ELSEVIER

Polymer 41 (2000) 2855–2863

polymer

# Determination of thermodynamic properties of poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and its copolymers at infinite dilution using inverse gas chromatography

İ. Kaya[a,*], K. Demirelli[b]

[a]*Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, Çanakkale, Turkey*
[b]*Department of Chemistry, Faculty of Sciences and Arts, Firat University, Elaziğ, Turkey*

Received 23 March 1999; received in revised form 25 June 1999; accepted 7 July 1999

**Abstract**

Some thermodynamic quantities were obtained for the interactions of poly[2-(3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], (PPCHEMA) poly[2-(3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] (PPCHEMA-AN) and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene] (PPCHEMA-S) with alcohols, ketones, acetates, aromatics and alkanes by inverse gas chromatography method in various temperatures. The specific retention volumes, $V_g^0$, weight fraction activity coefficients of solute probes at infinite dilution, $\Omega_1^\infty$, Flory–Huggins thermodynamic interaction parameters, $\chi_{12}^\infty$, between polymers and solvents are determined. The partial molar free energy, $\Delta G_1^\infty$, the partial molar heat of mixing, $\Delta H_1^\infty$, at infinite dilution and the solubility parameters of polymer, $\delta_2$, were calculated at various temperatures. The glass transition temperatures, $T_g$, of PPCHEMA, PPCHEMA-AN and PPCHEMA-S were found to be about 378, 377 and 375 K, respectively, by differential scanning calorimetry. Alcohols, ketones and acetates were found to be good solvent for PPCHEMA and PPCHEMA-AN but *n*-alkanes and aromatics (except for high temperatures) were found to be non-solvents. Whereas for PPCHEMA-S all solvents were found to be non-solvents at this temperatures. Also the solubility parameters for PPCHEMA, PPCHEMA-AN and PPCHEMA-S at infinite dilution were found by plotting the graph of $[(\delta_1^2/RT) - \chi_{12}^\infty/V_1]$ versus solubility parameters, $\delta_1$, of this probes.


*Keywords*: Poly2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethyl methacrylate and its copolymers; Inverse gas chromatography; Polymer–solvent interactions

## 1. Introduction

Recently, we demonstrated that the inverse gas chromatography (IGC) method can give, after careful analysis, a wealth of information on polymeric systems [1–7].

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, economical and provides valuable thermodynamic information for characterisation of polymeric materials. The inverse gas chromatography technique yielded a dependence of retention volumes on the chemical nature of the solvent used. It was found that the technique yielded useful for polymer–solvent and polymer–polymer interaction parameters. It was recognised that retention volumes of solvents $V_g^0$ measured by IGC may contain several dependencies, among them the carrier gas flow rate effect, the mass of the polymer in the stationary phase and the solid support contribution. It has been shown that the IGC method gives information on polymer–solvent and polymer–polymer systems such as solubility parameters, interaction parameters, diffusion constants, enthalpies of mixing, surface energies and areas, adsorption isotherms, glass transition temperatures, $T_g$, melting temperatures, $T_m$, and degree of crystallinity [8–16].

In this study, we examined the interactions of poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] (PPCHEMA), poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] (PPCHEMA-AN) and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene] (PPCHEMA-S) with alcohols, ketones, acetates, aromatics and alkanes solute probes by using the IGC method in temperatures range 423 to 473 K. On the other hand, we were determined to the solubility parameter, $\delta_2$, of the polymers.

* Corresponding author.

0032-3861/00/$ - see front matter 
PII: S0032-3861(99)00475-9

## 2. Data reduction

The probe specific retention volumes, $V_g^0$, corrected to 0°C were calculated from the standard chromatographic 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 [5–10].

The weight fraction activity coefficient, $\Omega_1^\infty$, the partial molar free energy, $\Delta G_1^\infty$ and the average partial molar enthalpy, $\Delta H_1^\infty$ at infinite dilution of the organic solvents were calculated according to the following equation

$$\Omega_1^\infty = 273.2\mathrm{R}/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/\mathrm{R}T] \quad (2)$$

$$\Delta G_1^\infty = \mathrm{R}T \ln \Omega_1^\infty \quad (3)$$

$$\Delta H_1^\infty = \mathrm{R}\partial \ln(\Omega_1^\infty)/\partial(1/T) \quad (4)$$

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 [7–14].

The molar volume of the solute, $V_1$ was calculated using the following relation [17].

$$V_1 = V_c/\rho_r \quad (5)$$

where $V_c$ is the critical molar volume and $\rho_r$ is the reduced density of the solute given as:

$$\rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)^{(0.8Z_c + 0.31)} \quad (6)$$

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

The Flory–Huggins parameters, $\chi_{12}^\infty$ characterising the interactions of a vapour-phase probe with a polymer are determined by the following equation:

$$\chi_{12}^\infty = \ln(273.2\mathrm{R}\nu_2/V_g^0 V_1 P_1^0/\mathrm{R}T(B_{11} - V_1) \quad (7)$$

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 [13–15].

$$\delta_1 = [(\Delta H_v - \mathrm{R}T)/V_1]^{0.5} \quad (8)$$

The solubility parameter of the polymer, $\delta_2$ can be calculated by using the following relation:

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

If the left-hand side of this equation is plotted against $\delta_1$, 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, $\delta_2$ can be determined from both the slope and intercept of the straight line [18–20].

## 3. Experimental

### 3.1. Materials

Fourteen polar and non-polar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. *N*-octane, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane were supplied from Aldrich Chemical Co. and methanol, ethanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate, benzene, toluene and *o*-xylene were supplied from Merck Chemical Co. as chromatographic grade. Chromosorb WHP [(silicone OV-210 + silicone OV-17,5 + 5%),(80–100 mesh)] was supplied from Shimadzu Chemical Co. 1,4-Dioxane and *n*-hexane (Aldrich) were dried over anhydrous $MgSO_4$ before use. Acrylonitrile and styrene Yalova Elyaf Comp. (Turkey) and KOH (Aldrich) were used as received. 1-Chloro-2,3-epoxy-5-methyl-5-hexene was received from the Institute of Polymeric Materials in the Academy of Sciences of Azerbaijan and freshly distilled before use. [2-(3-Phenyl-3-methyl-cyclobutyl)-2-hydroxyethylmethacrylate] was synthesised via the method given for the epoxy–carboxy reactions [21–25].

