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Thermodynamic interactions and characterisation of poly(isobornyl methacrylate) by inverse gas chromatography at various temperatures

İsmet Kaya[a,*], Eyüp Özdemir[b]

[a]*Department of Chemistry, K. Maraş Sütçü İmam University, K. Maraş, Turkey*
[b]*Department of Chemistry, Fırat University, Elazığ, Turkey*

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Abstract

The inverse gas chromatography (IGC) method was applied to poly(isobornyl methacrylate) (PIBORNMA) as a method for polymer characterisation and for the study of thermodynamic interactions. Six groups of solvents with different chemical natures and polarities were used to obtain information about PIBORNMA–solvent interactions. The PIBORNMA–solvent interaction parameters and the free energy of mixing were determined at a series of temperatures. The glass transition temperature (T_g) of PIBORNMA was found to be about 105°C by differential scanning calorimetry. The thermodynamic sorption functions for the sorption process of probes of differing chemical nature into PIBORNMA solution were obtained and discussed in terms of the probes' interactions with PIBORNMA. Furthermore, the contributions of $-CH_2$, –C=O, –C=O–OR, aromatic, cyclic ether and –OH functional groups in the six series of solvents to the sorption process were also obtained. Acetates, THF and ketones were found to be good solvents for PIBORNMA, whereas alkanes, aromatics and methanol were found to be non-solvents. Also the solubility parameter for PIBORNMA at infinite dilution was found by plotting the graph of $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ versus solubility parameters, δ_1, of some probes.

Keywords: Thermodynamic parameters; Solubility parameter; Poly(isobornyl methacrylate)

1. Introduction

Inverse gas chromatography (IGC) is a useful method in the study of some of the thermodynamic properties of polymers. IGC 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 [1]–[5]. 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 characterisation of polymers are beset by a number of technical difficulties. IGC is a reliable method for the characterisation of amorphous and semicrystalline polymers. The method is simple, fast, economical, and provides valuable thermodynamic information for characterisation of polymeric substances. In the past, IGC has been used extensively by many workers and applied to amorphous and semi-crystalline polymers and polymer blends [5].

IGC was developed by Smidsrod and Guillet [6] and was applied to many polymeric systems. It has been shown that IGC 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 point temperatures, and degrees of crystallinity. Furthermore, IGC is capable of obtaining physicochemical properties, the structure and chemical interactions of macromolecules [7]–[15].

DiPaola-Baranyi and Guillet [16] have recently shown that IGC, using a polymer as the stationary phase, can be a simple method for estimating solubility parameters of polymers. In principle, the technique of gas–liquid chromatography (GLC) should be ideally suited for determining solubility parameters directly for polymer substrates, since the method yields energies of mixing of polymer–solute systems. Moreover, the method is not restricted to the study of polymer–solvent systems but can also be used to investigate interactions between polymers and non-solvents. In addition, the system is amenable to high as well as to low temperatures. The use of GLC data to determine solubility parameters for polymers was first proposed by Guillet [17].

* Corresponding author.

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The method is based on the principle that the Flory-Huggins χ_{12}^{∞} parameter can be readily determined from retention data on various small molecule probes. These χ_{12}^{∞} parameters were determined by Eq. (3).

In this study we examine the polymer–solvent interaction parameters and the solubility parameters of amorphous poly(isobornyl methacrylate) (PIBORNMA) by using IGC in the temperature range 50–200°C.

2. Data reductions

The probe specific retention volumes, V_g^0, corrected to 0°C were calculated from the standard chromatographic relation [18]:

$$V_g^0 = (\Delta t F J \times 273.2)/wT_{room} \quad (1)$$

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_{room}; w is the mass of the polymeric stationary phase; and J is a correction factor for gas compressibility, defined by the following relation:

$$J = 3/2[(P_i/P_o)^2 - 1/(P_i/P_o)^3 - 1] \quad (2)$$

where P_i and P_o are the inlet and outlet pressures, respectively. The PIBORNMA–solute interaction parameters, χ_{12}^{∞}, at infinite dilution of different solutes used in this work are defined by the following equation:

$$\chi_{12}^{\infty} = \ln(273.2R\nu_2/V_g^0 V_1 P_1^0) - 1 - P_1^0/RT(B_{11} - V_1) \quad (3)$$

where R is the gas constant, ν_2 is the specific volume of the PIBORNMA, V_1 is the molar volume of the solute, P_1^0 is the vapour pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. V_1, P_1^0 and B_{11} were calculated at the column temperature. We will refer to the solute by the subscript 1 and to PIBORNMA by subscript 2.

