

Characterization of poly(ethyl methacrylate) by inverse gas chromatography

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The inverse gas chromatography (i.g.c.) method was applied to poly(ethyl methacrylate) (PEMA) as a method for polymer characterization. We have shown that the method was useful in obtaining meaningful thermodynamic data on PEMA-solvent systems, and information on the depolymerization of PEMA at a temperature close to its decomposition temperature. Three chemically different families were used to obtain some insights about PEMA-solvent interactions. PEMA was found to decompose above 245°C. However, above this temperature, the i.g.c. method can be utilized to detect the decomposition temperature. The PEMA-solvent interaction parameters and the free energy of mixing were found to be independent of the number of carbons in the series and temperature. The thermodynamic sorption functions for the sorption process of the three families of probes into PEMA solution were obtained and discussed in terms of their interactions with PEMA backbone. Furthermore, the contributions of CH₂, C=O and OH functional groups in the three series to the sorption process were also obtained. We found that the formation of hydrogen bonds between the C=O group of PEMA and the OH group of the alcohols is stronger than the dipole-dipole interactions between PEMA and the carbonyl groups of the acetates and the dispersive forces between PEMA and the alkanes. The latter was shown to be the weakest among the three series, and alkanes were found to be non-solvents of PEMA.

(Keywords: characterization; poly(ethyl methacrylate); inverse gas chromatography)

INTRODUCTION

Recently, we demonstrated that the inverse gas chromatography (i.g.c.) method can yield, after careful analysis, a wealth of information on polymeric systems¹⁻⁶. The term 'inverse' indicates that the polymeric stationary phase of the chromatographic column is of interest in contrast to conventional gas chromatography. The chromatographic column in this work contains the polymer under study. Because of the high viscosity of polymers, the existing methods for the characterization of polymers are beset by a number of technical difficulties. In our effort to promote the i.g.c. method as a reliable method for the characterization of amorphous and semi-crystalline polymers, we applied the i.g.c. method to many polymeric systems and we introduced many modifications to eliminate several contributions to the retention volumes of solvents. We concluded that the i.g.c. method is versatile, accurate and a fast method to obtain thermodynamic quantities on polymers and polymer blend systems.

In the past, the i.g.c. method has been used extensively by many workers and applied to amorphous and semi-crystalline polymers and polymer blends⁷⁻¹⁸. The i.g.c. method was developed by Smidsrod and Guillet⁷ and was applied to many polymeric systems. The method yielded a dependence of retention volumes on the chemical nature of the solvent used. Previous workers, however, limited their application of the i.g.c. method to

a temperature range 40-60°C above the polymer glass transition temperature. It has been shown that the equilibrium (diffusion across the layer) is established reasonably fast when the polymer is kept at a temperature significantly higher than the glass transition temperature¹⁹. However, polymers under their glass transition temperature are not penetrated by probe molecules under the conditions of a gas chromatography experiment. The method was beset by technical difficulties, which contributed to an extensive error in the interaction parameters of the polymer-solvent systems. We have contributed significantly to the modification of the i.g.c. method and improved the experimental precision by correcting for many experimental effects²⁻⁶. It has been shown that the i.g.c. method yields 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, melting temperatures and degree of crystallinity. Furthermore, the i.g.c. method is capable of obtaining physicochemical properties, the structure and chemical interactions of macromolecules.

In this paper, we will examine the application of the i.g.c. method to an amorphous poly(ethyl methacrylate) (PEMA) in a temperature range close to its decomposition (ceiling) temperature, and far above its glass transition temperature. It has been reported that the glass transition temperature of PEMA is in the range 65-66°C and it starts to decompose above 210°C²⁰. PEMA was heated at 200°C for about 10 min and no significant depolymerization was observed. We will use the i.g.c. method to examine the thermal depolymerization of PEMA, and we

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will show, for the first time, that the i.g.c. method is useful for obtaining meaningful thermodynamic parameters on PEMA-solvent systems in a temperature range close to PEMA's ceiling temperature. The dependence of the chemical nature of solvents on their miscibility with PEMA and the correlation of the thermodynamic quantities to PEMA structure will be discussed.

