Thermodynamic Interactions and Characterization of Poly (Acetyl Benzofuran Methylmethacrylate) and Poly(Acetyl Benzofuran Methylmethacrylate-co-Acrylonitrile) by Invers Gas Chromatography

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Summary: In this study, the thermodynamic and physical properties of poly(acetyl benzofuran methylmethacrylate) [poly(ABM)], poly(acetyl benzofuran methylmethacrylate%41-co-acrylonitrile) [poly(ABM%41-co-AN)] and poly(acetyl benzofuran methylmethacrylate%71-co-acrylonitrile) [poly(ABM%71-co-AN)] were researched by using inverse gas chromatography. Two groups of alcohols and alkanes with different chemical natures and polarities were used to determine certain properties of [poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN)]-solute systems. The specific retention volume, V_g^0, glass transition temperature, Tg; adsorption enthalpy, ΔHa; the sorption enthalpy, ΔH_1^S; sorption free energy, ΔG_1^S; sorption entropy, ΔS_1^S; the weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞, partial molar enthalpy of solute probes at infinite dilution, ΔH_1^∞; and Flory-Huggins interaction parameters, χ_{12}^∞; between polymer and solvents were determined in the temperature range of 493-343 K for poly(ABM) and 473-343 K for poly(ABM%41-coAN)-poly(ABM%71-coAN). Also, the solubility parameters of poly(ABM), poly(ABM%41-coAN) and poly(ABM%71-coAN) at infinite dilution were found out by plotting the graph of $[\delta_1^2 - (\Delta G_1^\infty/V_1)]$ versus solubility parameters, δ_1, of the probes.

Keywords: Poly(acetyl benzofuran methylmethacrylate) [poly(ABM)], poly(acetyl benzofuran methylmethacrylate-co-acrylonitrile) [poly(ABM-co-AN)], inverse gas chromatography, thermodynamic and physical properties.

Introduction

Inverse gas chromatography (IGC) is a useful method for studying certain thermodynamic and physical properties of polymer–solute systems. Thus, IGC has been used extensively to study the structures of polymers, the interactions of various liquids and gases with polymeric materials and polymer–polymer miscibility [1-5]. Furthermore, IGC is a reliable method for characterizing amorphous and semi-crystalline polymers. The IGC method is simple, fast, and economical and provides valuable thermodynamic data for characterizing polymeric substances.

IGC was developed by Smidsord and Guillet [6] and has been applied to many polymeric systems. In addition, IGC has been used to provide information regarding polymer-solvent and polymer-polymer systems, including 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 information on the physicochemical properties, structure and chemical interactions of macromolecules [7-13].

Dipaola-Baranyi and Guillet [14] have shown that IGC can serve as a simple method for estimating the solubility parameters of polymers when using a polymer as the stationary phase.

Data Reduction

Probe specific retention volumes, V_g^0, were calculated from the following standard chromatographic relation [15]:

$$V_g^0 = (F \times 273.2 \times t_r) / WxT \times 3/2 \times [\,[(P_i/P_0)^2 - 1] / [(P_i/P_0)^3 - 1]] \quad (1)$$

where t_r is the retention time of the probe, F is the flow rate of the carrier gas measured at room temperature, W is the mass of the polymeric stationary phase, T is the column temperature, and P_i and P_0 are the inlet and outlet pressures, respectively.

For the proble, the molar heat (enthalpy) (ΔH_1^S) and the molar free energy (ΔG_1^S) of sorption adsorbed by the polymer are given by the following equation:

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

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

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

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

where V_g^0 is the specific retention volume of the probe, T is the column temperature (K), M_1 is the molecular weight of the probe and R is the gas constant. The adsorption enthalpy of the probes adsorbed by the polymer, ΔH_a, was calculated using the following equation [16]:

$$\partial V_g^0/\partial (1/T) = -\Delta H_a/R \quad (5)$$

The partial molar free energy of mixing ΔG_1^∞ (cal/mol) and partial molar enthalpy ΔH_1^∞ (cal/mol) at infinite dilution were calculated according to the following equation [10]:

$$\Delta H_1^\infty = R(\delta \ln(a_1/w_1)^\infty / \delta(1/T)) \quad (6)$$

$$\Delta G_1^\infty = R \ln(a_1/w_1)^\infty \quad (7)$$

The weight fraction activity coefficient, Ω_1^∞, of the solute probe at infinite dilution was calculated according to the following equation [5]:

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

The [(PPBPDMA) and (PPCPDMA)]-solute interaction parameters of the different solutes, χ_{12}^∞, at infinite dilution were defined using the following equation:

$$\chi_{12}^\infty = \ln[(273.2xRxV_2)/(V_g^0 xV_1 xP_1^0)] - 1 - P_1^0/RT(B_{11}-V_1) \quad (9)$$

where R is the gas constant, V_2 is the specific volume of the polymer, V_1 is the molar volume of the solute, P_1^0 is the vapor pressure, and B_{11} is the second virial coefficient of the solute in the gaseous state. In addition, V_1, P_1^0 and B_{11} were calculated at the column temperature.