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

$$\log P_1^0 = A - B/(t + C) \quad (4)$$

where t is the temperature (in °C) and A, B and C are constants [19]. Second virial coefficients B_{11} were computed using the following equation [16]:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (5)$$

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 [19]. The molar heat (enthalpy) of sorption of the probe absorbed by the PIBORNMA, ΔH_1^s, is given by the following equation:

$$\Delta H_1^s = -R\,\partial \ln V_g^0/\partial(1/T) \quad (6)$$

where V_g^0 is the probe specific retention volume and T is the column temperature (K). The average partial molar heat of mixing at infinite dilution of the probe was calculated as follows:

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

where Ω_1^{∞} is the weight fraction activity coefficient of the solute probe at infinite dilution which is calculated according to the following equation [20]:

$$\Omega_1^{\infty} = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/RT] \quad (8)$$

where P_1^0, V_1 and B_{11} are as defined in Eq. (3) and M_1 is the molecular weight of the probe. The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient (Ω_1^{∞}) of the solute as follows:

$$\Delta G_1^{\infty} = RT \ln \Omega_1^{\infty} \quad (9)$$

where RT has the usual meaning.

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

$$\Delta G_1^s = -RT \ln(M_1 V_g^0/273.2R) \quad (10)$$

By incorporating Eqs. (6) and (10) we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \quad (11)$$

The adsorption enthalpy of probes adsorbed by the PIBORNMA ΔH_a is given by the following equation [21]:

$$\partial \ln V_g^0/\partial(1/T) = -\Delta H_a/R \quad (12)$$

where ΔH_a is the adsorption enthalpy and R is the ideal gas constant. Heats of vaporisation for the probes were obtained from the heats of solution and heats of mixing by using the following relation:

$$\Delta H_v = \Delta H_1^{\infty} - \Delta H_1^s \quad (13)$$

The solubility parameters of polymers, δ_2, can be determined by using the following relation:

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

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. Solubility parameters of polymer, δ_2, can be calculated from both the slope and intercept of the straight line [16], [22], [23].

Solubility parameters of probes are calculated from the relation [17]:

$$\delta_1 = [(\Delta H_v - RT/V_1)]^{1/2} \quad (15)$$

where ΔH_v is the molar enthalpy of vaporisation for the probe at temperature T.

3. Experimental

3.1. Materials

Thirteen 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 and methanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate, tetrahydrofuran, benzene, and *o*-xylene were supplied from Merck as chromatographic grade. Poly(isobornyl methacrylate) was supplied by Aldrich in powder form and Registry No. 64114-51-8. Chromosorb W (45–60 mesh) was supplied from Sigma.

3.2. Instrumentation and procedure

A Shimadzu GC-14A model gas chromatograph equipped with a dual flame ionisation dedector (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 (mmHg) at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rate was 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 column was prepared with a 2.1 m spiral glass column, 3.2 mm ID. The spiral glass column was washed with methylene chloride and was annealed prior to use. A column packing material was prepared by coating 45–60 mesh size chromosorb W with PIBORNMA: 0.5400 g was dissolved in 50 ml tetrahydrofuran (Merck) and 5.3990 g of the solid supporting material was then added to this solution and stirred. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a Rotavapor. The prepared material was packed into a spiral glass column (3.2 mm ID $\times$ 2.1 m). The column was conditioned at 80°C and a fast carrier gas 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 of 0.3 μl was selected. The retention times of the probes were measured by using chromatopac CR6A (Shimadzu). Methane was synthesised the laboratory by the reaction of sodium acetate with sodium hydroxide.

To ensure that PIBORNMA did not decompose on the column during our experiments, when it was heated to 200°C, we remeasured retention volumes of probes.