DATA REDUCTIONS

The probe specific retention volumes V_g corrected to 0°C were calculated from the standard chromatographic relation²¹:

$$V_g^\circ = \frac{\Delta t F J \times 273.15}{w T_{\text{room}}} \quad (1)$$

where $\Delta t = t_p - t_m$ is the difference between the retention times of the probe t_p and the marker t_m , F is the flow rate of the carrier gas measured at room temperature T_{room} , w is the mass of the polymeric stationary phase and J is a correction factor for gas compressibility, defined by the following relation:

$$J = \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o)^3 - 1} \quad (2)$$

where P_i and P_o are the inlet and outlet pressures, respectively.

The PEMA-solute interaction parameters χ_{12} at infinite dilution of different solutes used in this work are defined by the following equation:

$$\chi_{12} = \ln\left(\frac{273.15Rv_2}{V_g^\circ P_1^\circ V_1}\right) - 1 + \frac{V_1}{M_2 v_2} - \frac{(B_{11} - V_1)}{RT} P_1^\circ$$

or

$$\chi_{12} = \ln\left(\frac{273.15Rv_2}{V_g^\circ V_1 P_1^\circ}\right) - 1 - \frac{P_1^\circ}{RT} (B_{11} - V_1) \quad (3)$$

where R has the usual meaning as the gas constant, V_g is the specific volume of PEMA (ml g^{-1}), V_1 is the molar volume of the solute, P_1° is the vapour pressure, M_2 is the molecular weight of the polymer and B_{11} is the second virial coefficient of the solute in the gaseous state. It should be noted that the specific volume, V_1 , P_1° and B_{11} were calculated at the column temperature. Since M_2 is a large term, then the term V_1/M_2 becomes negligible. We will refer to the solute by the subscript 1 and PEMA by subscript 2.

The vapour pressure P_1° was calculated from the Antoine equation as follows:

$$\log P_1^\circ = A - B/(t + C) \quad (4)$$

where t is the temperature (°C) and the constants A , B and C were taken from Dreisbach's compilation²². The molar volumes of the solutes V_1 were calculated using:

$$V_1 = M_1/\rho_L \quad (5)$$

$$\rho_L + \rho_V = a - bt \quad (6)$$

$$\rho_V = P_1^\circ M_1/RT \quad (7)$$

where ρ_L and ρ_V are the densities of the liquid solute and its saturated vapour respectively, M_1 is the molecular weight of the solute and P_1° is the pressure calculated from equation (4). The constants a and b are also taken from Dreisbach's compilation²². Second virial coefficients

B_{11} were computed using the following equation²³:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (8)$$

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 alkanes or number of corresponding groups in non-alkane solutes.

The molar heat (enthalpy) of sorption of probe absorbed by the amorphous part of PEMA (ΔH_1^s) is given by the following equation (13):

$$\Delta H_1^s = -R \partial \ln V_g^\circ / \partial (1/T) \quad (9)$$

where V_g° is the net specific retention volume corrected for the loading dependence (as discussed in 'Results and discussion' section). By using the corrected V_g° in equation (9), we eliminated the contribution of the molar heat of probe adsorbed on the amorphous surfaces. In equation (9), T is the column temperature.

The average partial molar heat of mixing at infinite dilution of the probe was calculated as follows:

$$\Delta \bar{H}_1^\infty = R \partial \ln \Omega_1^\infty / \partial (1/T) \quad (10)$$

where Ω_1^∞ is the weight fraction activity coefficient of the solute probe at infinite dilution, which is calculated according to the following equation²⁴:

$$\Omega_1^\infty = \frac{273.15R}{V_g^\circ P_1^\circ M_1} \exp[-P_1^\circ (B_{11} - V_1)] RT \quad (11)$$

where P_1° , V_1 and B_{11} were defined in equation (3) and M_1 is the molecular weight of the probe. Equation (11) was developed by Patterson *et al.*^{17,24} to replace the original equation for infinite dilution activity coefficient developed by Everett²⁵. The original equation depended on an uncertain quantity, the molecular weight of the polymer.

The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient of the solute as follows:

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \quad (12)$$

where RT is the usual meaning.

The partial molar free energy of sorption at infinite dilution is calculated as follows:

$$\Delta G_1^s = -RT \ln(M_1 V_g^\circ / 273.15R) \quad (13)$$

By incorporating equations (9) and (13), we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^s = \Delta H_1^s - T \Delta S_1^s \quad (14)$$

EXPERIMENTAL

Materials

Fifteen polar and non-polar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. They were all purchased from Aldrich Chemical Co. as chromatographic grade, their purity being checked by gas chromatography prior to use. Poly(ethyl methacrylate) was supplied by Aldrich Chemical Co. in powder form. Its molecular weight was estimated from intrinsic viscosity, $[\eta] = 0.46 \text{ dl g}^{-1}$ in 2-butanone at 23°C, to be 215 000 using published Chinai and Samuels constants²⁶ ($a = 0.79$, $K = 0.00283 \text{ ml g}^{-1}$). Chromosorb W (AW-DMCS treated, 60/80 mesh) was obtained from Analabs.