### 3.2. Polymerisation of the monomer

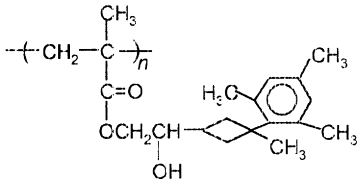
The monomer [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] was freed from inhibitor by washing with dilute KOH solution followed by reacting with distilled water and drying over anhydrous $MgSO_4$. Appropriate amounts of 2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethyl methacrylate and 1,4-dioxane and benzoyl peroxide (0.2% of the weight of the monomer) were placed into a reaction tube and purged with Ar for about 10 min. The sealed tube was kept at 60°C for 15 h. PPCHEMA was purified by reprecipitation in *n*-hexane from 1,4-dioxane solution and finally dried under vacuum. The yield was about 75% for PPCHEMA. Molecular weight of PPCHEMA was determined by gel permeation chromatography using polystyrene and tetrahydrofurane as standard and solvent, respectively. Weight-average molecular weight of PPCHEMA were found as 125 000 g/mol (polydispersity:2.62). The glass transition temperatures of PPCHEMA, is found about 105°C by differential scanning calorimeter (DSC) (Shimadzu, DSC-50). The monomer, polymer and copolymer were characterised by using FT-IR (Mattson 1000) and the $^1H$ and $^{13}C$ NMR spectra (Varian–Gemini 200 MHz) at 25°C $CDCl_3$ as solvent [25]. Density of PPCHEMA is 1.053 g cm$^{-3}$ by picnometer measurement.

Table 1
Stationary phase and column descriptions

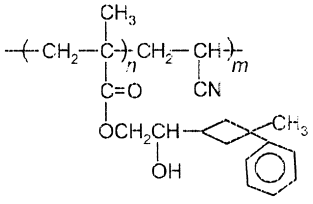
| Column | Solvent THF (ml) | Polymer loading (% w/w) | Mass of support mass of the polymer (g) | Chromosorb WHP (g) + polymer (g) | Column length (cm) |
|---|---|---|---|---|---|
| PPCHEMA | 25 | 7.80 | 0.2250 | 3.1250 | 110 |
| PPCHEMA-AN | 25 | 6.35 | 0.1715 | 2.8715 | 110 |
| PPCHEMA-S | 25 | 9.37 | 0.2403 | 2.8063 | 110 |

### 3.3. Copolymerization of the monomers

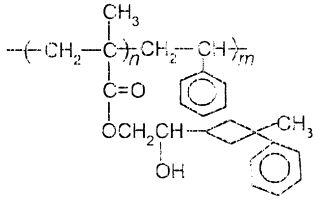
The monomer [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], acrylonitrile and styrene were freed from inhibitor by washing with dilute KOH solution followed by reacting with distilled water and drying over anhydrous $MgSO_4$. Appropriate amounts of [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], acrylonitrile and styrene and 1,4-dioxane and benzoyl peroxide (0.2% of the weight of the monomer) were placed into a reaction tube and purged with Ar for about 10 min. The sealed tube was kept at 60°C for 15 h. The PPCHEMA-AN and PPCHEMA-S were purified by reprecipitation in *n*-hexane from 1,4-dioxane solution and finally dried under vacuum. The monomer compositions have been determined by $^1$H NMR measurement. In the copolymer, the composition of [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethylmethacrylate] and acrylonitrile and [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethylmethacrylate] and styrene found as 55% and 45%, and 60% and 40%, respectively. The glass transition temperature of PPCHEMA-AN and PPCHEMA-S are found about 104 and 102°C, respectively, by differential scanning calorimeter (DSC). Densities of PPCHEMA-AN and PPCHEMA-S are 1.075 and 1.045 g cm$^{-3}$, respectively, by picnometer measurement.



PPCHEMA



PPCHEMA-AN



PPCHEMA-S

### 3.4. Instrumentation and procedure

A Shimadzu GC-14B model gas chromatography equipped with a dual flame ionisation defector, FID 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 and outlet of the column, read from a mercury manometer (mm Hg) 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 20 ml/min$^{-1}$ was used throughout our experiment. The spiral glass tubing was washed with methylene chloride and was annealed prior to use. Table 1 shows the description of these columns. Samples were achieved by dissolving certain weights of PPCHEMA, PPCHEMA-AN and PPCHEMA-S in the THF solution and depositing them on the solid support [ChromosorbWHP(silicone OV-210 + siliconeOV-17,5 + 5%), (80–100 mesh)]. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a Rotary evaporator. The prepared material was packed into a spiral glass tubing (3.2 mm I.D. × 1.1 m) [6]. Column was conditioned at temperature above the glass transition temperature,$T_g$, and fast carrier gas ($N_2$) flow rate for 24 h prior to use. 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 chromatopac CR6A, Shimadzu. Methane was synthesised in the laboratory by the reaction of sodium acetate with sodium hydroxide.

## 4. Results and discussion

The specific retention volumes $V_g^0$ of 14 probes were obtained by using one loading poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and its copolymers at a series of temperatures (423, 433, 443, 453, 463 and 473 K). Different chemical nature and polarity (alcohols, acetates, ketones, aromatics and *n*-alkane) were selected for this study. The $V_g^0$ values of these probes