4. Results and discussion

The specific retention volumes, V_g^0, of 13 probes were obtained by using one loading of PIBORNMA and at a series of temperatures. Probes of differing chemical nature and polarity (*n*-alkanes, *n*-acetates, *n*-ketones, aromatics, cyclic ethers and alcohols) were selected for this study. The V_g^0 values of these probes were calculated according to Eq. (1). The retention volume was confirmed to be independent of solute sample size in all cases studied [17]. The specific retention volume data are essential in the determination of physicochemical or thermodynamic properties of a polymer by IGC. In order to obtain these data, it is necessary to know the amount of the polymer that has been coated onto the support, gas flow rate, column pressures and temperature. The amount of injected sample also affects the retention volume [10]. The specific retention volumes, V_g^0, are given in Table 1. As can be seen from the table, the

Table 1
Changes in specific retention volumes as a function of temperature ($cm^3\,g^{-1}$ polymer)

T (K)	Meth.	Acet.	Met.Act.	Et.Act.	EMK	Benz.	THF	*o*-Xyl.	*n*-Oct.	*n*-Non.	*n*-Dec.	*n*-Undec.	*n*-Dodec.
323	23.43	36.50	54.29	78.12	64.76	82.20	38.52	149.50	19.05	27.16	38.88	127.93	231.24
333	16.43	22.67	41.01	48.95	48.84	62.53	30.53	114.42	9.78	18.16	28.15	83.28	159.14
343	10.54	15.39	21.90	30.00	27.12	49.26	24.03	70.29	6.26	10.84	21.16	53.05	89.05
353	7.93	11.13	14.77	22.35	21.15	41.92	18.05	42.59	5.84	8.83	14.22	27.11	60.61
363	6.24	8.62	10.79	14.62	14.23	29.24	14.29	36.47	4.74	6.76	9.44	17.87	31.57
373	5.20	7.25	7.91	10.61	10.95	16.16	8.42	20.85	4.21	5.14	7.38	10.67	19.53
378	4.58	5.68	6.20	8.11	8.00	12.28	7.56	16.63	4.03	4.63	4.85	6.88	11.15
383	4.68	5.80	6.59	8.35	8.27	12.47	7.62	17.02	4.58	4.73	5.96	7.86	12.08
388	4.55	5.40	5.99	7.48	7.72	10.66	5.72	16.61	4.58	4.70	5.53	7.22	10.36
393	4.43	5.13	5.64	6.19	6.72	8.38	5.39	14.07	4.56	4.56	5.28	6.59	8.86
403	4.18	4.63	4.97	5.77	5.87	6.50	4.45	11.29	4.35	4.42	4.61	5.48	7.06
413	4.04	4.34	4.48	4.91	5.10	5.85	4.20	8.96	4.13	4.34	4.41	4.91	5.86
423	3.86	4.07	1.23	4.52	4.64	5.36	3.55	7.72	3.90	4.11	4.15	4.52	5.22
433	3.71	3.87	3.99	4.23	1.27	4.91	3.54	6.73	3.71	3.87	3.99	4.33	4.93
443	3.63	3.80	3.83	4.07	4.10	4.56	3.44	6.56	3.70	3.85	4.02	4.32	4.74
453	3.49	3.64	3.67	3.87	3.91	4.21	3.42	7.83	3.66	4.10	3.96	4.23	4.58
463	3.48	3.54	3.62	3.75	3.82	3.97	3.35	6.12	3.62	3.93	3.90	3.93	4.54
473	3.38	3.48	3.48	3.62	3.71	3.72	3.19	6.08	3.48	3.75	3.71	3.74	4.45

Meth, methanol; Acet., acetone; Met.Act., methyl acetate; Et.Act., ethyl acetate; EMK, ethyl methyl ketone; Benz., benzene; THF, tetrahydrofuran; *o*-Xyl., *o*-xylene; *n*-Oct., *n*-octane; *n*-Non., *n*-nonane; *n*-Dec., *n*-decane; *n*-Undec., *n*-*undecane;* *n*-Dodec., *n*-dodecane.

