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Synthesis, characterization and thermodynamic properties of poly(3-mesityl-2-hydroxypropyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone)

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Abstract

Poly(3-mesityl-2-hydroxypropyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone) P(MHPMA-*co*-VP) was synthesized in 1, 4-dioxane solution using benzoyl peroxide (BPO) as initiator at 60 °C. The copolymer was characterized by ^{1}H ^{13}C NMR, FT-IR, DSC, TGA, size exclusion chromatography analysis (SEC) and elemental analysis techniques. According to SEC, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of PMHPMA-*co*-VP were found to be 58,000, 481,000 g/mol and 8.26, respectively. According to TGA, carbonaceous residue value of PMHPMA-*co*-VP was found to be 6% at 500 °C. Also, some thermodynamic properties of PMHPMA-*co*-VP such as the adsorption enthalpy, ΔH_a, molar evaporation enthalpy, ΔH_v, the sorption enthalpy, ΔH_1^s, sorption free energy, ΔG_1^s, sorption entropy, ΔS_1^s, the partial molar free energy, ΔG_1^∞, the partial molar heat of mixing, ΔH_1^∞, at infinite dilution was determined for the interactions of PMHPMA-*co*-VP with selected alcohols and alkanes by inverse gas chromatography (IGC) method in the temperature range of 323–463 K. According to the specific retention volumes, V_g^0, the weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞, and Flory–Huggins interaction parameters, χ_{12}^∞ between PMHPMA-*co*-VP-solvents were determined in 413–453 K. According to Ω_1^∞ and χ_{12}^∞, selected alcohols and alkanes were found to be non-solvent for PMHPMA-*co*-VP at 413–453 K. The glass transition temperature, T_g, of the PMHPMA-*co*-VP found to be 370 and 363 K, respectively, by IGC and DSC techniques, respectively.

Keywords: Poly(3-mesityl-2-hydroxypropyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone); Synthesis and characterization; Inverse gas chromatography

1. Introduction

Polymeric micelles formed from biodegradable amphiphilic block copolymers have attracted growing interest because of their unique morphological properties and their applicability in drug delivery. The outer hydrophilic shell makes the micelles soluble in aqueous solutions, whereas the inner hydrophobic core can serve as a microcontainer for various hydrophobic drugs. Polymeric micelles have been shown to solubilize poorly water-soluble drugs in high amounts, increase their half-life after intravenous administration, and enhance their efficiency [1].

Water-soluble carbon chain polymers with amide groups in side chains, mainly poly-*N*-vinylpyrrolidone (PVP) and *N*-vinylpyrrolidone (VP) copolymers are widely used, for instance, in medicine and as carriers of biologically active compounds [2].

Polymer hydro gels are three-dimensioned networks formed by chemical bonds and/or physical forces. They can absorb water to swell, but cannot dissolve in water. This reason, interest in the preparation of hydrogels with various properties has increased considerably in recent years, due to their versatile applications in biomedicine, biotechnology, food industry and others. They are used as controlled release systems of drugs, for the production of contact lenses and artificial organs in biomedicine, as an adsorbent for the removal of some agent in environmental applications [3].

Because of these properties, it is very important investigation of polymer-solute interactions of methacrylate polymers by IGC technique. The method had been developed by Smidsrod and Guillet and applied to many polymer–solvent and polymer–non-solvent systems. The physical–chemical properties which can be obtained for polymeric systems include the interaction parameters of polymer–solvent, polymer–non-solvent and polymer–polymer systems, solubility parameters, and weight fraction coefficients, the molar

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heat and free energy of mixing and sorption, the crystallinity degree of semi-crystalline polymers, the glass transition and melting points of polymers, the decomposition temperatures of polymers, the surface energy of polymers. The 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, and economical and provides valuable thermodynamic information for characterization of polymeric materials[4–11].

In this paper, we poly(3-mesityl-2-hydroxypropyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone) (PMHPMA-*co*-VP) was synthesized in 1, 4-dioxane solution using benzoyl peroxide as initiator at 60 °C. The copolymer was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, DSC, SEC and element analysis techniques. Then, we examined the interactions of PMHPMA-*co*-VP with alcohols (polar) and alkanes (nonpolar) solute probes by using IGC in the temperature range 323–463 K. Also, we were determined the solubility parameter, δ_2, and thermal properties of the PMHPMA-*co*-VP by using IGC and TGA techniques, respectively.

1.1. IGC methodology

IGC was used previously by many researchers to study the thermodynamic properties of polymers [7,8,12,13]. Only peak retention time data are needed and it is generally expresses as retention volume V_g^0. The specific retention volume at 0 °C was determined experimentally using the following relationship [14]:

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

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

where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe, t_p, and the methane, t_g, F the flow rate of the carrier gas at 273.15 K and 1 atm., T is column temperature (K), w is the mass of the polymeric stationary phase and J is the James–Martin correction factor for gas compressibility and P_i and P_o are the inlet and outlet pressures, respectively.

