, 54.20 (–*C*-ipso); 175.90, 177.10 (*C*=O); 40.20, 44.80 ($\underset{\diagdown O \diagup}{-CH-CH_2}$).

2.3. Characterisation

A Mattson 1000 FT-IR spectrometer was used. Thin films of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were prepared from dichloromethane solution. The solutions were cast on a clear sodium chloride window and the solvent was completely evaporated and the films were dried by heating to remove trace amounts of solvent before characterisation. The ^{1}H and ^{13}C NMR spectra of the copolymers were recorded with a Varian XL-200 NMR instrument. The copolymer samples were examined with 20% (w/v) solutions of CDCI$_3$ using tetramethylsilane as internal standard. The block copolymer compositions were determined by ^{1}H NMR measurements. In the block copolymers, the compositions of GMA and MMA; GMA and EMA; GMA and BMA were found to be 62 and 38%; 56 and 44%; 59 and 41%, respectively. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by HPLC of waters 510. For HPLC investigations were used a SGX (100 Å and 7 mm diameter loading material) 3.3 mm i.d. × 150 mm columns; eluent: THF (1.0 ml min^{-1}), polystyrene standards. A refractometric detector (at 25 °C) was used to analyse the product. The number average molecular weight (M_n), mass average molecular weight (M_w) and PDI were found as 5.55×10^5 g mol^{-1}, 7.10×10^5 g mol^{-1} and 1.28; 4.41×10^5 g mol^{-1}, 7.00×10^5 g mol^{-1} and 1.59; 5.30×10^5 g mol^{-1}, 7.38×10^5 g mol^{-1} and 1.39 for poly-(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA), respectively. TGA curves were recorded with a Shimadzu TGA-50 thermobalance (in air, rate 10 °C min^{-1}). The glass transition temperatures of poly-(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were determined as 100, 82 and 61 °C, respectively, by differential scanning calorimetry (DSC) using a Shimadzu DSC-50H thermal analyser. Densities are measured by determining the weight of a volume-calibrated pycnometer filled with a liquid of known density in which a certain quantity of the polymer sample [16]. Densities of poly(GMA-*co*-MMA), poly-(GMA-*co*-EMA) and poly-(GMA-*co*-BMA) were found as 1.204, 1.186, 1.178 g cm^{-3} at 25 °C, respectively.

2.4. Instrumentation and procedure of thermodynamic studies

A Packard 430 model gas chromatography equipped with a dual flame ionisation 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. 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 inlet of the column, read from a mercury manometer 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 20 cm^3 min^{-1} was used throughout our experiment. The copper (3.2 mm i.d. × 1 m) tubing was washed with methylenechloride and was annealed prior to use. A column packing material was prepared by coating 60–80 mesh size Chromosorb W treated with copolymers. 0.3 g of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were dissolved in 25 ml of 1,4-dioxane and an amount of 3 g of the solid supporting materials were, respectively, 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 a copper tubing [15]. The column was conditioned at temperature above the glass transition temperature and fast carrier gas (N_2) flow rate for 24 h prior to use. The 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 was selected 0.2 μl. The retention times of the probes were measured by using a Shimadzu CR2A Chromatopac model integrator. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide [13].

3. Results and discussion

3.1. Thermal behaviour

Thermogravimetric traces of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) are shown in Fig. 1. The relative thermal stabilities of the various samples were assessed by comparing the initial decomposition starting temperature (T_s), 20% weight loss, 50% weight loss final decomposition temperature (T_f), temperature of maximum rate of weight loss (T_{max}) and percent carbonaceous residue. The results of thermal behaviour are summarized in Table 1. All the copolymer samples showed a single decomposition step. According to TG, carbonaceous residue values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were found to be 3.00, 4.00 and 4.20%, respectively, at 500 °C.