Table 2
PIBORNMA–solute interaction coefficients χ_{12}^{∞} and weight fraction activity coefficients Ω_1^{∞} of alkanes, acetates, ketones, aromatics, THF and methanol at various temperatures

Probe	T (K)	Ω_1^{∞}						χ_{12}^{∞}					
		423	433	443	453	463	473	423	433	443	453	463	473
Methanol		14.49	12.22	10.25	8.79	7.41	6.51	1.250	1.039	0.819	0.611	0.387	0.195
THF		12.24	10.38	9.12	7.93	6.94	6.39	0.984	0.774	0.601	0.413	0.228	0.088
Acetone		9.88	8.71	7.59	6.86	6.12	5.51	0.757	0.583	0.398	0.246	0.074	− 0.087
EMK		12.42	11.16	9.72	8.69	7.62	6.80	1.054	0.907	0.726	0.573	0.391	0.223
Met.Act.		7.61	6.84	6.15	5.56	4.94	4.52	0.474	0.318	0.166	0.012	− 0.162	− 0.314
Et.Act.		9.77	8.65	7.60	6.84	6.06	5.49	0.785	0.620	0.446	0.293	0.116	− 0.035
Benzene		13.34	12.01	10.67	9.55	8.46	7.62	1.154	1.014	0.860	0.711	0.550	0.404
o-Xylene		24.93	22.50	18.54	13.14	12.50	10.99	1.885	1.762	1.546	1.226	1.150	0.941
n-Octane		29.46	24.77	20.28	16.95	14.33	12.60	1.977	1.770	1.536	1.317	1.107	0.934
n-Nonane		46.28	38.39	30.75	23.29	19.83	17.16	2.489	2.276	2.028	1.770	1.526	1.345
n-Decane		76.80	60.31	46.62	36.97	29.91	25.36	3.035	2.776	2.498	2.240	2.003	1.807
n-Undec.		117.65	90.71	68.58	53.95	45.27	37.49	3.490	3.216	2.920	2.662	2.465	2.252
n-Dodec.		172.22	130.45	100.11	77.29	59.40	47.15	3.889	3.601	3.325	3.052	2.773	2.524

specific retention volumes of probes on PIBORNMA are temperature dependent and decrease with increase of temperature. According to GC and DSC analyses the glass transition temperature (T_g) of PIBORNMA has been found to be 105°C [24].

PIBORNMA–solvent interaction parameters, such as the Flory-Huggins interaction parameter χ_{12}^{∞} at infinite dilution of the probe were calculated according to Eq. (3) for six different temperatures between 423 and 473K. Generally, χ_{12}^{∞} showed considerable dependence on the number of carbon atoms and temperature for alkanes, ketones, aromatics and acetates (Table 2). A consequence from theoretical considerations is that χ_{12}^{∞} has to be larger than 0.5 for the polymer–non-solvent systems and smaller than 0.5 for the polymer–solvent systems [25]. The values of χ_{12}^{∞} found in this experiment are high for alkanes, methanol and aromatics as usual for PlBORNMA–non-solvent systems, but are low for acetates, THF and ketones as usual for PIBORNMA–solvent systems. Similar results were obtained for the weight fraction activity coefficients (Ω_1^{∞}), as listed in Table 2.

We calculated the partial molar free energy of mixing (ΔG_1^{∞}) and partial molar free energies of sorption (ΔG_1^{s}) of probes according to Eqs. (9) and (10), respectively, and the results are listed in Table 3.

The Ω_1^{∞} data in Table 2 indicate that alkanes, methanol and aromatics are bad solvents but acetates, THF and ketones are moderate solvents for PIBORNMA. The following rules have been formulated by Guillet [26].

$\Omega_1^{\infty} < 5$: good solvents
$5 < \Omega_1^{\infty} < 10$: moderate solvents
$\Omega_1^{\infty} > 10$: bad solvents

ΔH_1^{∞} values of probes at infinite dilution were calculated using Eq. (8). For this reason, Ω_1^{∞} values were plotted against $1/T$ (K^{-1}) (Fig. 1).