The heat of vaporization of the pure solvent are calculated as follows [15]:

$$\Delta H_v = -R \frac{\partial \mathrm{Ln}\, P_1^0}{\partial(1/T)} \tag{3}$$

The sorption enthalpy (ΔH_a) of the probes adsorbed by the PMHPMA-*co*-VP is given by the following equation:

$$\frac{\partial \mathrm{Ln}\, V_g^0}{\partial(1/T)} = -\frac{\Delta H_a}{R} \tag{4}$$

The values of molar heat (enthalpy), ΔH_1^s, the molar free energy, ΔG_1^s, the entropy, ΔS_1^s, of sorption of the probe absorbed by the PMHPMA-*co*-VP and 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 like literature[16–18].

The molar heat (enthalpy), ΔH_1^s, the molar free energy, ΔG_1^s, and the molar entropy, ΔS_1^s, of sorption of the probe absorbed by the PMHPMA-*co*-VP is given by the following equations:

$$\Delta H_1^s = -R\delta \ln\left(\frac{V_g^0}{\delta(1/T)}\right) \tag{5}$$

$$\Delta G_1^s = -RT \ln\left(\frac{M_1 V_g^0}{273.15R}\right) \tag{6}$$

By incorporating Eqs. (5) and (6) we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \tag{7}$$

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 [6].

$$\Omega_1^\infty = \frac{273.15R}{V_g^0 P_1^0 M_1} \exp\left(-\frac{P_1^0(B_{11} - V_1)}{RT}\right) \tag{8}$$

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \tag{9}$$

$$\Delta \bar{H}_1^\infty = R\delta \ln\left(\frac{\Omega_1^\infty}{\delta(1/T)}\right) \tag{10}$$

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 molar volume of the solute, V_1 was calculated using the following relation [19].

$$V_1 = \frac{V_c}{\rho_r} \tag{11}$$

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

$$\rho_r = 1.20 + (5.565 - 11.03z_c)\left(1 - \frac{T}{T_c}\right)^{(0.8^{Z_c} + 0.31)} \tag{12}$$

where z_c is the critical compressibility factor and T_c is the critical temperature and these values were taken from literature [20].

The PMHPMA-*co*-VP-solute interaction parameters, χ_{12}^∞ at infinite dilution of different solutes used in this study are defined by the following equation:

$$\chi_{12}^\infty = \ln\left(\frac{273.2R\nu_2}{V_g^0 V_1 P_1^0}\right) - \frac{1 - P_1^0}{RT(B_{11} - V_1)} \tag{13}$$

where R is the gas constant, ν_2 is the specific volume of the polymer. The solubility parameter of the probe is calculated from the relation [20–24].

The vapour pressure P_1^0 was calculated from the Antonie equation as follows:

$$\log P_1^0 = \frac{A - B}{(t + C)} \tag{14}$$

where t is the temperature (in °C) and A, B and C are constants [20]. The second virial coefficients B_{11} were computed using the following equation [17]:

$$\frac{B_{11}}{V_c} = 0.430 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375(n - 1)\left(\frac{T_c}{T}\right)^{4.5} \tag{15}$$

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 molar volumes of the solutes V_1 were calculated as in the literature [21].

$$\delta_1 = \left[\frac{(\Delta H_v - RT)}{V_1}\right]^{0.5} \tag{16}$$

The molar evaporation enthalpy (ΔH_v) of the probes adsorbed by the PMHPMA-*co*-VP is given by the following equation [19]:

$$\Delta H_v = \Delta H_1^\infty - \Delta H_1^s \tag{17}$$

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

$$\left[\left(\frac{\delta_1^2}{RT}\right) - \frac{\chi_{12}^\infty}{V_1}\right] = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2^2}{RT} \tag{18}$$

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 [16].

2. Experimental

2.1. Materials

Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, hexane, heptane, octane, decane, methacrylic acid, pyridine, dichloromethane, toluene, mesitylene, *N*-vinyl-2-pyrrolidone, benzoyl peroxide (BPO), anhydrous $MgSO_4$, metallic sodium, diethyl ether, KOH, NaOH, epichlorohydrine, $CHCl_3$, anhydrous $AlCl_3$, 1,4-dioxane were supplied from Merck Chemical Co. as chromatographic grade. 3-mesityl-2-hydroxypropyl methyl methacrylate was synthesized as follows. Chromosorb W (80–100 mesh) was supplied from Sigma Chemical Co.