Instrumentation and procedure

Measurements were run on a modified Varian 1800 Aerograph gas chromatograph equipped with both thermal conductivity and flame ionization detectors (FID). The thermal conductivity detector was selected over the FID for reasons discussed elsewhere¹. Dried nitrogen gas (research grade) was used as a carrier gas; its flow rate was controlled by a series of valves, among them a precision needle valve to ensure stability of the flow. The flow rate was measured by a soap bubble flow meter with 50 ml volume thermostated at 25°C. Three readings usually taken agreed well within 0.3%. A flow rate of about 10 ml min⁻¹ was used throughout our experiment. The inlet and outlet pressures were frequently monitored (every hour) by a precision mercury manometer. The outlet pressure turned out to be always atmospheric while the inlet pressure ranged around 900 mmHg. The temperature of the column was monitored frequently within the range of 0.1°C using a high-precision temperature control and digital indicator (Omega model DP 701). A control of the mass of the polymer in the stationary phase has been under debate^{14,27,28}. A soaking-type method for coating the polymer on the support was recently developed with excellent precision².

Four columns were prepared with 5 ft long copper tubing, 1/4 inch OD. The copper tubings were washed with methanol and were annealed prior to use. Table 1 shows the description of these columns. Four loadings of PEMA were used ranging from 0 to 12% by weight of the polymer relative to the weight of the solid support. PEMA was dissolved in hot *N,N*-dimethylacetamide (DMA) solution and deposited onto the solid support. Columns were conditioned at 80°C and fast carrier gas flow rate for 24 h prior to use. Probes were injected onto the columns with 1 μ l Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume of 0.2 μ l was selected so as to remain within a safe region with minimum effect on the retention volumes⁵. The retention times of the probes were measured with high precision using an analogue-to-digital converter (digital multimeter interfaced with IEEE-488, Keithley), which was interfaced with an IBM-compatible personal computer (PC). This is an automated system for the detection and integration of the chromatographic signal, which was analysed as a function of time. The PC was used to control the operation, store the data, display the elution curves and perform extensive calculations using the stored data. The whole process was fully automated and controlled by a program developed by Munk and El-Hibri at the University of Texas at Austin, starting from the sample injection to the final retention volume calculations. The measured retention volumes of 15 probes used in this work for the zero loading column (support only) were

stored in a separate file and interpolated over a wide range of temperatures. The stored retention volumes of probes were then subtracted from the raw retention volumes of the probes using other columns with different loadings. This procedure was used to correct for the 'inert' solid support effect. Our data handling system saved us a tremendous amount of time in data acquisition and calculations, and offered a precision and reproducible results of ± 0.1 s in the retention time.

RESULTS and DISCUSSION

Specific retention volumes

Corrected specific retention volumes (V_g° of 15 solvents (probes) were obtained using four loadings of PEMA and at three temperatures (175, 185 and 195°C). Three different families with different chemical nature and polarity (n-alkanes, n-acetates and alcohols) were selected for this study. The alcohol series is a mixture of straight-chain and branched-chain alcohols. The V_g° values of these probes were calculated according to equation (1) using t_p as the maximum of the chromatographic peak in seconds. For several decades, chromatographers debated whether the maximum of the chromatographic peak represents the actual probe retention time. However, in some cases, peak parameters other than the peak maximum, such as the first moment or the first inflection point of the elution curve, may be used as a retention time. We compared retention times of all probes calculated using both the first moment, as the mean of the elution curve, and the peak maximum for 7% and 12% PEMA columns. After careful analysis of the retention volume of probes with different chemical nature, we concluded that the moment analysis is not reliable, in our case, to obtain meaningful retention volumes. The elution curves differed according to the chemical nature of the probes and in most cases the curves were not fully symmetrical (Gaussian). The moment analysis depended on the diffusivity of the probe. Our observations are in full agreement with previous results^{29,30}. Generally, larger values of retention volumes were obtained using the moment analysis than those obtained from the peak maximum. Thus all the forthcoming V_g° data were based on the peak maximum measurements.