ΔH_a and ΔH_1^{s} values of PIBORNMA–probe systems were calculated by plotting $\ln V_g^0$ against $1/T$ (K^{-1}) using

Table 3
Partial molar free energies of mixing ΔG_1^{∞} (kcal mol^{-1}) and partial molar free energies ΔG_1^{s} of sorption (kcal mol^{-1}) by using PIBORNMA as the stationary phase and alkanes, acetates, ketones, aromatics, THF and methanol as mobile phase

Probe	T (K)	ΔG_1^{∞}						ΔG_1^{s}					
		423	433	443	453	463	473	393	403	413	423	433	443
Methanol		2.25	2.15	2.05	1.97	1.84	1.76	3.95	4.10	4.23	4.37	4.51	4.63
THF		2.11	2.01	1.95	1.86	1.78	1.74	3.11	3.34	3.47	3.69	3.78	3.90
Acetone		1.93	1.86	1.78	1.73	1.67	1.61	3.37	3.54	3.68	3.83	3.96	4.07
EMK		2.12	2.08	2.00	1.95	1.87	1.80	3.00	3.18	3.37	3.54	3.69	3.81
Met.Act.		1.71	1.65	1.60	1.54	1.47	1.42	3.11	3.29	3.46	3.59	3.72	3.85
Et.Act.		1.92	1.86	1.79	1.73	1.66	1.60	2.90	3.03	3.24	3.39	3.52	3.64
Benzene		2.18	2.14	2.08	2.03	1.97	1.91	2.76	3.03	3.20	3.35	3.50	3.65
o-Xylene		2.70	2.68	2.57	2.37	2.27	2.25	2.12	2.35	2.59	2.78	2.97	3.06
n-Octane		2.84	2.76	2.65	2.55	2.45	2.38	2.94	3.05	3.17	3.29	3.42	3.50
n-Nonane		3.22	3.14	3.02	2.84	2.75	2.67	2.85	2.94	3.03	3.15	3.28	3.36
n-Decane		3.65	3.53	3.38	3.25	3.13	3.04	2.65	2.83	2.94	3.06	3.16	3.23
n-Undec.		4.01	3.88	3.72	3.59	3.51	3.41	2.41	2.61	2.77	2.91	3.01	3.08
n-Dodec.		4.33	4.19	4.06	3.91	3.76	3.62	2.11	2.34	2.55	2.71	2.83	2.93

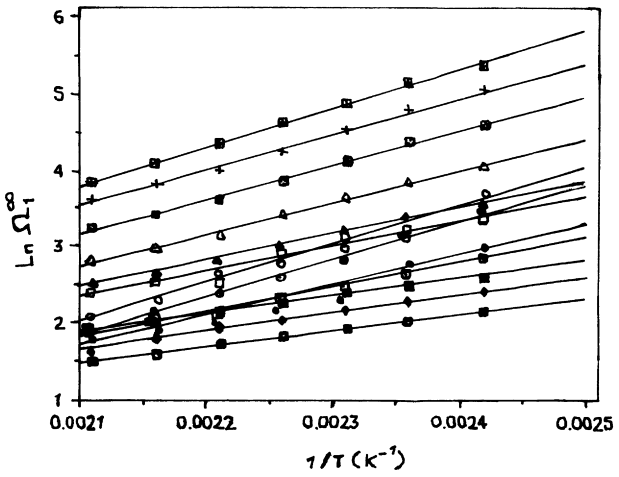
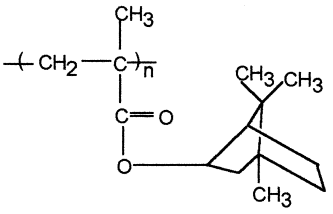


Fig. 1. Variation of $\ln \Omega_1^{\infty}$ against $1/T$ (K^{-1}) using 10% PIBORNMA: ⊡, methanol; ♦, acetone; ■, ethyl methyl ketone; ⊞, methyl acetate; ◇, ethyl acetate; ○, tetrahydrofuran; ⊙, benzene; □, *o*-xylene; ▲, *n*-octane; △, *n*-nonane; ⊠ *n*-decane; ＋, *n*-undecane; ⊞, *n*-dodecane.