Table 2
The change of specific retention volumes $V_g^0$ (ml/g) of alcohols, ketones, acetates, aromatics and alkanes using poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene] as stationary phase at the various temperatures

| | PPCHEMA | | | | | PPCHEMA-AN | | | | | PPCHEMA-S | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Probe/$T$(K) | 433 | 443 | 453 | 463 | 473 | 423 | 433 | 443 | 453 | 463 | 423 | 433 | 443 | 453 |
| Methanol | 4.85 | 4.72 | 4.74 | 4.41 | 4.08 | 5.82 | 5.36 | 5.22 | 4.88 | 4.59 | 5.50 | 4.54 | 3.67 | 3.39 |
| Ethanol | 5.11 | 5.02 | 4.97 | 4.56 | 4.34 | 6.21 | 5.70 | 5.27 | 5.10 | 4.75 | 4.80 | 4.05 | 3.70 | 3.68 |
| Acetone | 5.34 | 5.24 | 5.08 | 4.89 | 4.56 | 6.76 | 6.10 | 5.73 | 5.41 | 4.71 | 3.51 | 4.05 | 3.62 | 3.10 |
| Ethyl methyl ketone (EMK) | 7.13 | 6.96 | 6.48 | 6.16 | 5.85 | 7.73 | 6.95 | 6.50 | 5.77 | 5.36 | 4.93 | 4.65 | 4.06 | 3.94 |
| Methyl acetate | 5.42 | 5.30 | 5.29 | 5.02 | 4.78 | 6.37 | 5.56 | 5.22 | 4.92 | 4.89 | 3.51 | 3.51 | 3.23 | 3.10 |
| Ethyl acetate | 6.55 | 6.27 | 6.08 | 5.78 | 5.53 | 7.07 | 6.14 | 5.76 | 5.32 | 5.09 | 4.39 | 4.51 | 3.93 | 3.96 |
| Benzene | 7.88 | 7.09 | 6.93 | 6.46 | 5.90 | 8.07 | 6.78 | 6.41 | 6.06 | 5.66 | 6.32 | 7.08 | 6.41 | 5.58 |
| Toluene | 10.10 | 8.89 | 8.47 | 8.03 | 7.11 | 9.61 | 8.41 | 7.89 | 7.36 | 6.20 | 9.21 | 8.51 | 7.03 | 7.36 |
| *o*-Xylene | 16.16 | 13.52 | 12.22 | 10.39 | 9.78 | 14.33 | 11.87 | 10.05 | 9.14 | 6.16 | 23.31 | 18.91 | 15.68 | 13.22 |
| *n*-Octane | 6.98 | 6.49 | 6.35 | 5.90 | 5.48 | 7.47 | 6.75 | 6.31 | 5.70 | 5.52 | 8.16 | 7.08 | 6.46 | 5.99 |
| *n*-Nonane | 9.15 | 8.20 | 7.73 | 6.79 | 6.45 | 8.99 | 7.92 | 7.24 | 6.59 | 5.66 | 12.88 | 11.89 | 10.34 | 9.29 |
| *n*-Decane | 12.12 | 10.90 | 9.66 | 8.51 | 7.98 | 12.10 | 10.24 | 9.01 | 8.03 | 6.87 | 17.89 | 15.72 | 13.44 | 11.89 |
| *n*-Undecane | 17.46 | 14.71 | 12.25 | 10.89 | 9.41 | 16.32 | 13.29 | 10.96 | 9.38 | 7.92 | 27.68 | 24.72 | 18.35 | 13.92 |
| *n*-Dodecane | 25.16 | 21.39 | 18.31 | 15.63 | 12.40 | 23.50 | 18.53 | 14.62 | 12.75 | 10.00 | 27.91 | 25.66 | 20.39 | 16.72 |

were calculated according to Eq. (1). The specific retention volumes $V_g^0$ are given in Table 2. Such as shown in Table 2, $V_g^0$ values changed for each group solvents with temperature. That is, the specific retention volumes, $V_g^0$, of the probes decreased with increasing temperature.

$\Omega_1^\infty$ and $\chi_{12}^\infty$ values obtained using Eqs. (2) and (7), respectively, are also collected in Tables 3 and 4. The partial molar free energy of mixing, $\Delta G_1^\infty$, and the partial molar heats of mixing at infinite dilution of solutes, $\Delta H_1^\infty$, calculated from Eqs. (3) and (4) are collected in Tables 5 and 6.

It has been proposed that $\Omega_1^\infty$ values greater than 5 are indicative of poor polymer-solute systems while lower values characterise good solubility for such a system [26]. Values of $\chi_{12}^\infty$ greater than 0.5 represent unfavourable polymer–solvent interactions while values lower than 0.5 indicate favourable interactions in dilute polymer solutions [27].

It will be seen that these values (in Table 3) acetates, ketones and methanol, ethanol, benzene, toluene (at high temperature) are good solvents but *n*-alkanes and *o*-xylene are non-solvents PPCHEMA. Acetates, ketones, and alcohols and benzene (at high temperature) are good solvents but *n*-alkanes, *o*-xylene and toluene are non-solvents for PPCHEMA-AN. All probes (except for acetates, at 453 K) are non-solvents for PPCHEMA-S.

Similarly, according to the interaction parameters, $\chi_{12}^\infty$, acetates, ketones and ethanol, benzene, toluene (at high temperature) are good solvents but *n*-alkanes, methanol and *o*-xylene are non-solvents PPCHEMA. Acetates, ketones, and alcohols and benzene (at high temperature)

Table 3
Weight fraction activity coefficient $\Omega_1^\infty$ of poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and its copolymers-alcohols, ketones, acetates, aromatics and *n*-alkanes systems