Second virial coefficients, B_{11}, were computed using the following equation/[14]:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (10)$$

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 solubility parameters of the polymers, δ_2, were determined using the following relation:

$$\delta_1^2 - \Delta G_1^\infty/V_1 = 2\delta_1\delta_2 - \delta_2^2 \quad (11)$$

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

If the left-hand side of this equation is plotted against δ_1, then a straight line with a slope of $(2\delta_1\delta_2)$ and an intercept of $-\delta_2^2$ are obtained. The solubility parameters of the polymer, δ_2, can be calculated from the slope and intercept of the straight line [14].

Experimental

Materials

The chromatographic grade molecular probes used in this study, including ethyl alcohol (C_2), 1-propyl alcohol (C_3), 1-butyl alcohol (C_4), n-hexane (C_6), n-heptane (C_7), and n-octane (C_8), were obtained from Merck Chemical Co. Methane was used as a non-interacting marker to correct the dead volume in the column. The poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN) were supplied from the Chemistry Department of Fırat University, Elazığ, Turkey, and the Chromosorb W (80-100 mesh) was obtained from Sigma Chemical Co.

Instrumentation and Procedure

The polymer was accounted for 10% of the charging material. The glass transition temperature, T_g, was approximately 423K for poly(ABM), 393K for poly(ABM%41-co-AN) and poly(ABM%71-co-AN).

Schimadzu GC-2010 gas chromatography was made convenient for colon analysis. A Schimadzu GC-2010 model gas chromatograph equipped with a dual flame ionization detector (FID) was used in this analysis. Dry helium gas (research grade) was used as a carrier gas. The pressures (mm-Hg) read at the inlet and outlet of the column from software of GC 2010**,** were used to compute corrected retention volumes by standard procedure. A flow rate of about 30 ml min^{-1} was used throughout our experiment. The column consisted of a 1 m steel pipe with 3.2 mm ID. The steel column was washed with distilled water, benzene and acetone, and then was dried. A column packing material was prepared by coating 80-100 mesh size Chromosorb W with poly(ABM), poly(ABM%41-co-AN) and

poly(ABM%71-co-AN). The prepared material was packed into the steel column (3.2 mm IDx1 m) with colon filling apparatus. The column was conditioned at 220 ^{0}C with a fast carrier gas flow rate for 24h prior to use. Probes were injected into the column with 1 µl Hamilton syringes. Three consecutive injections were performed for each probe, each set of measurements. An injection volume of 0.3 µl was selected and the retention times of the probes were measured using software of GC-2010 (Schimadzu).

Results and Discussion

The V_g^0 of probes were obtained using one polymer loading and at a series of temperatures. The V_g^0 values of these probes were calculated according to the Eq. (1). The retention volume was confirmed to be independent of solute sample size in all of studied cases [17]. Specific retention volume data are essential in the determining the physicochemical or thermodynamic properties of a polymer by IGC. To obtain these data, the amount of the polymer that has been coated onto the support, the gas flow rate, the column pressures and the temperature must be known. The V_g^0values are given in Table-1 (a), (b) and (c). The specific retention volumes of probes on poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN) varied with temperature for each of the probe and generally decreased with increasing temperature. The T_g of poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN) are given in Fig. 1 (a), (b) and (c). As shown in Fig. 1 (a), the T_g of poly(ABM) was approximately 423 K. As shown in Fig. 1 (b) and (c), the T_g of poly(ABM%41-co-AN) and poly(ABM%71-co-AN) were approximately 393 K. In the study carried out with DSC, the Tg of poly(ABM) was approximately 423 K, poly (ABM%71-ko-AN) and (ABM0.41-ko-AN) were approximately 398 K[18]. Similar results were obtained from the study performed with IGC.

Table-1: (a) The variation of logarithm of specific retention volumes, Vg^0 (ml/g), of alcohols and alkanes with temperature using poly(ABM) as stationary phase.