Eqs. (12) and (6), respectively. Table 4 shows the experimentally obtained sorption heats (ΔH_1^s), molar heats of mixing (ΔH_1^{∞}) and adsorption heats (ΔH_a) in temperature ranges 383–403 K, 413–473 K and 323–373 K, respectively. Since the chemical nature and number of carbon atoms of each probe are different from each other, the heat of sorption becomes more exothermic as more CH_2 groups are added to the four families of probes. The attraction forces between PIBORNMA and acetates and ketones are actually a combination of two types: dispersive forces between the CH_2 groups of the acetates, ketones and the methyl group of PIBORNMA, and the interaction of the C=O groups of the acetates and ketones with the C=O groups of PIBORNMA via dipole–dipole interactions. We calculated the contribution of the C=O groups of the acetates and ketones to the sorption functions by subtracting the contribution of the alkane and aromatic sorption functions (ΔG_1^s) from that of the acetates and ketones (Table 5). The sorption functions of ΔH_1^s and ΔH_1^s) showed a linear relationship with the number of carbons in the four series. Similarly, 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 dependent on the number of carbons in the series and on temperature.

As seen from Table 4 the ΔH_1^s value of methanol is the smallest. The reason for this small value is the exertion of the steric effect by the branched isobornyl group in the structure of PIBORNMA



partially blocking the formation of a hydrogen bond between the C=O group of the polymer and the –OH group of the alcohol. In linear chain hydrocarbons, the higher the chain length the bigger the sorption energy values. The ΔH_1^s values of *n*-C_8–*n*C_{12} changed from 1.31 to 4.41 kcal mol^{-1}. Similarly these values showed an increasing trend in acetates, ketones and aromatics with increasing molecular weight.

The ΔH_1^{∞} values of probes found from the slope of straight lines in Fig. 1 are given in Table 4. ΔH_v values of probes were found according to Eq. (13) and are given in Table 4. ΔH_1^{∞} values of *n*-hydrocarbons changed from 6.78 to 20.06 kcal mol^{-1} as seen from Table 4. ΔH_1^{∞} values for methanol and *o*-xylene were found to be 6.45 kcal mol^{-1} while the values for methyl acetate, ethyl acetate, acetone and THF varied between 4.14 and 4.71 kcal mol^{-1}. Based upon these results the probes having ΔH_1^{∞} values in the range 4.14–4.71 kcal mol^{-1} were accepted as solvent–polymer sytems and the others were taken as non-solvent–polymer systems.

Baranyi and Guillet [16] determined that ΔH_1^{∞} values for aromatic solvents changed from − 0.01 to 0.3 cal mol^{-1} in PS and from 0.3 to 1.1 kcal mol^{-1} in PMA. These values for the same polymers were reported to change from 0.6 to 2.5 and from 2.5 to 4.1 kcal mol^{-1} in *n*-hydrocarbons. According to these results the probes having small ΔH_1^{∞} values were suitable for solvent–polymer systems and those with large ΔH_1^{∞} values were suitable for nonsolvent–polymer systems [16].

Table 4
Partial molar heats of sorption ΔH_1^s (kcal mol^{-1}) (383–403 K) and molar heats of mixing ΔH_1^{∞} (413–473 K), and adsorption heats ΔH_a (kcal mol^{-1}) (323–373 K), ΔH_v [a] (kcal mol^{-1}), ΔH_v [b] (kcal mol^{-1}) of alkanes, ketones, acetates, aromatics, THF and methanol on PIBORNMA

	Meth.	THF	Acet.	EMK	Met.Act.	Et.Act.	Benz.	*o*-Xyl.	*n*-Oct.	*n*-Non.	*n*-Dec.	*n*-Undec.	*n*-Dodec.
ΔH_1^s	− 1.41	− 3.12	− 2.14	− 3.57	− 2.69	− 3.15	− 4.04	− 5.60	− 1.31	− 1.60	− 1.90	− 2.97	− 4.41
ΔH_a	− 3.44	− 6.12	− 4.36	− 6.07	− 5.35	− 5.81	− 6.28	− 6.69	− 2.38	− 4.63	− 5.57	− 7.04	− 8.40
ΔH_1^{∞}	6.45	4.71	4.57	4.62	4.14	4.54	4.45	6.45	6.82	8.07	8.88	9.19	10.06
ΔH_v [a]	7.86	7.83	6.71	8.19	6.83	7.69	8.49	12.06	8.42	9.38	10.78	12.15	14.46
ΔH_v [b]	8.43	7.07	6.96	7.46	7.20	7.70	7.35	8.80	8.23	8.82	9.39	9.92	10.43

[a]Calculated according to Eq. (13).
[b]From Ref. [19].