| | PPCHEMA | | | | PPCHEMA-AN | | | | PPCHEMA-S | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Probe/$T$(K) | 433 | 443 | 453 | 463 | 433 | 443 | 453 | 463 | 433 | 443 | 453 |
| Methanol | 8.41 | 6.98 | 5.64 | 5.01 | 7.63 | 6.33 | 5.48 | 4.85 | 8.98 | 8.93 | 7.81 |
| Ethanol | 7.52 | 5.95 | 4.65 | 3.99 | 6.75 | 5.68 | 4.53 | 3.84 | 9.45 | 8.02 | 6.21 |
| Acetone | 5.46 | 4.70 | 4.14 | 3.69 | 6.01 | 5.39 | 4.86 | 4.75 | 7.15 | 6.71 | 6.64 |
| EMK | 5.95 | 5.03 | 4.55 | 4.05 | 6.10 | 5.38 | 5.09 | 4.62 | 9.05 | 8.51 | 7.37 |
| Methyl acetate | 4.35 | 3.80 | 3.27 | 2.99 | 4.24 | 3.86 | 3.50 | 3.06 | 6.61 | 6.16 | 5.42 |
| Ethyl acetate | 4.93 | 4.30 | 3.75 | 3.35 | 5.25 | 4.67 | 4.26 | 3.77 | 7.09 | 6.76 | 5.66 |
| Benzene | 6.73 | 6.09 | 5.10 | 4.52 | 7.50 | 6.72 | 5.80 | 5.13 | 7.68 | 6.72 | 6.29 |
| Toluene | 7.24 | 6.62 | 5.61 | 4.74 | 8.67 | 7.45 | 6.44 | 6.09 | 8.57 | 8.34 | 6.44 |
| *o*-Xylene | 8.85 | 8.42 | 7.42 | 7.09 | 11.91 | 11.19 | 9.80 | 9.00 | 7.57 | 7.29 | 6.87 |
| *n*-Octane | 11.94 | 10.34 | 8.61 | 7.62 | 12.35 | 10.63 | 9.57 | 8.14 | 11.78 | 10.39 | 9.12 |
| *n*-Nonane | 15.18 | 13.34 | 11.27 | 10.32 | 17.52 | 15.10 | 13.20 | 12.36 | 11.69 | 10.60 | 9.40 |
| *n*-Decane | 18.96 | 16.27 | 14.18 | 12.68 | 22.43 | 19.68 | 17.04 | 15.69 | 14.63 | 13.21 | 11.53 |
| *n*-Undecane | 21.80 | 19.38 | 17.78 | 15.43 | 28.63 | 25.99 | 23.20 | 21.20 | 18.38 | 15.54 | 15.05 |
| *n*-Dodecane | 25.03 | 21.60 | 18.71 | 16.58 | 33.98 | 31.60 | 26.85 | 25.88 | 24.55 | 22.66 | 20.48 |

Table 4
Solute interaction coefficients $\chi_{12}^{\infty}$ of poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene]-alcohols, ketones, acetates, aromatics and *n*-alkanes systems

| | PPCHEMA | | | | PPCHEMA-AN | | | | PPCHEMA-S | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Probe/*T*(K) | 433 | 443 | 453 | 463 | 433 | 443 | 453 | 463 | 433 | 443 | 453 |
| Methanol | 0.725 | 0.523 | 0.289 | 0.147 | 0.651 | 0.449 | 0.286 | 0.133 | 0.831 | 0.815 | 0.665 |
| Ethanol | 0.581 | 0.331 | 0.059 | −0.121 | 0.498 | 0.308 | 0.060 | −0.136 | 0.853 | 0.676 | 0.400 |
| Acetone | 0.325 | 0.154 | 0.002 | −0.145 | 0.218 | 0.004 | −0.197 | −0.219 | 0.785 | 0.564 | 0.536 |
| EMK | 0.374 | 0.193 | 0.077 | −0.058 | 0.426 | 0.329 | 0.247 | −0.105 | 0.842 | 0.772 | 0.615 |
| Methyl acetate | 0.195 | 0.036 | −0.143 | −0.266 | 0.195 | −0.030 | −0.135 | −0.282 | 0.669 | 0.572 | 0.432 |
| Ethyl acetate | 0.291 | 0.139 | −0.025 | −0.155 | 0.382 | 0.111 | 0.013 | −0.116 | 0.705 | 0.646 | 0.444 |
| Benzene | 0.586 | 0.478 | 0.288 | 0.154 | 0.762 | 0.605 | 0.448 | 0.313 | 0.733 | 0.619 | 0.545 |
| Toluene | 0.670 | 0.575 | 0.400 | 0.229 | 0.879 | 0.721 | 0.566 | 0.514 | 0.862 | 0.850 | 0.581 |
| *o*-Xylene | 0.837 | 0.781 | 0.648 | 0.596 | 1.171 | 1.103 | 0.965 | 0.923 | 0.720 | 0.673 | 0.610 |
| *n*-Octane | 0.932 | 0.781 | 0.586 | 0.463 | 0.992 | 0.836 | 0.720 | 0.556 | 0.958 | 0.826 | 0.685 |
| *n*-Nonane | 1.182 | 1.047 | 0.873 | 0.780 | 1.353 | 1.198 | 1.058 | 0.988 | 0.961 | 0.855 | 0.729 |
| *n*-Decane | 1.454 | 1.294 | 1.151 | 1.034 | 1.648 | 1.510 | 1.362 | 1.274 | 1.234 | 1.125 | 0.984 |
| *n*-Undecane | 1.623 | 1.498 | 1.405 | 1.258 | 1.922 | 1.818 | 1.698 | 1.602 | 1.375 | 1.325 | 1.317 |
| *n*-Dodecane | 1.777 | 1.622 | 1.471 | 1.343 | 2.109 | 2.029 | 1.859 | 1.815 | 1.797 | 1.710 | 1.602 |

are good solvents but *n*-alkanes, *o*-xylene and toluene are non-solvents for PPCHEMA-AN. All probes (except for acetates, at 453 K) are non-solvents for PPCHEMA-S. The interaction parameters, $\chi_{12}^{\infty}$, the partial molar free energy of mixing, $\Delta G_1^{\infty}$, and the weight fraction activity coefficients, $\Omega_1^{\infty}$, were found to be dependent of the number of carbons in the series and temperature.

The interaction parameters, $\chi_{12}^{\infty}$, the partial molar free energy of mixing, $\Delta G_1^{\infty}$, the weight fraction activity coefficients, $\Omega_1^{\infty}$, and the partial molar heats of mixing, $\Delta H_1^{\infty}$, at infinite dilution of the solutes did show dependence with change in the number of carbons in the series (except for alcohols). That is, these values ($\chi_{12}^{\infty}$, $\Omega_1^{\infty}$, $\Delta G_1^{\infty}$ and $\Delta H_1^{\infty}$) increased with increasing in the number of carbons in the series. But, in all series, $\chi_{12}^{\infty}$, $\Omega_1^{\infty}$, $\Delta G_1^{\infty}$, the values decreased with increase in the column temperature.