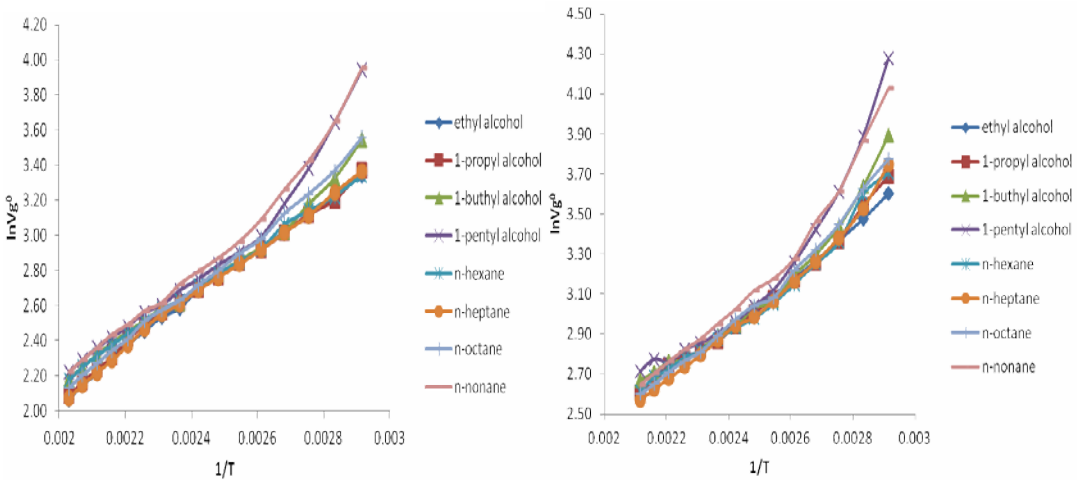
Temperature (1/T) 10^{-3}	Ethyl Alcohol	1-Propyl Alcohol	1-Buthyl Alcohol	1-Pentyl Alcohol	n-Hexane	n-Heptane	n-Octane	n-Nonane
2.028	7.88	8.081	8.83	9.185	8.791	7.924	8.397	9.185
2.07	8.55	8.682	9.483	9.862	9.483	8.55	9.061	9.862
2.114	9.131	9.354	10.16	10.563	10.115	9.175	9.668	10.563
2.159	9.935	10.03	10.881	11.212	10.739	9.84	10.408	11.402
2.207	10.772	11.123	11.574	11.925	11.474	10.722	11.123	12.075
2.257	11.609	12.035	12.354	12.94	12.248	11.768	12.301	13.047
2.309	12.602	12.943	13.227	13.454	13.227	12.829	13.113	13.681
2.364	13.268	13.63	13.69	14.655	13.811	13.569	13.871	15.198
2.421	14.763	14.763	15.02	15.661	15.02	14.763	15.148	16.368
2.481	15.873	15.873	16.147	16.968	16.147	15.805	16.42	17.652
2.544	17.14	17.14	17.432	18.234	17.286	17.067	18.088	19.401
2.611	18.75	18.517	18.75	19.917	18.594	18.517	19.684	22.018
2.681	20.454	20.371	20.537	24.029	21.368	20.454	22.699	26.108
2.755	22.475	22.653	24.074	29.404	23.097	22.475	25.407	30.826
2.833	25.126	24.559	27.865	38.256	25.126	25.693	28.999	38.445
2.915	28.262	29.072	34.846	51.56	28.262	28.971	35.049	52.27

Table-1: (b) The variation of logarithm of specific retention volumes, Vg^0 (ml/g), of alcohols and alkanes with temperature using poly(ABM%71-co-AN) as stationary phase.