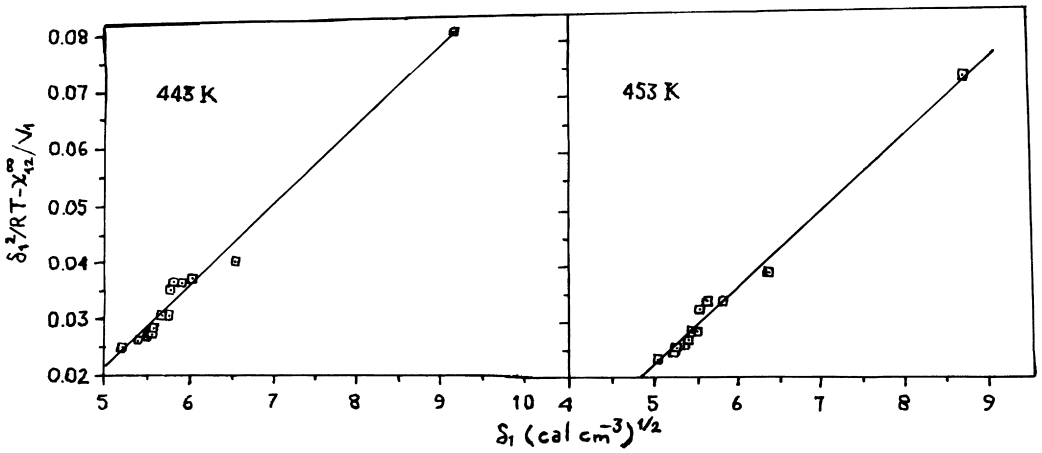


Fig. 2. Variation of δ_1 (cal cm^{-3})$^{1/2}$ against $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$.

Using the solubility parameter δ_1, with probes at the same temperature, values of δ_2 for PIBORNMA were obtained from the slopes and intercepts of plots of $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ against δ_1 (Fig. 2). The values are shown in Table 6. It is seen that solubility parameters obtained from the slopes and intercepts of the plots are in good agreement with each other. In comparing the δ_2 values of PIBORNMA at different temperatures, it is seen that solubility parameters decrease with increasing temperature. According to swelling coefficient (Q) method [27] the solubility parameter δ_2 of PIBORNMA has been calculated as 8.30 (cal cm^{-3})$^{1/2}$ at 25°C [24]. DiPaola-Baranyi and Guillet have determined the solubility parameters of polystyrene and poly(methyl acrylate) to be 7.6 and 8.7 (cal cm^{-3})$^{1/2}$ using Eqs. (14) and (15) at 193 and 100°C, respectively [16].

Table 5
Alkanes, ketones, acetates and aromatics group contributions to ΔH_1^s (kcal mol^{-1}) and ΔG_1^s (kcal mol^{-1})

Group	ΔH_1^s	ΔG_1^s
Alkanes	− 0.78	− 0.16
Ketones	− 1.43	− 0.30
Acetates	− 0.46	− 0.20
Aromatics	− 1.56	− 0.62

Table 6
Variation of solubility parameter δ_2 of PIBORNMA

T (K)	Slope	Intercept	δ_2 (cal cm^{-3})$^{1/2}$ from Eq. (14)		r
			From slope	From intercept	
443	0.0144	− 0.0508	6.34	6.69	0.99
453	0.0138	− 0.0471	6.21	6.51	0.99

The solubility parameter δ_2 of PIBORNMA determined from the χ_{12}^{∞} data in Table 6 at 443 K was 6.34 (cal cm^{-3})$^{1/2}$ (from the slope) and 6.69 (cal cm^{-3})$^{1/2}$ (from the intercept). These results indicate that δ_2 values calculated from the χ_{12}^{∞} data are in better compliance with the solubility parameter determined for PIBORNMA at 25°C.

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