$\Delta H_1^{\infty}$ values (at 443–453 K) of probes found from the slope of straight lines are shown in Fig. 1 (a)–(c) and are given in Table 6. $\Delta H_1^{\infty}$ values (at 443–453 K) of alcohols, ketones, acetates, aromatics and *n*-hydrocarbons changed from 8.35 to 9.54 kcal/mol from 3.97 to 5.17 kcal/mol from 5.56 to 5.96 kcal/mol from 5.17 to 7.15 kcal/mol from 3.18 to 7.55 kcal/mol; 5.96 to 9.14 kcal/mol from 1.99 to 4.37 kcal/mol from 3.58 to 3.97 kcal/mol from 5.56 to 5.96 kcal/mol from 3.97 to 6.36 kcal/mol; 5.17 to 9.94 kcal/mol from 3.97 to 5.56 kcal/mol from 5.17 to 7.15 kcal/mol from 2.38 to 10.33 kcal/mol from 1.19 to 5.17 kcal/mol for PPCHEMA, PPCHEMA-AN and PPCHEMA-S, respectively. Based upon these results the ones having $\Delta H_1^{\infty}$ low

Table 5
The Partial molar free energies of mixing, $\Delta G_1^{\infty}$, (kcal/mol) poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and its copolymers-alcohols, ketones, acetates, aromatics and *n*-alkanes systems at the various temperatures

| | PPCHEMA | | | | | PPCHEMA-AN | | | | | PPCHEMA-S | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Probe/*T*(K) | 433 | 443 | 453 | 463 | 473 | 423 | 433 | 443 | 453 | 463 | 423 | 433 | 443 | 453 |
| Methanol | 1.83 | 1.71 | 1.56 | 1.48 | 1.42 | 1.83 | 1.77 | 1.62 | 1.53 | 1.45 | 1.88 | 1.89 | 1.93 | 1.85 |
| Ethanol | 1.74 | 1.57 | 1.38 | 1.27 | 1.11 | 1.74 | 1.64 | 1.53 | 1.36 | 1.24 | 1.95 | 1.93 | 1.83 | 1.64 |
| Acetone | 1.46 | 1.36 | 1.28 | 1.20 | 1.16 | 1.58 | 1.54 | 1.48 | 1.42 | 1.43 | 1.93 | 1.69 | 1.68 | 1.70 |
| Ethyl methyl ketone (EMK) | 1.53 | 1.42 | 1.36 | 1.29 | 1.22 | 1.60 | 1.56 | 1.48 | 1.47 | 1.41 | 1.98 | 1.90 | 1.89 | 1.80 |
| Methyl acetate | 1.27 | 1.18 | 1.07 | 1.01 | 0.95 | 1.26 | 1.24 | 1.19 | 1.13 | 1.03 | 1.74 | 1.63 | 1.60 | 1.52 |
| Ethyl acetate | 1.37 | 1.28 | 1.19 | 1.11 | 1.05 | 1.45 | 1.43 | 1.36 | 1.31 | 1.22 | 1.84 | 1.69 | 1.68 | 1.56 |
| Benzene | 1.64 | 1.59 | 1.47 | 1.39 | 1.33 | 1.76 | 1.73 | 1.68 | 1.58 | 1.50 | 1.96 | 1.73 | 1.68 | 1.66 |
| Toluene | 1.70 | 1.66 | 1.55 | 1.43 | 1.38 | 1.89 | 1.86 | 1.77 | 1.68 | 1.66 | 1.92 | 1.85 | 1.87 | 1.67 |
| *o*-Xylene | 1.88 | 1.88 | 1.80 | 1.80 | 1.72 | 2.13 | 2.13 | 2.13 | 2.05 | 2.02 | 1.73 | 1.74 | 1.75 | 1.74 |
| *n*-Octane | 2.13 | 2.06 | 1.94 | 1.87 | 1.81 | 2.13 | 2.16 | 2.08 | 2.03 | 1.93 | 2.15 | 2.12 | 2.06 | 1.99 |
| *n*-Nonane | 2.34 | 2.28 | 2.18 | 2.15 | 2.05 | 2.52 | 2.46 | 2.39 | 2.32 | 2.31 | 2.22 | 2.12 | 2.08 | 2.02 |
| *n*-Decane | 2.53 | 2.46 | 2.39 | 2.34 | 2.23 | 2.72 | 2.68 | 2.62 | 2.55 | 2.53 | 2.39 | 2.31 | 2.27 | 2.20 |
| *n*-Undecane | 2.65 | 2.61 | 2.59 | 2.52 | 2.48 | 2.91 | 2.89 | 2.87 | 2.83 | 2.81 | 2.46 | 2.51 | 2.42 | 2.44 |
| *n*-Dodecane | 2.77 | 2.71 | 2.64 | 2.58 | 2.61 | 3.05 | 3.03 | 3.04 | 2.96 | 2.99 | 2.91 | 2.75 | 2.75 | 2.72 |

Table 6
The partial molar enthalpy, $\Delta H_1^{\infty}$, (kcal/mol) of poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and its copolymers-alcohols, ketones, acetates, aromatics and *n*-alkanes systems at 443–453 K

| | PPCHEMA | PPCHEMA-AN | PPCHEMA-S |
|---|---|---|---|
| Methanol | 8.35 | 5.96 | 5.17 |
| Ethanol | 9.54 | 9.14 | 9.94 |
| Acetone | 5.17 | 4.37 | 3.97 |
| Ethyl methyl ketone | 3.97 | 1.99 | 5.56 |
| Methyl acetate | 5.96 | 3.97 | 5.17 |
| Ethyl acetate | 5.56 | 3.58 | 7.15 |
| Benzene | 7.15 | 5.96 | 2.78 |
| Toluene | 6.36 | 5.96 | 10.33 |
| *o*-Xylene | 5.17 | 5.56 | 2.38 |
| *n*-Octane | 7.55 | 3.97 | 5.17 |
| *n*-Nonane | 6.76 | 5.56 | 4.77 |
| *n*-Decane | 5.56 | 5.56 | 5.17 |
| *n*-Undecane | 3.18 | 4.77 | 1.19 |
| *n*-Dodecane | 5.56 | 6.36 | 3.97 |

values were accepted as solvent–polymer and the others were taken as non-solvents–polymer systems (except for *n*-undecane and *n*-dodecane values for PPCHEMA-S).

Baranyi and Guillet in their study determined that $\Delta H_1^{\infty}$ values for aromatic solvents changed from −0.01 to 0.3 cal/mol in PS and from 0.3 to 1.1 kcal/mol in PMA, respectively. These values for the same polymers were reported to change from 0.6 to 2.5 and 2.5 to 4.1 kcal/mol, respectively, in *n*-hydrocarbons. According to these result the ones having small $\Delta H_1^{\infty}$ values were suitable for solvent–polymer and the ones with large $\Delta H_1^{\infty}$ values are suitable for non-solvents–polymer systems [18].