To eliminate the diffusion effect of the carrier gas, we performed our experiments using a slow flow rate (10 ml min⁻¹). Retention volumes of probes showed a dependence on the loading of PEMA. Four loadings of PEMA were used (0–12%) in order to explore this effect. This dependence is due to two retention mechanisms: adsorption of probes on the surface of PEMA and absorption of probes into the PEMA layer. Since we are only interested in the interaction of probes with PEMA, we eliminated the adsorption effect of probes by plotting retention volumes versus the inverse of PEMA mass. Fifteen plots like Figure 1 were generated for each probe and at three temperatures. The curves were extrapolated to infinite loading of PEMA and the intersection of the curves with the Y-axis is the corrected retention volume at the indicated temperatures. Table 2 shows the net specific retention volumes of probes corrected for the solid support, flow rate and PEMA loading. The corrected V_g° values differed from the uncorrected (raw) V_g° values by 42%, 43% and 51% at 175, 185 and 195°C, respectively. One would expect that the uncorrected V_g°

Table 1 Stationary phase and column description

Column no.	PEMA loading (% w/w)	Mass of PEMA (g)	Mass of support (g)	Column length (cm)
I	0	0	7.9670	152.40
II	3	0.2402	8.0009	152.40
III	7	0.5635	8.0023	152.40
IV	12	0.9663	8.0025	152.40

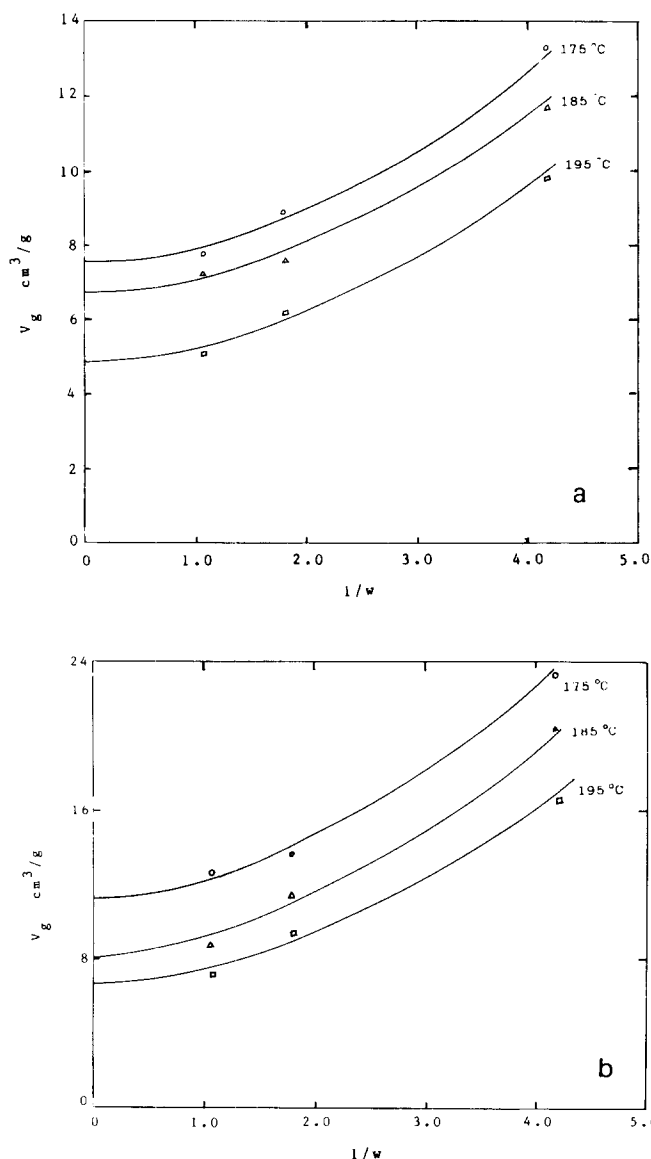


Figure 1 (a) Specific retention volumes of propyl acetate vs. the inverse mass of PEMA at 175, 185 and 195°C. (b) Specific retention volumes of 2-pentanol vs. the inverse mass of PEMA at 175, 185 and 195°C

Table 2 Corrected specific retention volumes (mlg^{-1}) of alkanes, acetates and alcohols at 175, 185 and 195°C using PEMA as stationary phase