2.2. Synthesis of 3-mesityl-2-hydroxypropyl chloride

Mesitylene (M) (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 1-chloro-2, 3-epoxypropane (1.2 mol, 11.2 g). 1-chloro-2, 3-epoxypropane was added drop wise over of solution between 0–5 °C for 5–6 h. Then, the reaction mixture was stirred at 30 °C for 1 h and then mixture was added to HCl and freezing water solution. Organic phase was extracted several times with diethyl ether and dried over anhydrous $MgSO_4$. Diethyl ether was removed with vacuum evaporator. Unreacted mesitylene was removed by vacuum distillation. The product was distilled under vacuum (5 mmHg, 90 °C) [25].

2.3. 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) epichlorohidryne. The chlorohydrins was added drop wise over of solution and mixture was heated between 30–35 °C for 8–9 h. Organic phase was extracted several times with diethyl ether and washed with water (50 ml × 3) and dried over anhydrous $MgSO_4$. Diethyl ether was removed with vacuum evaporator. The product was distilled under vacuum (5 mmHg, 95 °C). The product was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR techniques.

FT-IR (KBr, cm^{-1}): ν (C–H aryl) 3100–3000, ν (C–H aliphatic) 2918–2860, ν (C=C) 1635, ν (C–O) 1095, ν (epoxy-C–H) 3100–3000. ^{1}H NMR ($CDCl_3$):δ ppm, 1.80–2.40(s,9H, Aryl–C*H*$_3$);2.63 (d, 2H,–C*H*$_2$); 2.92(d, 2H, oxyrane C*H*$_2$); 3.80 (m, 1H, oxyrane–C*H*); 6.60–7.00 (s, 2H, Aromatic). ^{13}C NMR ($CDCl_3$):δ ppm, 20–21.30(s,3C, Aryl–*C*H$_3$); 46.70 (s, 1C,–*C*H$_2$); 31.80 (s, 1C, oxyrane *C*H$_2$); 51.60 (s, 1C, oxyrane *C*H); 129.60 (s, 2C, Aromatic–*C*H); 131.20 (s, 1C, Aromatic, –C–, ipso carbon); 135.90 (s, 1C, Aromatic, –C–, ipso carbon); 137.30 (s, 2C, Aromatic C, ipso carbon).

2.4. Synthesis of 3-mesityl-2-hydroxypropyl methacrylate

3-Mesityl-1, 2-epoxy propane (15 g), methacrylic acid (18 g), toluene (150 ml) and pyridine (3 ml, as catalyst) were placed in a 250 ml single-necked flask. The solid hydroquinone was added over of the mixture for prevent to polymerisation. The mixture was heated between 85–90 °C for 30 h. 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 vacuum evaporator. The product was distilled under vacuum (5 mmHg, 135–140 °C). The product was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR techniques.

Analytical calcd for MHPMA.: C, 73.28; H, 8.40. Found: C, 73.05; H, 8.15. FT-IR (KBr, cm^{-1}): ν (O–H) 3480–3458, ν (C–H aryl and alkene C=C) 2946–2903, ν (C–H aliphatic) 2827–2816, ν (vinylic C=C) 1615, ν (C=O) 1735, ν (C–O–C) 1274. ^{1}H NMR ($CDCl_3$):δ ppm, 1.96 (s, 3H, C*H*$_3$); 2.00–2.40 (s,9H, Aryl-C*H*$_3$); 2.50–3.10 (d, 2H,–C*H*$_2$); 4.17 (d, 2H, O–C*H*$_2$); 3.66 (m, 1H,–C*H*); 5.58–6.14 (s, 2H, vinylic C*H*$_2$); 6.90 (s, 2H, Aromatic). ^{13}C NMR ($CDCl_3$): δ ppm, 17.10 (s, 1C, *C*H$_3$); 19.00–19.80 (s,3C, Aryl-*C*H$_3$); 32.27 (s, 1C,–*C*H$_2$); 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).