3.2. Thermodynamic properties

The specific retention volumes, V_g^0 of 11 probes were obtained by using three columns loading poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) between 333 and 443 K. The values of specific retention volumes, V_g^0 of these probes were calculated according to Eq. (1) and are given in Tables 2–4. As shown in Tables

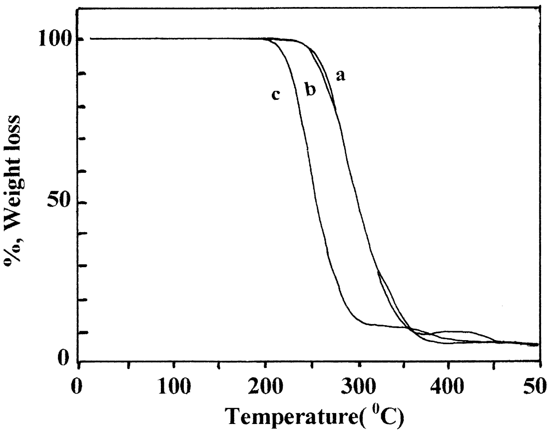


Fig. 1. TG curves of poly(GMA-*co*-MMA) (a), poly(GMA-*co*-EMA) (b) and poly(GMA-*co*-BMA) (c).

Table 1

The thermo-oxidative degradation values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA)

Copolymers	T_s (°C)	20% Mass	50% Mass	T_{max} (°C)	T_f (°C) %	Carb. residue
PGMA-*co*-MMA	245	278	300	319	365	3.00
PGMA-*co*-EMA	237	270	299	320	365	4.00
PGMA-*co*-BMA	220	244	260	274	301	4.20

Table 2

Variation of specific retention volumes, V_g^0 (cm^3 g^{-1}) of some *n*-alkanes, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane with temperature using poly(GMA-*co*-MMA) as stationary phase

Probe	T (K)											
	343	353	363	373	383	388	393	403	413	423	433	443
n-Pentane	14.36	13.13	12.18	11.43	10.54	10.28	9.87	9.29	8.63	7.69	7.15	6.75
n-Hexane	16.12	14.73	12.70	11.98	10.94	10.53	10.02	9.29	8.63	7.87	7.23	6.75
n-Heptane	19.03	17.08	14.01	12.48	11.44	10.72	10.55	9.74	9.71	8.22	7.56	6.90
n-Octane	24.91	22.42	15.85	13.84	12.35	11.53	11.19	10.23	14.55	8.75	8.06	7.46
n-Nonane	29.50	25.55	19.39	16.31	13.93	12.88	12.40	11.32	10.53	9.64	8.64	8.02
n-Decane	52.65	37.87	28.03	21.50	17.31	15.54	14.67	13.13	12.29	11.10	10.22	9.52
Benzene	17.88	16.37	14.47	13.96	13.64	13.87	13.98	13.35	12.52	11.45	10.39	9.52
Toluene	23.08	21.07	16.31	15.76	15.84	16.46	16.62	16.32	13.07	13.84	12.88	12.03
Xylene	35.08	30.89	19.65	18.23	18.55	19.44	19.79	20.17	18.46	9.64	15.46	14.57
1,4-Dioxane	25.14	23.28	18.53	13.47	19.62	19.00	23.21	19.63	17.81	16.05	14.96	14.13
CCl_4	16.96	15.09	13.03	12.36	11.39	11.21	10.87	10.38	9.88	9.46	8.56	7.94
C_3H_5Cl	16.81	14.38	12.97	12.36	11.44	11.31	11.13	10.38	10.02	9.28	8.31	7.70
C_4H_9Cl	18.11	16.44	13.88	12.91	12.29	12.02	11.92	11.27	10.76	10.03	9.22	8.49

Table 3

Variation of specific retention volumes, V_g^0 (cm^3 g^{-1}) of some *n*-alkanes, aromatics, CCl_4, 1-chloro-propane and 1-chloro-butane with temperature using poly(GMA-*co*-EMA) as stationary phase