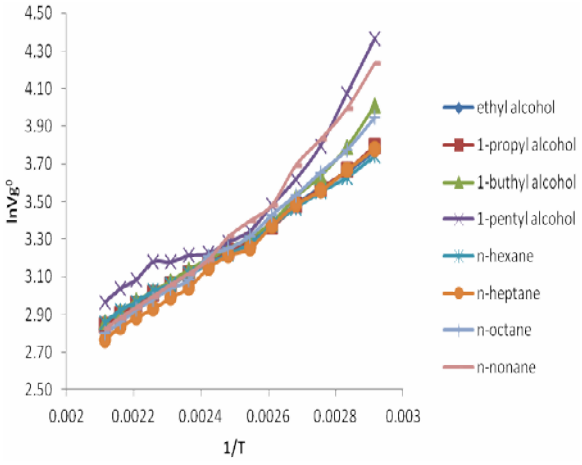
Temperature (1/T) 10^{-3}	Ethyl Alcohol	1-Propyl Alcohol	1-Buthyl Alcohol	1-Pentyl Alcohol	n-Hexane	n-Heptane	n-Octane	n-Nonane
2.114	13.383	13.563	14.39	15.038	13.67	13.023	13.455	14.066
2.159	14.641	14.299	14.983	16.01	14.641	13.766	14.146	14.907
2.207	15.473	15.553	15.835	15.715	15.271	14.546	15.03	15.835
2.257	16.342	16.171	15.872	16.813	16.171	15.401	15.872	16.813
2.309	16.514	16.649	16.829	17.324	16.694	16.334	16.604	17.729
2.364	17.96	17.529	17.96	18.199	17.672	17.624	18.007	19.109
2.421	18.874	18.823	18.976	19.282	18.772	18.874	19.537	20.558
2.481	20.531	20.204	20.585	20.857	19.659	19.768	20.912	22.546
2.544	22.042	21.752	21.519	22.624	21.228	21.403	21.81	23.962
2.611	23.984	23.798	24.357	25.973	23.363	23.674	24.979	26.532
2.681	26.192	25.859	27.059	30.657	25.925	26.059	27.725	31.924
2.755	28.997	28.782	31.073	37.016	28.782	29.383	31.359	37.087
2.833	32.28	34.52	37.995	48.807	36.528	33.979	37.455	47.726
2.915	36.707	40.036	49.109	72.249	40.786	42.45	43.532	62.094

Table-1: (c) The variation of logarithm of specific retention volumes, Vg^0 (ml/g), of alcohols and alkanes with temperature using poly(ABM%41-co-AN) as stationary phase.

Temperature (1/T) 10^{-3}	Ethyl Alcohol	1-Propyl Alcohol	1-Buthyl Alcohol	1-Pentyl Alcohol	n-Hexane	n-Heptane	n-Octane	n-Nonane
2.114	16.873	17.235	17.442	19.409	17.391	15.941	16.511	16.821
2.159	17.977	18.195	18.522	20.864	18.631	17.051	17.432	17.868
2.207	18.978	19.207	19.551	21.902	19.436	17.888	18.691	18.863
2.257	20.233	20.354	20.536	24.049	20.596	18.779	19.688	19.991
2.309	21.473	21.345	21.665	24.037	21.345	19.87	20.896	21.281
2.364	22.655	22.587	23.062	24.893	22.519	21.027	21.841	22.587
2.421	24.274	23.987	24.346	25.136	23.772	23.269	24.844	24.274
2.481	25.945	25.448	25.793	26.706	25.108	24.88	25.793	27.467
2.544	26.968	26.887	27.291	28.34	26.483	25.837	27.533	29.875
2.611	29.798	29.025	29.627	32.546	29.283	29.197	30.915	32.546
2.681	32.64	32.458	33.916	37.29	32.093	32.64	34.281	40.116
2.755	35.692	35.595	37.916	44.615	34.916	35.11	38.699	46.07
2.833	38.664	39.181	44.247	58.824	37.734	39.181	43.523	54.275
2.915	43.28	44.605	54.984	78.501	42.286	43.832	51.671	68.895



(a) (b)



(c)

Fig. 1: Variation of logarithm of specific retention volumes, Vg^0 (ml/g) of alcohols and alkanes with reciprocal of absolute column temperature and the glass transition temperature, Tg, for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN).

Table-2: (a) Partial molar enthalpy, ΔH_1^s (cal/mol), partial molar free energy of mixing, ΔG_1^s (cal/mol) and partial molar entropy ΔS_1^s (cal/mol) of poly(ABM) with alcohols and alkanes.

	ΔH1s (cal/mol)	ΔG1s (cal/mol)				ΔS1s (cal/mol)			
Probes/T(K)	**423-453**	**423**	**433**	**443**	**453**	**423**	**433**	**443**	**453**
Ethyl alcohol	**-2688.013**	**3026.388**	**3142.242**	**3287.057**	**3428.613**	**-13.509**	**-13.465**	**-13.488**	**-13.502**
1-propyl alcohol	**-2593.035**	**2780.355**	**2890.582**	**3021.364**	**3160.499**	**-12.703**	**-12.664**	**-12.674**	**-12.701**
1-buthyl alcohol	**-2171.791**	**2600.341**	**2691.416**	**2813.677**	**2935.895**	**-11.282**	**-11.231**	**-11.254**	**-11.275**
1-pentyl alcohol	**-2503.023**	**2397.419**	**2527.662**	**2620.325**	**2753.002**	**-11.585**	**-11.618**	**-11.565**	**-11.603**
n-hexane	**-2405.66**	**2466.291**	**2561.768**	**2688.619**	**2808.069**	**-11.518**	**-11.472**	**-11.500**	**-11.509**
n-heptane	**-3011.099**	**2354.398**	**2458.307**	**2591.067**	**2733.344**	**-12.684**	**-12.631**	**-12.646**	**-12.681**
n-octane	**-2756.763**	**2225.78**	**2326.749**	**2436.752**	**2582.368**	**-11.779**	**-11.740**	**-11.724**	**-11.786**
n-nonane	**-2812.201**	**2051.642**	**2190.617**	**2282.976**	**2404.198**	**-11.498**	**-11.554**	**-11.502**	**-11.515**