The solubility parameter of a polymer, $\delta_2$, can be determined by using Eq. (9). The solubility parameter, $\delta_2$, is determined from either slope or intercept of a straight line obtained by plotting the left-hand-side of Eq. (9) versus $\delta_1$. The solubility parameter of PPCHEMA, PPCHEMA-AN and PPCHEMA-S were evaluated from either the slope or intercept of Fig. 2 (I–III) as 6.95 $(cal/cm^3)^{0.5}$, 6.94 $(cal/cm^3)^{0.5}$ at 443 K, respectively. The values of solubility parameters of PPCHEMA, PPCHEMA-AN and PPCHEMA-S, $\delta_2$, decreased with increasing temperature (see Table 7).

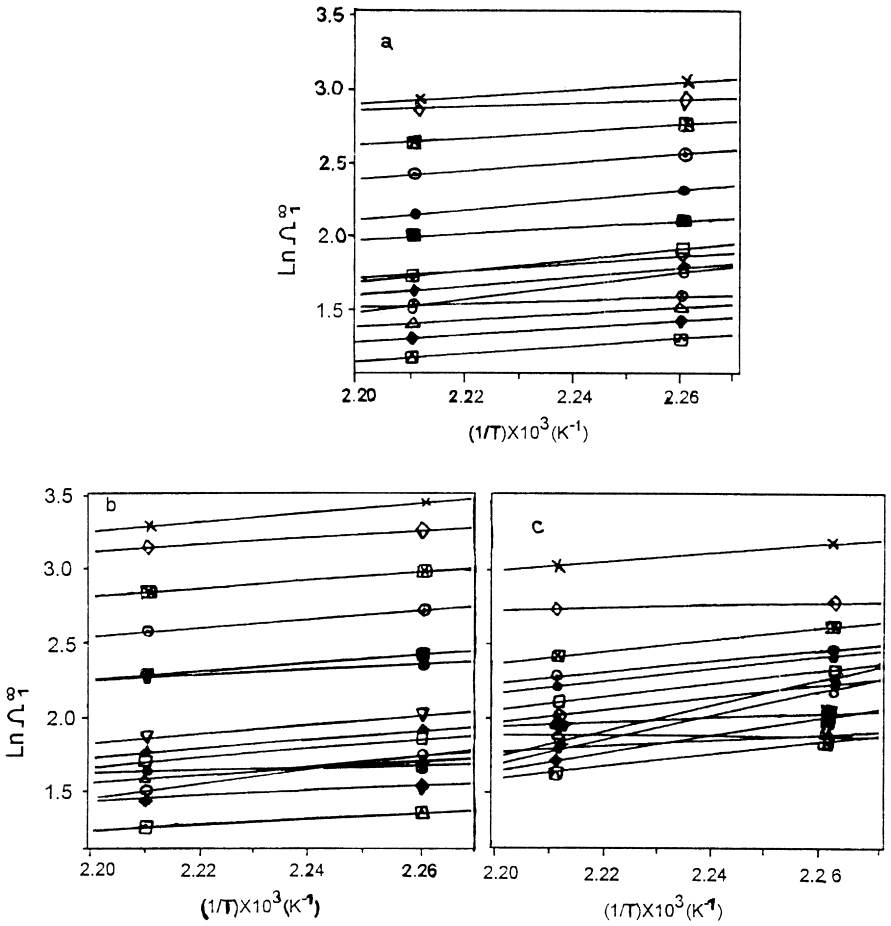


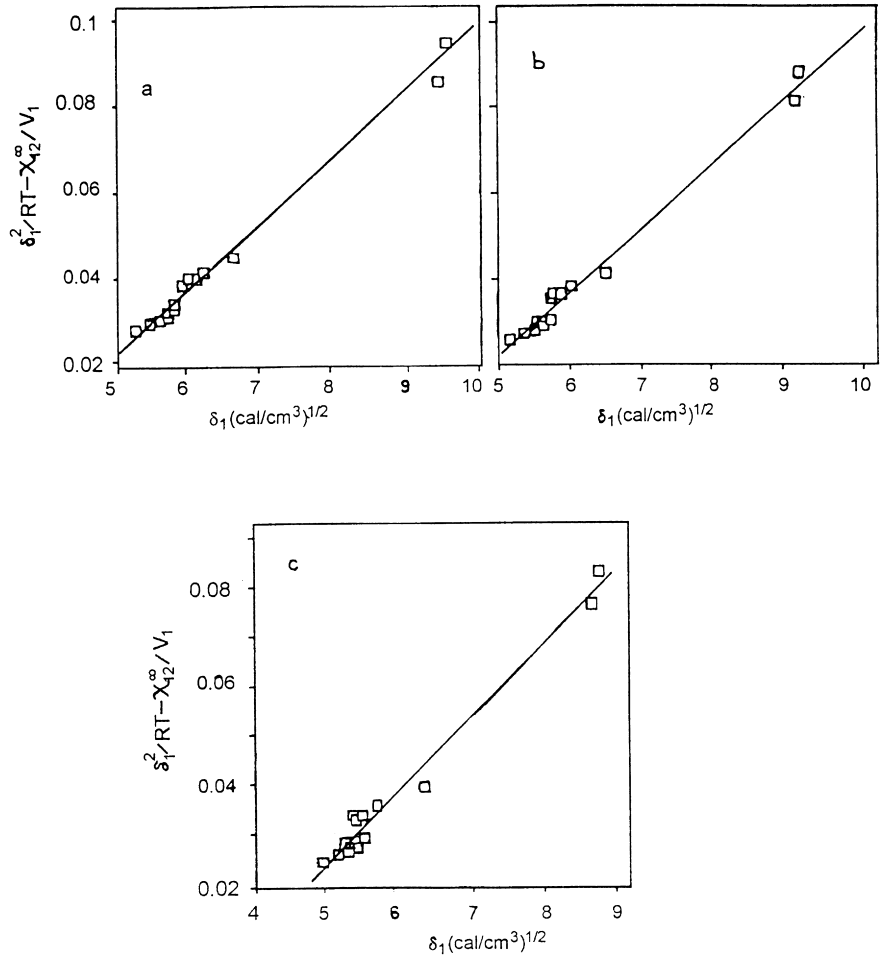

Fig. 1. Variation of logarithm of weight fraction activity coefficients, $\Omega_1^{\infty}$ with reciprocal of absolute column temperature, $1/T(K^{-1})$ for some solutes on (a) PPCHEMA, (b) PPCHEMA-AN and (c) PPCHEMA-S: □: Methanol, ○: Ethanol, △: Acetone, ⊗: EMK., ⍓: Methyl Acetate, ◆: Ethyl Acetate, ★: Benzene, ▽: Toluene, ■: *o*-Xylene, ●: *n*-Octane, ⊙: *n*-Nonane, ⍓: *n*-Decane, ◇: *n*-Undecane, ×: *n*-Dodecane