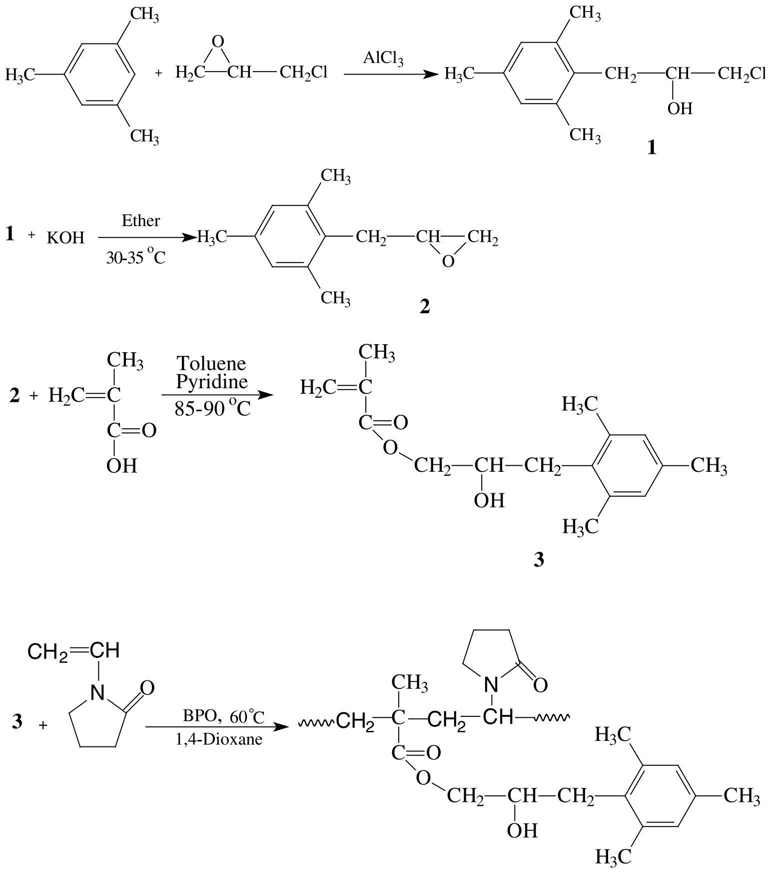
2.5. Copolymerisation of PMHPMA with VP

PMHPMA-*co*-VP was prepared by free-radical polymerisation of MHPMA and *N*-vinyl-2-pyrrolidine with BPO (2% of the monomer weight) in 1, 4-dioxane in a sealed tube at 60 °C for 15 h with 50% conversion (Scheme 1).The copolymer was precipitated in excess hexane. After a few reprecipitations from hexane solution using 1, 4-dioxane, the copolymer was dried under vacuum at 40 °C for 24 h [25].

Analytic Calcd for PMHPMA-*co*-VP: C, 70.78; H, 8.31; N, 3.75.Found: C, 69.18; H, 7.16; N, 3.32. FT-IR (KBr, cm^{-1}): ν (O–H) 3506, ν (C–H aryl and alkene) 3100–3040, ν (C–H aliphatic) 3000–2850, ν (C=O) 1725, ν (C=C aromatic) 1600, ν (C–O–C) 1228. ^1H NMR (DMSO):δ ppm, 1.09–1.93 (s and d, 7H, CH_3 and CH_2 protons of main chain); 2.30–3.50 (t and m, 6H, CH_2 protons of pyrrolidone); 3.80 (d, 1H,–N–CH); 2.05 (s, 9H, Aryl-CH_3); 2.95 (d, 2H,–CH_2); 3.74 (d, 2H, O–CH_2); 3.60 (m, 1H, –CH); 4.47 (s, 1H, –OH); 6.42 (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); 18.00, 3310 and 44.30 (s, 3C, carbons of pyrrolidone) and 174.00 (s, 1C, C=O, carbonyl carbon of pyrrolidone).

2.6. Analysis

The copolymer and its beginning matters were characterized by using Mattson FT-IR-1000 spectrometer and ^1H and ^{13}C NMR spectra (Bruker AC FT NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded at 25 °C by using deuteriated DMSO as solvent. TMS was used as internal standard. Elemental analysis was carried out with a Carlo Erba 1106. The FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}). According to ^1H NMR results, ratios of *N*-vinyl-2-pyrrolidone and 3-mesityl-2-hydroxypropyl methacrylate were found to be 45.75 and 54.25%, respectively, at the copolymer. GPC analyses were performed at 30 °C using THF as eluent at a flow rate of 1.0 ml/min. A refractive index detector was used as a detector. The instrument (Hawlet Packard GPC-SEC system) was calibrated with a mixture of polystyrene standards using 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 copolymer



Scheme 1.

sample. The glass transition temperature of PMHPMA-*co*-VP is found about 380 K by Shimadzu differential scanning calorimeter (DSC) DSC-50 model. Thermal data was obtained by using TG-50H Shimadzu Thermal Analysis. TGA measurement was taken between 20–500 (in air, rate 10 /min). Density is 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 [26]. Density of PMHPMA-*co*-VP was found as 1.040 g/cm^3 by pycnometric measurement at 25 .

2.7. Instrumentation and procedure

A Packard 430 model gas chromatography 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 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 molecule 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 from the end of the column with a soap bubble flow meter. A flow rate of about 15 cm^3 min^{-1} was used throughout our experiment. The copper (3.2 mm I.D. × 1 m.) tubing was washed with acetone and was annealed prior to use. A column packing material was prepared by coating 80–100 mesh size Chromosorb W treated with PMHPMA-*co*-VP. 0.300 g of PMHPMA-*co*-VP was dissolved in 25 ml of dichloromethane and 3.000 g of the solid supporting materials were 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 spiral glass tubing. 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 onto 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 [27].