Probe	175°C	185°C	195°C
n-Heptane	3.21	2.48	2.29
n-Octane	5.46	4.26	3.69
n-Nonane	9.02	7.58	5.87
n-Decane	13.46	11.62	8.41
n-Undecane	22.52	18.61	13.46
n-Dodecane	35.35	26.92	20.69
n-Methyl acetate	3.11	2.73	2.19
n-Ethyl acetate	4.91	4.01	3.32
n-Propyl acetate	7.56	6.74	4.85
n-Butyl acetate	11.75	9.41	7.24
Methanol	2.14	1.78	1.54
Ethanol	2.66	2.26	1.83
2-Propanol	3.35	2.67	2.18
1-Butanol	9.57	8.02	5.87
2-Pentanol	11.36	8.19	6.74

values would have contributed to very high error in the interaction parameters. Thus correction of V_g° values is necessary to obtain meaningful thermodynamic data. Our corrected V_g° values are then amenable for thermodynamic calculations and we believe that the error in V_g° after correction is better than 2%. To make sure that PEMA did not decompose on the column during our experiments, when it was heated up to 195°C, we remeasured retention volumes of probes at 175°C after cooling the column and reheating it to 175°C. Comparison of retention volumes of probes revealed that thermal decomposition did not occur when PEMA was heated at 195°C for a period of 8 h. Table 3 shows that retention volumes after reheating of PEMA differed less than 10% from the original retention volumes. Figure 2 shows a typical retention diagram, a linear dependence of corrected

Table 3 Uncorrected specific retention volumes of alkanes, acetates and alcohols at 175°C after cooling and reheating 12% PEMA column

Probe	V_g° before	V_g° after	Difference (%)
n-Heptane	3.02	3.30	8.5
n-Octane	4.98	5.23	4.9
n-Nonane	8.12	8.79	7.6
n-Decane	13.63	13.82	1.4
n-Undecane	21.84	22.41	2.7
n-Dodecane	34.79	34.37	1.2
n-Methyl acetate	3.47	3.28	5.8
n-Ethyl acetate	4.14	4.30	3.7
n-Propyl acetate	7.81	8.22	4.9
n-Butyl acetate	11.21	11.72	4.4
Methanol	2.26	2.43	7.0
Ethanol	2.73	2.71	0.7
2-Propanol	3.51	3.35	4.8
1-Butanol	9.51	9.96	4.5
2-Pentanol	12.58	12.94	2.8

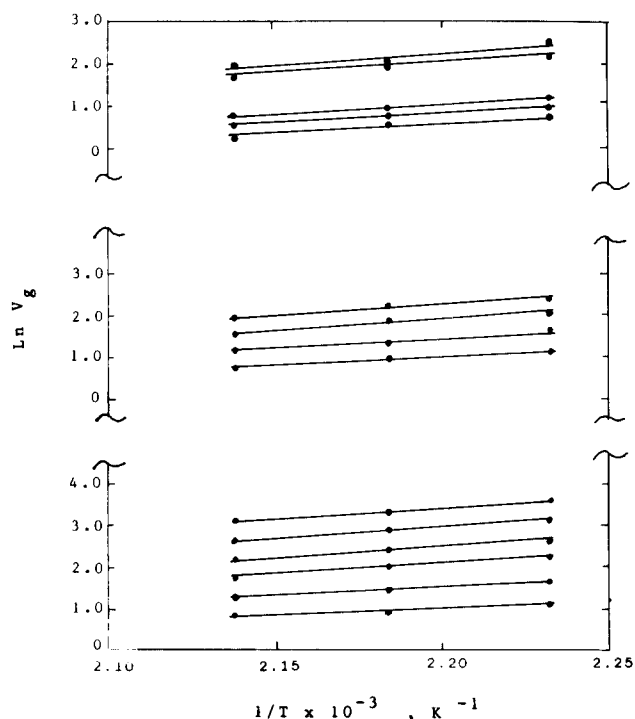


Figure 2 Retention diagram of three families. Corrected specific retention volumes vs. the inverse of temperature (175–195°C): upper, alcohol series; middle, acetate series; lower, alkane series

V_g° data with change in temperature being observed for alkanes, acetates and alcohols. This linear relationship indicates that equilibrium is established for the sorption of probes into the PEMA layer in the temperature range used. However, as we will show later, the linear relationship was also observed when experiments were performed up to 245°C.