Probe	T (K)											
	333	343	353	358	363	373	383	393	403	413	423	433
n-Pentane	15.87	14.48	12.82	12.54	12.58	11.30	10.65	9.92	9.29	8.66	8.12	7.54
n-Hexane	16.82	15.65	13.42	12.90	12.72	11.49	10.83	10.08	9.55	9.06	8.49	7.85
n-Heptane	20.38	16.61	14.97	15.11	13.71	12.89	11.55	10.92	10.28	9.64	9.05	8.33
n-Octane	22.21	20.15	18.90	15.93	15.42	14.36	12.74	12.03	11.38	10.67	9.52	8.77
n-Nonane	52.64	34.89	29.06	20.54	19.33	17.44	15.30	14.32	13.31	12.73	10.27	8.50
n-Decane	65.74	58.25	52.05	56.88	27.65	22.86	20.36	18.50	16.91	15.37	14.47	11.32
Benzene	21.42	21.38	21.35	22.85	25.16	24.42	19.64	17.27	14.82	13.81	10.08	8.95
Toluene	32.69	32.08	31.51	28.33	39.23	32.42	27.50	23.57	19.63	17.33	14.47	13.47
Xylene	52.30	51.35	56.50	35.39	57.00	49.93	41.32	32.39	26.52	23.31	18.44	16.67
CCl_4	17.52	17.00	18.83	15.06	16.77	15.18	13.45	12.42	11.90	11.36	15.81	9.65
C_3H_5Cl	20.55	17.96	15.94	20.90	18.62	17.18	13.65	11.92	10.80	10.88	9.85	8.77
C_4H_9Cl	22.55	20.36	19.87	23.21	20.47	18.73	18.04	20.98	12.47	11.50	10.55	9.03

2–4 V_g^0 values changed with molecular weight of each group solvents.

ΔH_1^s values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA)-probe systems were calculated by plotting ln V_g^0 against $1/T$ (K^{-1}) using Eq. (2). Table 5 shows the experimentally obtained sorption heats, ΔH_1^s, in the temperature range 363–393, 383–403 and 358–368 K, respectively, for poly(GMA-*co*-MMA), poly-(GMA-*co*-EMA) and poly(GMA-*co*-BMA)-probe systems. The $T\Delta S_1^s$ values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA), poly(GMA-*co*-BMA)-probe systems were calculated from Eq. (4). The enthalpy data in Table 5 indicated that most of the solvents showed a less interaction with poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly-(GMA-*co*-EMA. The $T\Delta S_1^s$ values of *n*-alkanes and aromatics changed from -9.49 to -18.02 kJ mol^{-1} and from -19.40 to -22.36 kJ mol^{-1}, respectively, for poly-(GMA-*co*-MMA). The $T\Delta S_1^s$ values of *n*-alkanes and aromatics changed from -18.64 to -23.28 kJ mol^{-1} and from -6.40 to -8.78 kJ mol^{-1}, respectively, for poly(GMA-*co*-EMA).

Table 4
Variation of specific retention volumes, V_g^0 (cm^3 g^{-1}) of some *n*-alkanes, aromatics, CCl$_4$, 1-chloro-propane and 1-chloro-butane with temperature using poly(GMA-*co*-BMA) as stationary phase

Probe	*T* (K)										
	358	363	368	373	378	383	388	393	403	413	423
n-Pentane	6.72	6.61	6.48	6.35	6.18	5.85	5.50	5.44	5.02	4.68	4.46
n-Hexane	7.81	7.59	7.29	7.12	6.81	6.51	6.25	6.01	5.51	5.08	4.75
n-Heptane	7.81	7.59	9.31	8.68	8.20	7.52	7.11	6.82	6.17	5.58	5.23
n-Octane	9.40	12.80	13.09	11.53	10.98	9.67	8.83	8.51	7.22	6.48	5.89
n-Nonane	21.55	20.68	19.98	17.62	16.03	13.74	12.04	11.23	9.21	7.98	7.03
n-Decane	39.93	37.99	33.35	29.68	26.12	21.14	17.89	16.11	12.56	10.47	8.94
Benzene	26.62	24.55	20.12	18.01	16.28	13.62	11.81	11.00	9.21	8.08	7.13
Toluene	49.19	44.60	34.57	30.07	26.00	20.90	17.66	16.11	12.67	10.67	9.13
Xylene	83.18	80.90	60.63	50.94	42.91	33.33	26.96	24.05	18.22	14.66	12.07
CCl$_4$	12.73	12.10	11.61	11.33	11.23	10.15	9.29	8.96	7.75	6.88	6.18
C$_3$H$_5$Cl	11.28	10.83	9.72	9.26	8.77	7.76	7.22	6.92	6.17	5.70	5.23
C$_4$H$_9$Cl	17.36	16.77	14.17	12.96	11.86	10.15	9.29	8.73	7.54	6.78	6.08

The $T\Delta S_1^s$ values of *n*-alkanes and aromatics changed from -13.67 to -41.97 kJ mol^{-1} and from -36.70 to -42.59 kJ mol^{-1}, respectively, for poly(GMA-*co*-BMA).