3. Results and discussion

3.1. Structure of PMHPMA-co-VP

According to molecular weight distribution, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of PMHPMA-*co*-VP were found to be 58,000, 481,000 g/mol and 8.26, respectively. When the FT-IR spectra of PMHPMA-*co*-VP and its monomer are compared, both have 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 polymer and monomer were observed at 1735, 1618, 1735 and 1615 cm^{-1}, respectively. According to ^{1}H and ^{13}C NMR spectra, the signals at 6.42 ppm and 129.60–137.30 ppm, respectively, are assigned to aromatic protons for copolymer. The signals at 2.05 ppm are due to methyl protons of the aromatic ring. The ^{1}H ^{13}C NMR and FT-IR results showed the formation of macromolecules from MHPMA-*co*-VP by the 1, 4-dioxane solution using benzoyl peroxide (BPO) as initiator at 60 °C.

3.2. Thermal behavior

Thermo gravimetric trace of PMHPMA-*co*-VP is shown in Fig. 1. PMHPMA-*co*-VP was demonstrated the relative thermal stability. The initial decomposition starting temperature (T_s), 26% weight loss, 50% weight loss, final decomposition temperature (T_f), temperature of maximum rate of weight loss (T_{max}) and percent carbonaceous residue values of PMHPMA-*co*-VP were found to be 185, 300, 347, 450, 350 and 6%, respectively.

3.3. Thermodynamic properties

In this study, we were obtained in the specific retention volumes, V_g^0 of 9 probes by using one loading PMHPMA-*co*-VP (about 10%, w/w) at 323–463 K. The values of specific retention volumes, V_g^0 of these probes were calculated according to Eq. (1) and are given in Table 1. The specific retention volumes, V_g^0 of the probes decreased with increasing temperature for each group solvents. The T_g of PMHPMA-*co*-VP was found about 370 K by inverse gas chromatography.

ΔH_a and ΔH_1^s values of PMHPMA-*co*-VP-probe systems were calculated by plotting ln V_g^0 against $1/T\,K^{-1}$. Table 2 shows the experimentally obtained adsorption enthalpy, ΔH_a, sorption heats, ΔH_1^s, in temperatures ranges 323–363 and 373–413 K, respectively. The ΔG_1^s and ΔS_1^s values of PMHPMA-*co*-VP-probe systems were calculated as literature [28] and given in Table 2. The sorption values ΔH_1^s and ΔS_1^s (see Table 2) and the average partial molar heats of mixing, ΔH_1^∞, (Table 4) were found to be negative and positive, respectively. Chen et al. had been used to three loading of PEMA (3–12%, w/w) and they

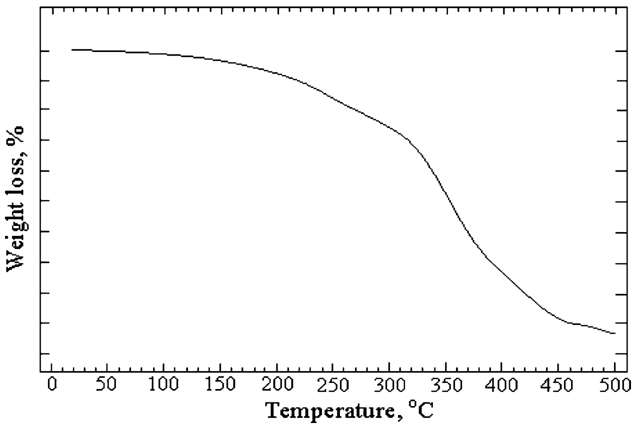


Fig. 1. TG curve of PMHPMA-*co*-VP.

Table 1
The variation of specific retention volumes, V_g^0 (cm^3/g) of selected some alcohols and alkanes with temperature using PMHPMA-*co*-VP as stationary phase

T (K)/probe	Hexane	Heptane	Octane	Decane	MeOH	EtOH	1-Propanol	1-Butanol	1-Pentanol
323	3.415	3.598	3.842	4.452	4.527	4.466	4.405	4.589	4.527
333	3.055	3.285	3.285	4.034	4.037	3.979	3.749	4.210	4.210
343	2.712	2.875	2.874	3.688	3.643	3.588	3.154	3.860	3.752
353	2.412	2.464	2.515	3.336	3.342	3.394	2.931	3.497	3.497
363	2.243	2.243	2.292	2.877	3.031	3.031	2.738	3.227	3.276
373	2.132	2.197	2.203	2.540	2.413	2.502	2.465	2.497	2.759
383	2.293	2.435	2.317	2.670	2.694	2.710	2.620	2.643	2.965
393	1.957	2.054	2.081	2.207	2.433	2.416	2.291	2.375	2.662
403	1.894	2.013	2.034	2.053	2.338	2.258	2.219	2.298	2.457
413	1.845	1.995	1.995	2.070	2.264	2.227	2.189	2.264	2.404
423	1.832	1.940	1.977	2.048	2.194	2.194	2.122	2.287	2.338
433	1.813	1.882	1.917	1.985	2.132	2.166	2.203	2.269	2.321
443	1.805	1.871	1.912	2.035	2.041	2.107	2.173	2.238	2.370
453	1.861	1.876	1.861	2.030	2.022	2.117	2.117	2.306	2.338
463	1.819	1.879	1.857	2.004	2.034	2.079	2.094	2.247	2.307