Experiments were performed at temperatures higher than 195°C in order to explore the effectiveness and the ability of the i.g.c. method to characterize the thermal depolymerization of PEMA and the detection of PEMA decomposition temperature. We measured retention volumes of selected probes in the range 205–280°C. Since PEMA was reported to decompose above 210°C²⁰, we examined the retention volumes of probes before, at and above the proposed decomposition temperature. Retention volumes of selected probes from the three families (C_{10} – C_{12} alkanes, C_3 – C_4 acetates and C_3 – C_4 alcohols) on 12% PEMA were plotted *versus* the inverse of temperature for the temperature range 175–225°C (Figure 3). Again, a linear relationship was observed between V_g° values and the inverse of temperature. This indicates that the equilibrium of sorption between these probes and PEMA is stationary at a temperature range up to 225°C.

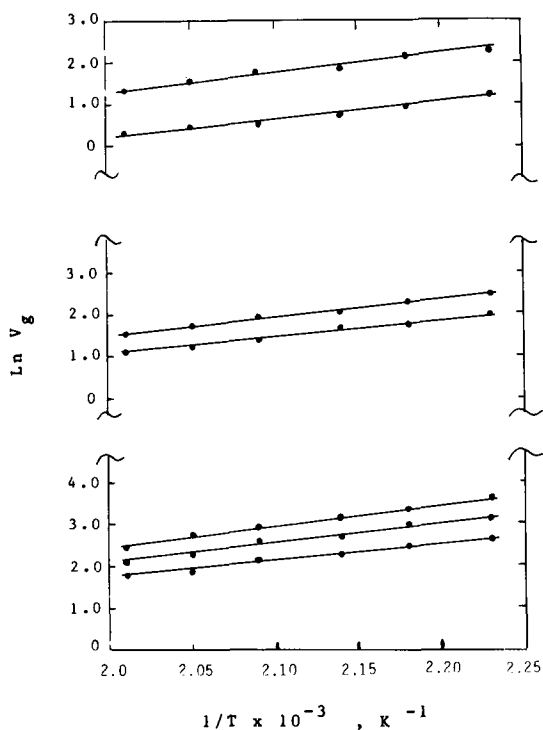


Figure 3 Uncorrected V_g° values of the three families vs. the inverse of temperature (175–225°C) using 12% PEMA: upper, C_3 and C_4 alcohols; middle, C_3 and C_4 acetates; lower, C_{10} – C_{12} alkanes

No decomposition is observed at 225°C. However, when the temperature was increased to 245°C, there has been a change in the shape of the elution curves of probes due to the partial depolymerization of PEMA. Thus, we concluded that the decomposition temperature of high-molecular-weight PEMA occurred above 245°C. A linear relationship of V_g° values with increasing temperature was continued up to 280°C. Our interpretation is that at 280°C, PEMA has not fully decomposed and the retention volume becomes independent of the amount of PEMA left on the column at such a high temperature. Therefore, the i.g.c. method could be utilized to study the decomposition process of polymers. However, it is limited to the temperature range at which probe vapours approach non-ideal behaviour.

Interaction and other thermodynamic parameters

PEMA–solvent interaction parameters, such as Flory–Huggins interaction parameter χ_{12} at infinite dilution of the probe, were calculated according to equation (3), in a temperature range just below the PEMA decomposition temperature. Since Antoine equation constants for the acetate and alcohol series are not available in the temperature range used, we only calculated χ_{12} for the alkane series. We eliminated the low-boiling alkanes like pentane and hexane from the series to avoid the non-ideality of these probes in the temperature range of our experiments. Generally, χ_{12} did not show considerable dependence with change in the number of carbons and temperature (Table 4); it was only changed within experimental error. Similar results were obtained for the weight fraction activity coefficients Ω_1° listed in Table 4. However, χ_{12} of heptane at 195°C shows a 7% error from that at 185°C; this may be due to the high volatility of heptane at this temperature. In order to check our results, we calculated the partial molar free energy of mixing (ΔG_1°) of alkanes at three temperatures (Table 4). All data in Table 4 indicate that alkanes are poor solvents for PEMA.