According to the literature, at infinite dilution of the solutes, the values of the weight fraction activity coefficient, Ω_1^∞, the Flory–Huggins interaction parameter χ_{12}^∞, partial molar free energy of mixing ΔG_1^∞ and the partial molar heats of mixing, ΔH_1^∞, can only be determined at temperatures above T_g by IGC technique. As a rule, 40–50 °C above T_g is sufficient [13]. The values of Ω_1^∞ and χ_{12}^∞ obtained using Eqs. (6) and (11), respectively, are also collected in Tables 6 and 7. The values of ΔH_1^∞ of the probes were found from the slopes of ln Ω_1^∞ versus $1/T$ (K^{-1}). The partial molar free energy of mixing ΔG_1^∞ and the partial molar heats of mixing at infinite dilution of the solutes, ΔH_1^∞ calculated from Eqs. (7) and (8) are collected in Table 8.

It has been proposed that the values of Ω_1^∞ greater than 5 are indicative of poor polymer–solute systems while lower values characterize good solubility for such a system [17]. 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 [18].

The values of the weight fraction activity coefficient Ω_1^∞ and χ_{12}^∞ (Tables 6 and 7) have shown that *n*-pentane, *n*-hexane, *n*-heptane, benzene, toluene, xylene (moderate solvent), CCl$_4$, 1-chloro-propane and 1-chloro-butane are good solvent for poly(GMA-*co*-MMA), poly(GMA-*co*-EMA)

Table 5
The sorption free energy, ΔG_1^s (kJ mol^{-1}) and the sorption enthalpy, ΔH_1^s (kJ mol^{-1}) of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) with some *n*-alkanes, aromatics, CCl$_4$, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane systems

Probe	ΔG_1^s (kJ mol¯1)									ΔH_1^s (kJ mol^{-1})		
	Copoly[a]			Copoly[b]			Copoly[c]			Copoly[a]	Copoly[b]	Copoly[c]
	$T = 373$	$T = 383$	$T = 393$	$T = 383$	$T = 393$	$T = 403$	$T = 358$	$T = 363$	$T = 368$	$T = 363–393$	$T = 383–403$	$T = 358–368$
n-Pentane	9.78	10.2	10.7	9.36	9.74	10.1	10.9	11.2	11.4	−8.90	−5.43	−3.93
n-Hexane	9.07	9.61	10.1	8.78	9.11	9.53	10.0	10.2	10.5	−10.6	−5.43	−7.27
n-Heptane	8.49	8.95	9.45	8.07	8.44	8.74	9.57	9.82	9.32	−10.2	−5.23	−18.1
n-Octane	7.82	8.32	8.86	7.31	7.69	7.98	8.69	7.86	7.86	−12.7	−6.52	−34.2
n-Nonane	7.06	7.61	8.11	6.40	6.77	7.06	5.81	6.06	6.27	−13.3	−8.40	−7.90
n-Decane	6.02	6.73	7.27	5.10	5.52	5.89	3.68	3.89	4.35	−17.8	−12.5	−18.8
Benzene	8.69	8.86	9.24	6.73	7.52	8.07	6.69	7.02	7.73	−1.92	−12.6	−29.1
Toluene	7.69	4.93	4.97	5.35	5.94	6.52	4.35	4.72	5.56	−1.05	−16.6	−36.6
Xylene	6.73	6.69	6.81	3.59	4.18	4.93	2.39	2.51	3.43	−4.60	−18.3	−33.0
CCl$_4$	7.11	7.44	7.77	6.14	6.60	6.94	6.86	7.11	7.32	−6.27	−8.78	−9.66
C$_3$H$_5$Cl	9.20	9.53	10.0	7.82	8.65	9.24	9.20	9.49	9.95	−6.90	−15.0	−15.6
C$_4$H$_9$Cl	8.49	8.82	9.20	7.06	7.31	8.11	7.44	7.65	8.28	−5.73	−9.91	−18.6
1,4-Dioxane	7.15	7.23	7.57	–	–	–	–	–	–	−0.71	–	–

Temperature is in K.

[a] MMA.

[b] EMA.

[c] BMA.