Table 2
The partial molar sorption free energies, ΔG_1^s (kcal/mol), the partial molar sorption enthalpy, ΔH_1^s (kcal/mol), adsorption enthalpy ΔH_a (kcal/mol) and sorption entropy, ΔS_1^s (cal/mol) of PMHPMA-*co*-VP with selected some alcohols and alkanes systems

Probe/*T* (K)	ΔG_1^s (kcal/mol)				ΔH_1^s (kcal/mol)	ΔH_a (kcal/mol)	ΔS_1^s (kcal/mol)			
	373	383	393	403	373–413	323–363	373	383	393	403
Methanol	4.20	4.23	4.42	4.57	−2.18	−6.24	−33.88	−33.15	−33.26	−33.15
Ethanol	3.91	3.95	4.14	4.30	−2.80	−7.25	−35.59	−34.89	−34.97	−34.89
1-Propanol	3.72	3.77	3.98	4.10	−2.57	−7.00	−33.35	−32.76	−32.93	−32.75
1-Butanol	3.56	3.61	3.78	3.91	−2.16	−9.21	−30.31	−29.79	−29.93	−29.79
1-Pentanol	3.35	3.39	3.56	3.71	−2.87	−9.64	−33.02	−32.34	−32.39	−32.34
Hexane	3.56	3.44	3.66	3.77	−2.95	−4.47	−34.57	−33.87	−34.11	−33.86
Heptane	3.43	3.44	3.66	3.77	−2.95	−5.11	−33.82	−33.01	−33.29	−33.00
Octane	3.33	3.38	3.55	3.66	−2.01	−6.10	−28.33	−27.85	−28.01	−27.85
Decane	3.06	3.10	3.33	3.48	−4.04	−8.54	−37.70	−36.94	−37.16	−36.94

had been determined ΔH_1^s, ΔG_1^s and ΔS_1^s values of alkanes, acetates and alcohols-PEMA. ΔH_1^s and ΔS_1^s and ΔG_1^s values of alkanes, acetates and alcohols had been found to be negative and positive, respectively, for PEMA at 458 K [29]. The values of Ω_1^∞ and χ_{12}^∞ calculated and also collected in Table 3. All two series showed an exothermic heat of sorption and negative entropy of sorption, which is responsible for the endothermic free energy of sorption. The enthalpy change of the sorption process is dependent on the interaction between the probe-PMHPMA-*co*-VP. Because of the chemical nature and number of carbons of each probe are different from each other, the heat of sorption becomes more exothermic as more CH_2 groups are added to the two families of probes. This is an indication that the individual CH_2 group, regardless of the chemical nature of the probe, has a significant interaction with the PMHPMA-*co*-*N*-VP. Alcohols showed more exothermic values than alkanes. While alcohols have two contributions to the sorption process interaction with PMHPMA-*co*-VP via OH and CH_2, alkanes have only one contribution, which is the interaction of CH_2 groups with PMHPMA-*co*-VP. Our interpretation is that

Table 3
The weight fraction activity coefficients, Ω_1^∞ and Flory–Huggins interaction parameters, χ_{12}^∞, of PMHPMA-*co*-VP with selected some alcohols and alkanes systems

Probe/*T* (K)	Ω_1^∞					χ_{12}^∞				
	413	423	433	443	453	413	423	433	443	453
Methanol	28.63	23.09	18.81	15.73	12.84	1.91	1.69	1.48	1.29	1.09
Ethanol	28.56	22.16	17.40	14.03	11.09	1.95	1.69	1.45	1.23	1.00
1-Propanol	42.09	32.90	24.39	19.31	15.69	2.34	2.09	1.79	1.55	1.35
1-Butanol	63.98	46.93	35.68	27.73	20.94	2.78	2.46	2.18	1.93	1.65
1-Pentanol	98.95	74.69	56.29	41.96	32.88	3.23	2.94	2.65	2.35	2.11
Hexane	23.36	19.30	16.17	13.59	11.13	1.65	1.46	1.28	1.11	0.91
Heptane	38.29	31.51	26.30	21.66	17.86	2.15	1.96	1.78	1.58	1.39
Octane	67.35	53.01	43.22	34.68	28.84	2.73	2.48	2.28	2.06	1.87
Decane	198.92	148.90	115.72	86.37	67.20	3.82	3.52	3.26	2.97	2.71