The thermodynamic sorption functions for the sorption process of the three families of probes into PEMA solution were calculated using equations (9), (13) and (14). Table 5 shows the calculated sorption functions at 185°C; all three 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 and PEMA backbone. Since 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 three families of probes. This is an indication that the individual CH_2 group, regardless

Table 4 PEMA–solute interaction coefficients χ_{12} , weight fraction activity coefficients Ω_1° and partial molar free energies of mixing ΔG_1° (kcal mol⁻¹) of alkanes at 175–195°C

Probe	χ_{12}			Ω_1°			ΔG_1°		
	175°C	185°C	195°C	175°C	185°C	195°C	175°C	185°C	195°C
n-Heptane	1.43	1.55	1.67	22.29	25.71	29.66	2.77	2.96	3.16
n-Octane	1.39	1.45	1.49	20.22	22.03	23.38	2.68	2.82	2.93
n-Nonane	1.37	1.34	1.37	19.05	18.85	19.63	2.63	2.67	2.77
n-Decane	1.44	1.37	1.33	19.94	18.76	18.26	2.67	2.67	2.70
n-Undecane	1.41	1.35	1.34	18.71	17.97	18.02	2.61	2.63	2.69
n-Dodecane	1.43	1.35	1.31	18.75	17.56	16.93	2.61	2.61	2.63

Table 5 Partial molar heats of sorption ΔH_1^s , partial molar free energies of sorption ΔG_1^s and entropies of sorption $T \Delta S_1^s$ (kcal mol⁻¹) of alkanes, acetates and alcohols at 185°C using PEMA as stationary phase

Probe	ΔH_1^s	ΔG_1^s	$T \Delta S_1^s$
n-Heptane	-7.08	4.57	-11.65
n-Octane	-8.09	3.96	-12.05
n-Nonane	-8.87	3.33	-12.20
n-Decane	-9.67	2.84	-12.51
n-Undecane	-10.51	2.33	-12.84
n-Dodecane	-11.17	1.92	-13.09
n-Methyl acetate	-7.21	4.76	-11.97
n-Ethyl acetate	-8.07	4.26	-12.33
n-Propyl acetate	-9.04	3.64	-12.68
n-Butyl acetate	-9.92	3.22	-13.14
Methanol	-6.84	5.91	-12.75
Ethanol	-7.84	5.36	-13.20
2-Propanol	-8.89	4.97	-13.86
1-Butanol	-10.11	3.77	-13.88
2-Pentanol	-10.79	3.60	-14.39

of the chemical nature of the probe, has a significant interaction with the PEMA backbone. Comparison of the heat of sorption for probes with a similar number of carbons and different functional groups revealed that alcohols show more exothermic heat of sorption than acetates and alkanes. Acetates, however, show more exothermic values than alkanes. Alcohols and acetates have two contributions to the sorption process (interaction with PEMA via OH or C=O and via CH₂ groups), while alkanes have only one contribution, which is the interaction of CH₂ groups with PEMA. Branching of alcohols did not show any significant effect on the sorption process. Close examination of the heat-of-sorption values cited in Table 5 shows a systematic increment of about 0.80 kcal mol⁻¹ for each CH₂ group added to the alkane series, about 0.90 kcal mol⁻¹ for each CH₂ added to the acetate series, and about 1.0 kcal mol⁻¹ for each CH₂ group added to the alcohol series. It is clear that the CH₂ group of alcohols show the largest contribution to the heat of mixing, followed by acetates and alkanes. These results are meaningful as one can interpret these values in terms of the individual functional group contribution to the heat of sorption. The sorption functions ΔH_1^s , ΔG_1^s and $T \Delta S_1^s$ showed a linear relationship with the number of carbons in the three series. We plotted the sorption functions *versus* the number of carbons in the series of three families in a typical family plot (Figure 4). A linear dependence was obtained. The slope of the straight lines was used to interpret the strength and the type of the interaction forces between PEMA and probe functional groups. From the slopes of the straight lines for the three series, we obtained the contributions of the functional group in each series to the sorption functions (Table 6). Table 6 shows that more exothermic heats of sorption are obtained with acetates and alcohols than alkanes; however, alcohols showed more exothermic heat-of-sorption values than acetates. Our interpretation is that acetates and alcohols form stronger attraction forces with PEMA backbone sites than do alkanes. The attraction forces between PEMA and acetates are actually a combination of two types: dispersive forces between the CH₂ groups of the acetates and the ethyl group of PEMA, and the interaction of the C=O group of the acetates with the C=O group of

PEMA via dipole-dipole interactions. Similarly, alcohols interact via dispersive forces between the CH₂ groups in both alcohols and PEMA, plus the formation of hydrogen bonds between the OH group of the alcohols and the carbonyl group of PEMA. In the light of this analysis, we calculated the contribution of the C=O groups of the acetates and the OH groups of the alcohols to the sorption functions, by subtracting the contribution of alkane sorption functions from that of the acetates and alcohols (Table 6). The contribution of the C=O group of the acetate to the heat of sorption differed significantly from that of the OH group in the alcohols, suggesting that dipole-dipole interactions in PEMA-acetate systems are weaker than the hydrogen-bond interactions in PEMA-alcohol systems.