Table 6
The weight fraction activity coefficients, Ω_1^∞ of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) with some *n*-alkanes, aromatics, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane systems at various temperatures

Probe	Copoly[a]			Copoly[b]			Copoly[c]		
	$T = 413$	$T = 423$	$T = 433$	$T = 423$	$T = 433$	$T = 443$	$T = 383$	$T = 393$	$T = 403$
n-Pentane	2.96	2.82	2.74	2.82	2.71	2.56	7.78	7.12	6.54
n-Hexane	4.66	3.97	3.81	4.40	4.17	3.48	13.07	10.79	9.81
n-Heptane	6.55	5.85	5.41	6.63	5.75	5.08	19.50	17.22	15.06
n-Octane	10.16	8.89	7.99	9.98	9.03	7.81	29.23	24.45	22.21
n-Nonane	15.14	13.17	11.61	14.30	12.73	12.79	37.94	34.33	30.30
n-Decane	21.51	18.15	15.36	19.88	16.00	15.68	49.04	44.84	39.84
Benzene	4.67	4.26	3.93	4.56	5.10	4.73	11.21	10.76	10.00
Toluene	5.29	4.66	4.32	5.09	4.88	4.25	10.78	9.84	9.76
Xylene	8.66	7.53	6.48	7.74	7.53	6.68	16.02	15.75	15.22
1,4-Dioxane	3.53	3.11	2.75						
CCl_4	0.88	0.85	0.84	0.76	0.76	0.72	1.64	1.58	1.51
C_3H_5Cl	2.20	2.14	1.94	2.45	2.16	2.15	6.24	5.91	5.33
C_4H_9Cl	2.38	2.03	1.85	3.75	3.49	3.21	9.33	8.60	7.97

Temperature is in K.

[a] MMA.

[b] EMA.

[c] BMA.

but *n*-octane, *n*-nonane and *n*-decane are non-solvents for poly(GMA-*co*-MMA), poly(GMA-*co*-EMA). 1,4-dioxane is solvent for poly(GMA-*co*-MMA). *n*-Heptane, CCl_4 and 1-chloro-propane are solvents for poly(GMA-*co*-BMA) but *n*-alkanes (*n*-heptane is moderate solvent), aromatics and 1-chloro-butane are non-solvents for poly(GMA-*co*-BMA). The interaction parameters, χ_{12}^∞, the partial molar free energy of mixing, ΔG_1^∞, the weight fraction activity coefficients, Ω_1^∞, and the partial molar heats of mixing at infinite dilution of the solutes, ΔH_1^∞ showed depending on according to change in the number of carbons in the series. That is, these values (χ_{12}^∞, Ω_1^∞, ΔG_1^∞ and ΔH_1^∞) increased with increase in the number of carbons in the series. But, in all series, the values of χ_{12}^∞, Ω_1^∞, ΔG_1^∞, decreased with increasing column temperature.

The solubility parameter of a polymer, δ_2, can be determined by using Eq. (12) [11,19]. The solubility parameter, δ_2, is determined from either slope or intercept of a straight line obtained by plotting the left-hand-side of Eq. (12) versus δ_1 (Fig. 2). The solubility parameters, δ_2, of the poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) was found to be 30.85, 25.83, 25.00 $(\mathrm{J\ cm^{-3}})^{0.5}$ and 31.94, 26.59, 25.71 $(\mathrm{J\ cm^{-3}})^{0.5}$ from slope and intercept of $[(\delta_1^2/RT) - \chi_{12}^\infty/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT$ equation, at 433, 423 and 393 K, respectively (Table 9).

Table 7
The interaction parameters, χ_{12}^∞ of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) with some *n*-alkanes, aromatics, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane systems at various temperatures