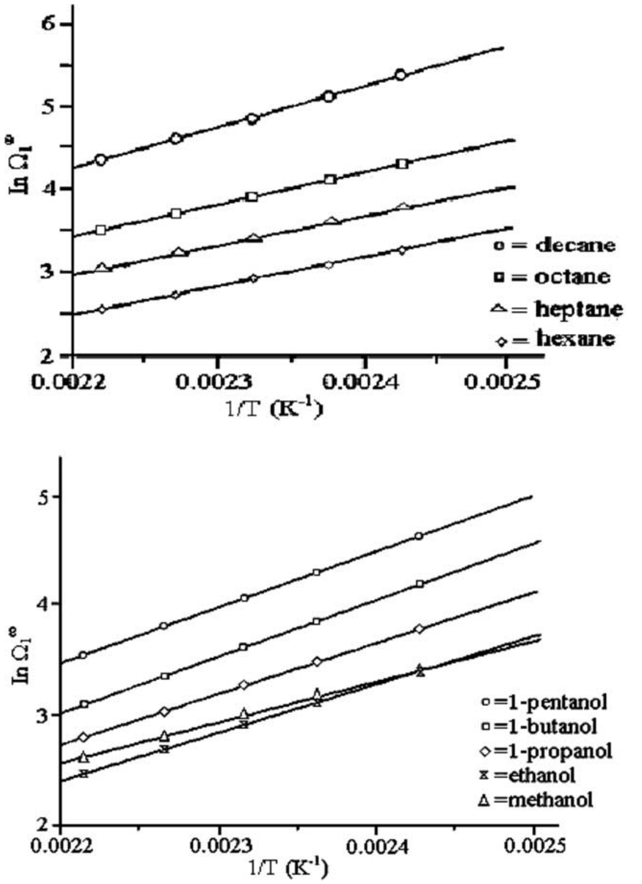


Fig. 2. Variation of logarithm of weight fraction activity coefficients, Ln Ω_1^∞, with reciprocal of absolute column temperature, $1/T\,\mathrm{K}^{-1}$ for some selected alkanes and alcohols on PMHPMA-*co*-VP.

alcohols form stronger attraction forces with PMHPMA-*co*-VP than do alkanes. The attraction forces between PMHPMA-*co*-VP and alcohols are actually a combination of two types. The first of these dispersive forces between the CH_2 groups of the alcohols and the 3-mesityl-2-hydroxypropyl group of PMHPMA-*co*-VP, the second is dipole–dipole interaction of the OH group of the alcohols with the C=O group of PMHPMA-*co*-VP.

The $\Delta\bar{H}_1^\infty$ values of the probes were found from the slopes of ln Ω_1^∞ versus $1/T\,\mathrm{K}^{-1}$ (Fig. 2). According to the literature, the partial molar free energy of mixing, ΔG_1^∞, and the partial molar heats of mixing at infinite dilution of the solutes,$\Delta\bar{H}_1^\infty$, calculated and collected in Table 4.

The $\Delta\bar{H}_1^\infty$ values of alcohols and alkanes changed from 7.61–10.61 kcal/mol and from 6.97–10.33 kcal/mol, respectively, as seen from Table 4.

It has been proposed that the values of Ω_1^∞ greater than five are indicative of poor polymer–solute systems while lower values characterize good solubility for such a system [30]. The values of χ_{12}^∞ greater than 0.5 represent unfavorable polymer–solvent interactions while the values lower than 0.5 indicate favorable interactions in dilute polymer solutions [31].

It will be seen that these values (in Table 3), according to Ω_1^∞ and χ_{12}^∞, selected some alcohols and alkanes are non-solvent for PMHPMA-*co*-VP. These values increased with increasing in the number of carbon in the alcohols and alkanes. The 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 at infinite dilution of the solutes,$\Delta\bar{H}_1^\infty$, did show dependence on change in the number of carbon atoms in the series. χ_{12}^∞, Ω_1^∞ and ΔG_1^∞ values decreased with increasing in the column temperature for all probes.

According to Ω_1^∞ and χ_{12}^∞, while methanol and ethanol are good solvent for poly [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and poly [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] at 453 K, there are non-solvent for poly [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene]. Alkanes had been found to be non-solvents for each polymer and copolymer [32].

According to the literature [15], the molar evaporation enthalpy, ΔH_v, calculated and collected in Table 4. The ΔH_v values of alcohols and alkanes changed from 9.79 to 13.48 kcal/mol and from 9.93 to 14.37 kcal/mol, respectively, as seen from Table 4.