Table 7
Variation of the solubility parameters $\delta_2$ (cal/cm$^3$)$^{0.5}$ poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate], poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene] at temperature 433–453 K

| | *T*(K) | Slope | Intercept | Cal. from slope | Cal. from intercept | *r* |
|---|---|---|---|---|---|---|
| | 433 | 0.0163 | −0.0573 | 7.01 | 7.02 | 0.995 |
| PPCHEMA | 443 | 0.0150 | −0.0560 | 6.60 | 7.02 | 0.994 |
| | 453 | 0.0130 | −0.0532 | 5.85 | 6.92 | 0.990 |
| | 433 | 0.0164 | −0.0594 | 7.06 | 7.15 | 0.991 |
| PPCHEMA-AN | 443 | 0.0150 | −0.0562 | 6.60 | 7.03 | 0.991 |
| | 453 | 0.0135 | −0.0522 | 6.08 | 6.85 | 0.985 |
| | 433 | 0.0152 | −0.0544 | 6.54 | 6.84 | 0.993 |
| PPCHEMA-S | 443 | 0.0140 | −0.0511 | 6.16 | 6.71 | 0.994 |
| | 453 | 0.0124 | −0.0480 | 5.58 | 6.57 | 0.993 |

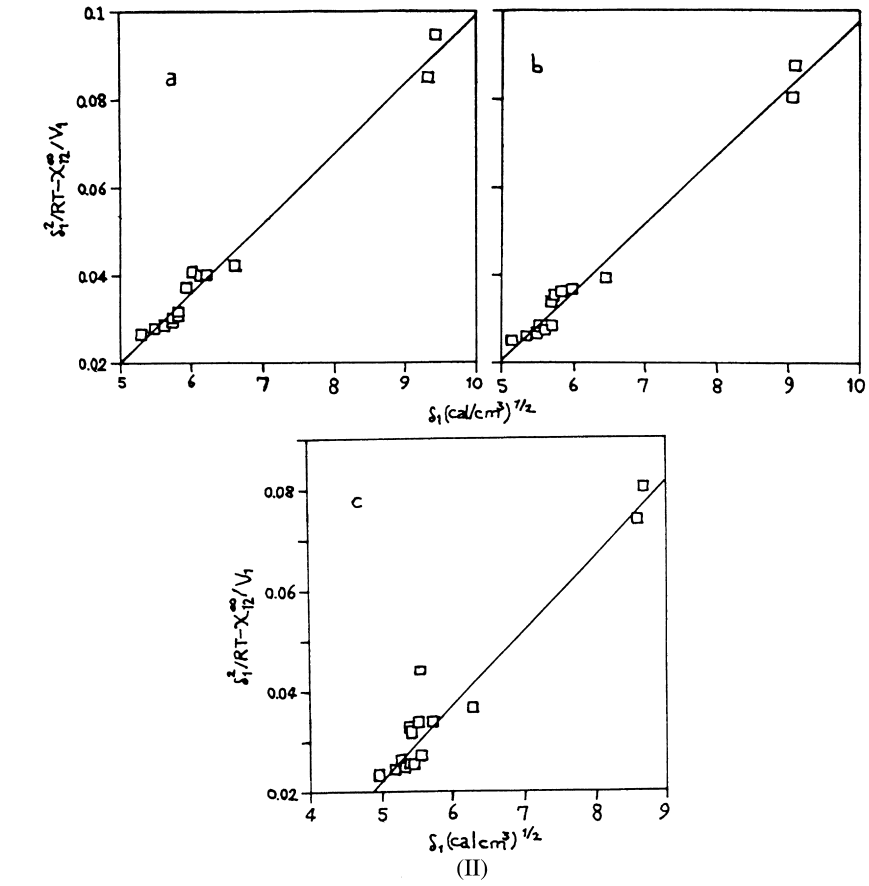
Kaya et al. [4] has determined the solubility parameters of poly(methyl methacrylate), poly(ethyl methacrylate), poly(isobuthyl methacrylate) and poly(-*t*-buthyl methacrylate) were found to be 6.85, 5.99, 6.02, 6.45 (cal/cm$^3$)$^{0.5}$ using Eq. (9) at 453 K.

The solubility parameters were determined as the mean of the upper limits and lower limits of the solubility parameters using pairs of solvent–non-solvent. The following solubility parameters were found to be 9.45 (cal/cm$^3$)$^{0.5}$, 9.25 (cal/cm$^3$)$^{0.5}$ and 9.15 (cal/cm$^3$)$^{0.5}$