Probe	Copoly[a]			Copoly[b]			Copoly[c]		
	$T = 413$	$T = 423$	$T = 433$	$T = 423$	$T = 433$	$T = 443$	$T = 383$	$T = 393$	$T = 403$
n-Pentane	0.236	0.221	0.200	0.213	0.204	0.197	0.456	0.413	0.382
n-Hexane	0.365	0.346	0.315	0.310	0.302	0.288	1.156	1.032	0.913
n-Heptane	0.356	0.343	0.325	0.358	0.345	0.321	1.210	1.117	1.010
n-Octane	0.612	0.514	0.496	0.561	0.520	0.493	1.816	1.514	1.416
n-Nonane	1.205	1.183	1.100	1.110	0.990	0.983	2.185	2.003	1.814
n-Decane	1.415	1.286	1.072	1.214	1.105	1.076	2.293	2.055	1.842
Benzene	0.355	0.312	0.275	0.352	0.348	0.340	0.683	0.605	0.526
Toluene	0.416	0.401	0.353	0.405	0.386	0.341	0.592	0.545	0.510
Xylene	0.584	0.510	0.466	0.515	0.500	0.485	1.102	1.014	0.977
1,4-Dioxane	0.291	0.273	0.215	–	–	–	–	–	–
CCl_4	0.052	0.041	0.026	0.076	0.042	0.010	0.079	0.055	0.034
C_3H_5Cl	0.154	0.129	0.086	0.220	0.203	0.192	0.442	0.391	0.315
C_4H_9Cl	0.162	0.114	0.077	0.297	0.274	0.240	0.519	0.492	0.458

Temperature is in K.

[a] MMA.

[b] EMA.

[c] BMA.

Table 8
The partial molar free energies of mixing, ΔG_1^{∞} (kJ mol^{-1}) and partial molar enthalpy, ΔH_1^{∞} (kJ mol^{-1}) of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) with *n*-alkanes, aromatics, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane systems

Probe	ΔG_1^{∞} (kJ mol^{-1})									ΔH_1^{∞} (kJ mol^{-1})		
	Copoly[a]			Copoly[b]			Copoly[c]			Copoly[a]	Copoly[b]	Copoly[c]
	$T = 413$	$T = 423$	$T = 433$	$T = 423$	$T = 433$	$T = 443$	$T = 383$	$T = 393$	$T = 403$	$T = 403–423$	$T = 403–423$	$T = 403–423$
n-Pentane	3.80	3.72	3.72	3.55	3.51	3.39	6.52	6.40	6.27	3.76	3.47	3.93
n-Hexane	5.39	4.97	4.93	5.10	5.01	4.47	8.19	7.94	7.65	5.10	4.89	5.56
n-Heptane	6.60	6.35	6.23	6.48	6.14	5.85	9.45	9.28	9.07	6.40	4.89	6.90
n-Octane	8.15	7.86	7.65	7.90	7.73	7.40	10.7	10.4	10.3	7.90	7.73	8.07
n-Nonane	9.53	9.28	9.03	9.11	9.20	9.15	11.5	11.5	11.4	9.28	9.20	9.61
n-Decane	10.7	10.4	10.0	10.2	9.32	9.91	12.3	12.4	12.3	10.4	9.99	10.7
Benzene	5.43	5.23	5.06	5.23	5.73	5.60	7.69	7.73	7.69	5.23	5.52	5.85
Toluene	5.85	5.56	5.43	5.60	5.56	5.23	7.57	7.48	7.65	5.60	5.48	6.19
Xylene	7.61	7.27	6.90	7.02	7.10	6.86	8.82	8.99	9.11	7.23	6.98	7.73
CCl_4	−0.46	0.59	−0.63	−0.92	−0.96	−1.21	1.59	1.46	1.38	0.59	1.05	0.63
C_3H_5Cl	2.76	2.76	2.42	3.09	2.72	2.76	5.81	5.81	5.60	2.63	2.84	3.05
C_4H_9Cl	3.05	2.55	2.26	0.46	0.46	0.42	7.11	6.94	6.94	2.63	4.39	3.68
1,4-Dioxane	4.43	4.10	3.72	–	–	–	–	–	–	4.10	–	–

Temperature is in K.
[a] MMA.
[b] EMA.
[c] BMA.

According to swelling coefficient (Q) [20] and titration [21, 22] methods, the solubility parameters δ_2 of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) have been calculated as 45.98, 45.14, 47.23 (J cm^{-3})$^{0.5}$; 45.77, 43.47, 44.39 (J cm^{-3})$^{0.5}$, respectively, at 25 °C.