The solubility parameter of a polymer, δ_2, can be determined by using Eq. (18) [33]. 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. (18) versus δ_1. The solubility parameter of PMHPMA-*co*-VP was evaluated from either the slope or intercept of Fig. 3 as 6.10 $(\mathrm{cal/cm^3})^{0.5}$, 7.00 $(\mathrm{cal/cm^3})^{0.5}$ at 413 K, respectively. The values of solubility parameters of

Table 4
The partial molar free energies of mixing, ΔG_1^∞ (kcal/mol) and the partial molar enthalpy of mixing, ΔH_1^∞ (kcal/mol), molar evaporation enthalpy, ΔH_v (kcal/mol) of PMHPMA-*co*-VP with selected some alcohols and alkanes systems

Probe/*T* (K)	ΔG_1^∞					ΔH_1^∞	ΔH_v (Eq. (17))	ΔH_v (Eq. (3))
	413	423	433	443	453	413–453		
Methanol	2.75	2.64	2.53	2.43	2.30	7.61	9.79	8.85
Ethanol	2.57	2.60	2.46	2.33	2.17	8.90	11.70	9.72
1-Propanol	3.07	2.94	2.75	2.61	2.48	9.59	12.15	10.45
1-Butanol	3.41	3.23	3.08	2.93	2.74	10.55	12.70	11.47
1-Pentanol	3.77	3.63	3.47	3.29	3.14	10.61	13.48	12.16
Hexane	2.59	2.49	2.40	2.30	2.17	6.97	9.93	10.56
Heptane	2.99	2.90	2.81	2.71	2.60	7.22	10.17	8.98
Octane	3.46	3.34	3.24	3.12	3.03	8.07	10.08	9.18
Decane	4.35	4.21	4.09	3.93	3.79	10.33	14.37	11.27

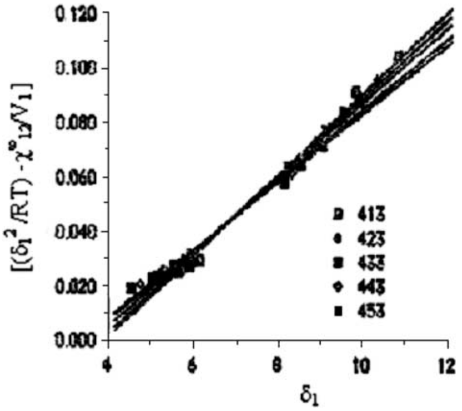


Fig. 3. Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 (cal/cm^3)$^{0.5}$ at different temperatures.

Table 5
The solubility parameter, δ_2 (cal/cm^3)$^{0.5}$ of PMHPMA-*co*-VP between 413–453 K

T (K)	Slope	Intercept	Cal. from slope, δ_2	Cal. from intercept, δ_2	*r*
413	0.0149	−0.0589	6.10	7.00	1.00
423	0.0143	−0.0546	6.00	6.80	1.00
433	0.0136	−0.0504	5.80	6.60	1.00
443	0.0128	−0.0446	5.60	6.30	1.00
453	0.0124	−0.0421	5.50	6.20	0.99

PMHPMA-*co*-VP, δ_2, decreased with increasing temperature (Table 5). Also, according to swelling coefficient (Q) method the solubility parameter, δ_2, of PMHPMA-*co*-VP has been calculated as 10.45 (cal cm^{-3})$^{0.5}$ at 25 °C [34].

4. Conclusion

The inverse gas chromatography technique is simple, fast, and economical and provides valuable thermodynamic and physical chemistry information for characterization of polymeric materials. This technique was successfully applied to determine of polymer–solvent and polymer–non-solvent interactions. IGC technique was successfully applied to determine some thermodynamic properties of PMHPMA-*co*-VP such as the adsorption enthalpy, molar evaporation enthalpy, the sorption enthalpy, sorption free energy, sorption entropy, Flory–Huggins interaction parameters, the partial molar free energy of mixing, the weight fraction activity coefficients, solubility parameter of polymer and the partial molar heats of mixing, at infinite dilution. Alcohols showed a stronger interaction with PMHPMA-*co*-VP than did alkanes. The effects the ΔH_1^s, ΔS_1^s and ΔG_1^s sorption parameters of contributions of alcohols (–OH) and alkanes (–CH$_2$) functional groups were calculated as -0.99, -0.49 kcal mol^{-1}; -0.21, -0.23 cal mol^{-1} and -20, -0.12 kcal mol^{-1}, respectively. The hydroxyl group showed more interaction than the methyl group with PMHPMA-*co*-VP. According to Flory–Huggins interaction parameters and the weight fraction activity coefficients as selected alcohols and alkanes non-solvent for PMHPMA-*co*-VP were determined. Also, from the IGC results, the solubility parameter of a copolymer, δ_2, can be determined from either slope or intercept of a straight line obtained by plotting the left-hand-side of Eq. (18) versus δ_1. The solubility parameters, δ_2, of PMHPMA-*co*-VP found to be 6.10 (cal cm^{-3})$^{0.5}$ and 7.00 (cal 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 413 K, respectively.

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