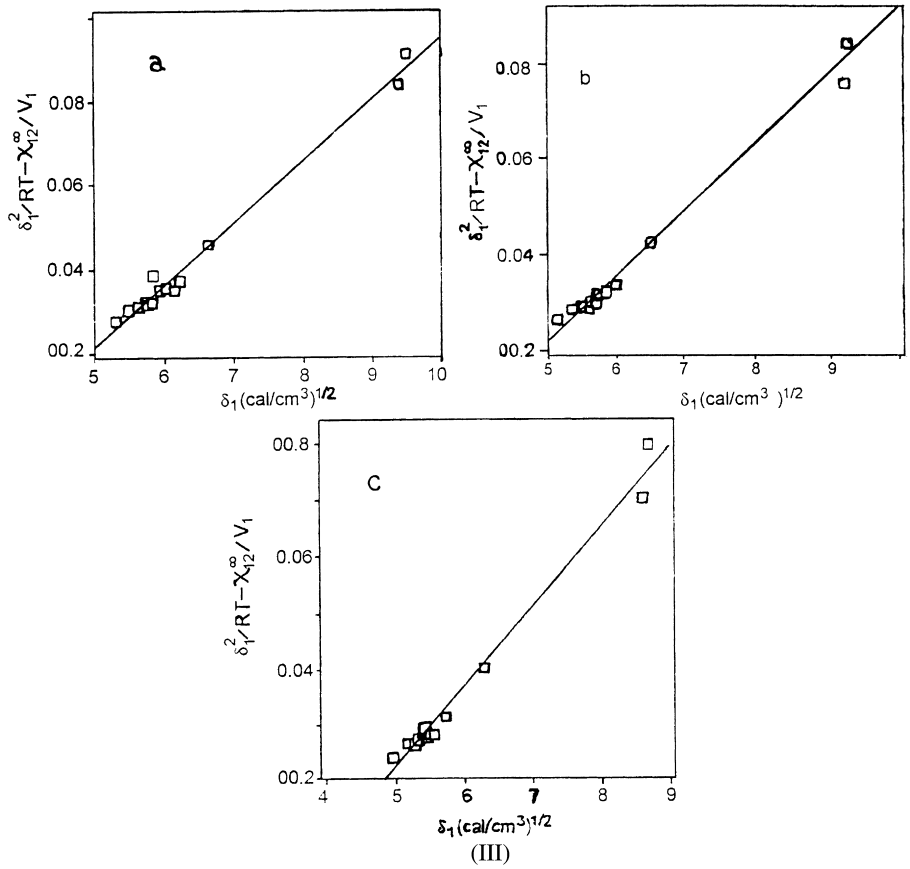



(I)

Fig. 2. I Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, $\delta_1$ (cal/cm$^3$)$^{0.5}$ at temperatures (a) = 433 K; (b) = 453 K; and (c) = 463 K (for PPCHEMA). II Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_{1]}$ with solubility parameters of the solutes, $\delta_1$ (cal/cm$^3$)$^{0.5}$ at temperatures (a) = 433 K; (b) = 453 K; and (c) = 463 K (for PPCHEMA-AN). III Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, $\delta_1$ (cal/cm$^3$)$^{0.5}$ at temperatures (a) = 433 K; (b) = 443 K; and (c) = 453 K (for PPCHEMA-S).




(II)




(III)

Fig. 2. *(continued)*

for PPCHEMA, PPCHEMA-AN and PPCHEMA-S, respectively.

## 5. Conclusion

Inverse gas chromatography technique was successfully applied to determine the glass transition temperature of PPCHEMA, PPCHEMA-AN and PPCHEMA-S and the Flory–Huggins interaction parameters, $\chi_{12}^{\infty}$, the partial molar free energy of mixing, $\Delta G_1^{\infty}$, the weight fraction activity coefficients, $\Omega_1^{\infty}$, and the partial molar heats of mixing, $\Delta H_1^{\infty}$, at infinite dilution of the solutes of alcohols, ketones, acetates, aromatics and alkanes on PPCHEMA, PPCHEMA-AN and PPCHEMA-S and the solubility parameter of a polymer, $\delta_2$. The results obtained are in good agreement with that of polymer–solvents and polymer–non-solvents systems. The technique is relatively uncomplicated and the data reduction is carried out by a computer.

## References

[1] Kaya İ, Ceylan K. Doğa-Tr J Chem 1993;17:1.
[2] Kaya İ, Özdemir E. J Macromol Sci Pure Appl Chem A 1995;32(3):377.
[3] Kaya İ, Ceylan K, Özdemir E. Tr J Chem 1995;19:94.
[4] Kaya İ, Özdemir E. J Macromol Sci Pure Appl Chem A 1995;32(3):369.
[5] Kaya İ. PhD Thesis, Study of physical and thermodynamic properties of alkyl methacrylates, Firat University, Elaziğ, 1995. p. 106.
[6] Kaya İ, Özdemir E. Polymer 1999;40:2405.
[7] Kaya İ, Özdemir E, Coskun M. J Macromol Sci Pure Appl Chem A 1996;33(1):37.
[8] Braun JM, Guillet JE. Macromolecules 1975;8:882.
[9] Gray DG, Guillet JE. Macromolecules 1974;7:244.
[10] Chein-Tai C, Al-Saigh ZY. Macromolecules 1989;22:2974.
[11] Chein-Tai C, Al-Saigh ZY. Polymer 1990;31:1170.
[12] Smidsrod O, Guillet JE. Macromolecules 1969;2:272.
[13] Galin M. Macromolecules 1989;10:1239.
[14] Deshpande DD, Tyagi OS. Macromolecules 1978;11:746.
[15] Munk P, Al-Saigh ZY, Card TW. Macromolecules 1985;18:2196.
[16] DiPaola-Baranyi G, Guillet JE, Klein JE, Jeberien HE. J Chromatogr 1978;166:349.
[17] Reid CR, Prausnitz JM, Sherwood TK. The properties of gases and liquids, 3rd ed. New York: McGraw-Hill, 1977.
[18] DiPaola-Baranyi G, Guillet JE. Macromolecules 1978;11:228.
[19] Guillet JE. J Macromol Sci Chem 1970;4:1669.
[20] Sanetra R, Klarz BN, Wlochowicz A. Polymer 1988;28:1753.
[21] Madec PJ, Mareshal E. Makromol Chem 1983;184:323.
[22] Boutevin B, Pietrasanta Y, Parisi JP. Makromol Chem 1987;188:1621.
[23] Brosse JC, Soutif JC, Pirazzi C. Makromol Chem 1979;180:2109.
[24] Bauduin G, Boutevin B, Mistraj JP, Parisi JP, Pietrasanta Y. Makromol Chem 1987;188:1055.
[25] Coskun M, Demirelli K, Erol I, Ahmetzade M. J Polym Sci A Polym Chem 1997;35:2123.
[26] Guillet JE, Purnel JH. Advances in analytical chemistry and instrumentation, gas chromatography. New York: Wiley, 1973.
[27] Klein J, Jeberien HE. Macromol Chem 1980;181:1237.