4. Conclusion

Some copolymers of GMA with MMA, EMA and BMA were formed in 1,4-dioxane by using AIBN at 60 °C. The copolymers were characterised by FT-IR, $^1H-^{13}C$ NMR,

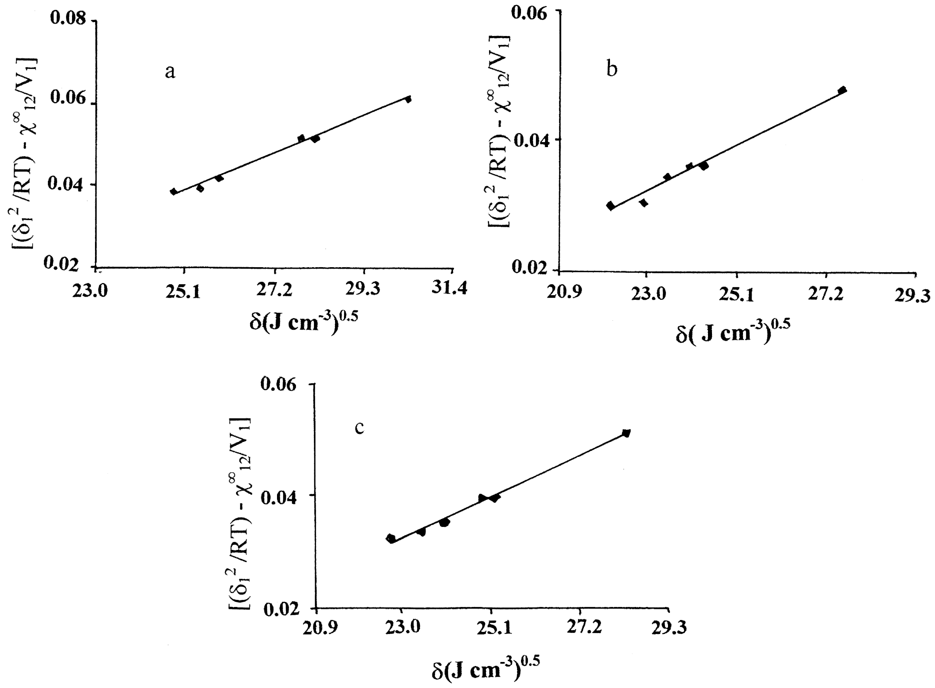


Fig. 2. Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 (J cm^{-3})$^{0.5}$ at various temperatures (a) = 393 K, (for poly(GMA-*co*-BMA)) (b) = 423 K, (poly(GMA-*co*-EMA)) (c) = 433 K, (poly(GMA-*co*-MMA)).

Table 9
The solubility parameter, δ_2 (J cm^{-3})$^{0.5}$ of copolymers at 393, 423 and 433 K, respectively

T (K)	Copolymers	Slope	Intercept	Calcd from slope, δ_2	Calcd from intercept, δ_2	r
433	Poly(GMA-*co*-MMA)	0.0139	−0.0440	25.0	25.7	0.9788
423	Poly(GMA-*co*-EMA)	0.0147	−0.0481	25.8	26.5	0.9860
393	Poly(GMA-*co*-BMA)	0.0189	−0.0747	30.8	31.9	0.9803

HPLC, TGA and DSC. The percentages of GMA, MMA, EMA and BMA in the copolymers were established by ^{1}H NMR analysis. The glass transition temperatures of the poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were found to be 100, 82 and 61 °C, respectively. IGC technique was successfully applied to determine some thermodynamic properties of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) such as the sorption enthalpy, ΔH_1^s, sorption free energy, ΔG_1^s, sorption entropy, ΔS_1^s, Flory–Huggins interaction parameters, χ_{12}^∞, the partial molar free energy of mixing, ΔG_1^∞, the weight fraction activity coefficients, Ω_1^∞, and the partial molar heats of mixing, ΔH_1^∞, at infinite dilution. Flory–Huggins interaction parameters of copolymers with *n*-alkanes, aromatics, CCl_4, 1-chloro-propane, 1-chloro-butane and 1,4-dioxane solvents were determined. The results obtained are in good agreement with polymer–solvents and polymer–non-solvents systems. The technique is relatively uncomplicated and the data reduction is carried out by a computer. According to TG, carbonaceous residue values of poly(GMA-*co*-MMA), poly(GMA-*co*-EMA) and poly(GMA-*co*-BMA) were found to be 3.00, 4.00 and 4.20%, respectively, at 500 °C.

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