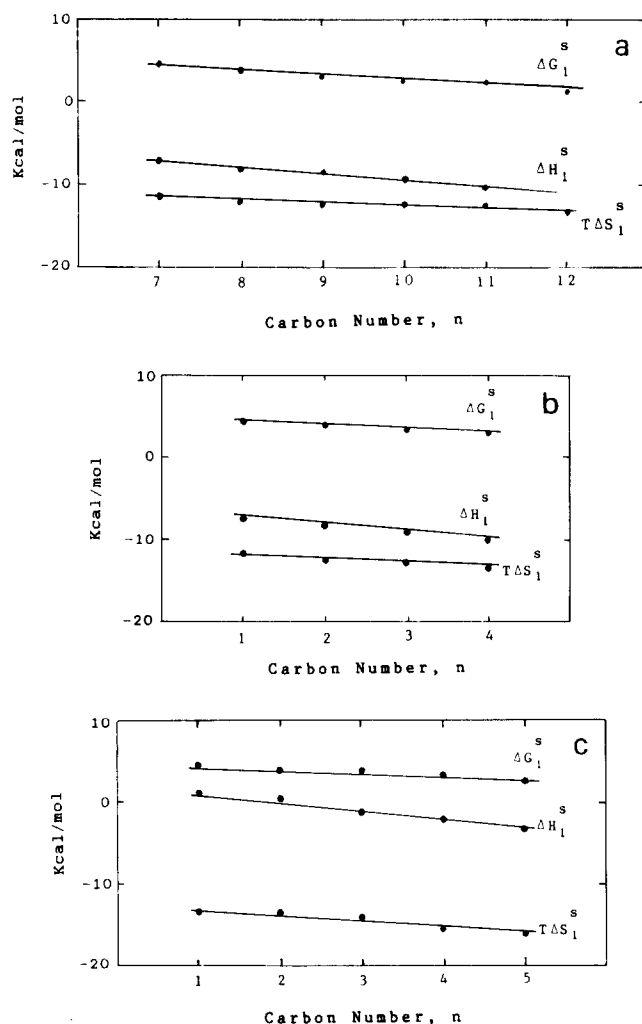


Figure 4 Family plot. Calculated sorption functions ΔH_1^s , ΔG_1^s and $T \Delta S_1^s$ vs. number of carbons in the three series: (a) alkane series; (b) acetate series; (c) alcohol series

Table 6 CH₂, C=O and OH group contributions to ΔH_1^s , ΔG_1^s and $T \Delta S_1^s$ (kcal mol⁻¹)

Group	ΔH_1^s	ΔG_1^s	$T \Delta S_1^s$
Alkanes, CH ₂	-0.81	-0.53	-0.28
Acetates, CH ₂	-0.91	-0.39	-0.52
Alcohols, CH ₂	-1.02	-0.40	-0.62
Acetates, C=O	-0.10	0.14	-0.24
Alcohols, OH	-0.21	0.13	-0.34

CONCLUSION

We have found in this report that the i.g.c. method is capable of obtaining information about the thermal-depolymerization of polymers and the ceiling temperature of polymers. We have shown that PEMA decomposes above 245°C, and decomposition was not complete at 280°C. Retention volumes of 15 chemically different probes were obtained and corrected for many effects. The peak maximum of the elution curves was used to calculate the retention volumes of probes. The first moment of the elution curves was shown to be unreliable, in our case, in the calculations of retention volumes of probes. Retention volumes of three families used in this work showed a linear relationship with temperature in the equilibrium sorption region. The slopes of the straight lines were used to obtain the sorption quantities, ΔH_1^s , ΔG_1^s and $T \Delta S_1^s$. Probes of the three families showed an exothermic heat of sorption, which was increased as a CH₂ group was added in the series. On the other hand, the interaction parameters χ_{12} , the partial molar free energy of mixing ΔG_1^∞ and the weight fraction activity coefficients Ω_1^∞ were found to be independent of the number of carbons in the series and temperature. Generally, alkanes were found to be non-solvents for PEMA while alcohols and acetates showed a stronger interaction with PEMA than did alkanes. The contributions of the three functional groups, OH, C=O and CH₂, to the sorption functions were obtained. The hydroxyl group showed more interaction than the carbonyl and methyl groups with PEMA backbone.

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