Table-2: (b) Partial molar enthalpy, ΔH_1^s (cal/mol), partial molar free energy of mixing, ΔG_1^s (cal/mol) and partial molar entropy ΔS_1^s (cal/mol) of poly(ABM%71-co-AN) with alcohols and alkanes.

	ΔH1s (cal/mol)	ΔG1s (cal/mol)						ΔS1s (cal/mol)					
Probes/T(K)	**393-443**	**393**	**403**	**413**	**423**	**433**	**443**	**393**	**403**	**413**	**423**	**433**	**443**
Ethyl alcohol	**-2181.527**	**2415.374**	**2533.699**	**2665.627**	**2771.891**	**2909.639**	**2986.052**	**-11.697**	**-11.700**	**-11.736**	**-11.710**	**-11.758**	**-11.665**
1-propyl alcohol	**-2117.744**	**2218.153**	**2333.711**	**2449.721**	**2568.899**	**2673.944**	**2761.34**	**-11.033**	**-11.046**	**-11.059**	**-11.080**	**-11.066**	**-11.014**
1-buthyl alcohol	**-2154.504**	**2062.746**	**2150.765**	**2270.924**	**2372.161**	**2484.202**	**2593.109**	**-10.731**	**-10.683**	**-10.715**	**-10.701**	**-10.713**	**-10.717**
1-pentyl alcohol	**-2085.157**	**1888.303**	**2001.471**	**2115.569**	**2215.379**	**2310.146**	**2389.853**	**-10.111**	**-10.141**	**-10.171**	**-10.167**	**-10.151**	**-10.102**
n-hexane	**-1893.849**	**1955.706**	**2066.957**	**2156.133**	**2259.094**	**2361.483**	**2444.038**	**-9.795**	**-9.828**	**-9.806**	**-9.818**	**-9.828**	**-9.792**
n-heptane	**-2258.225**	**1831.534**	**1941.772**	**2027.933**	**2134.629**	**2250.493**	**2354.24**	**-10.407**	**-10.422**	**-10.378**	**-10.385**	**-10.413**	**-10.412**
n-octane	**-2331.545**	**1714.517**	**1791.811**	**1892.087**	**2006.443**	**2123.667**	**2212.4**	**-10.295**	**-10.232**	**-10.227**	**-10.255**	**-10.289**	**-10.257**
n-nonane	**-2537.796**	**1550.591**	**1638.822**	**1755.238**	**1859.171**	**1967.614**	**2059.752**	**-10.403**	**-10.364**	**-10.395**	**-10.395**	**-10.405**	**-10.378**

Table-2: (c) Partial molar enthalpy, ΔH_1^s (cal/mol), partial molar free energy of mixing, ΔG_1^s (cal/mol) and partial molar entropy ΔS_1^s (cal/mol) of poly(ABM%41-co-AN) with alcohols and alkanes.

	ΔH1s (cal/mol)	ΔG1s (cal/mol)						ΔS1s (cal/mol)					
Probes/T(K)	**393-443**	**393**	**403**	**413**	**423**	**433**	**443**	**393**	**403**	**413**	**423**	**433**	**443**
Ethyl alcohol	**-2046.411**	**2257.868**	**2346.287**	**2459.139**	**2576.698**	**2683.716**	**2798.053**	**-10.952**	**-10.900**	**-10.909**	**-10.929**	**-10.924**	**-10.936**
1-propyl alcohol	**-1956.837**	**2052.638**	**2148.93**	**2250.773**	**2355.817**	**2460.17**	**2558.834**	**-10.202**	**-10.188**	**-10.188**	**-10.195**	**-10.201**	**-10.193**
1-buthyl alcohol	**-1974.859**	**1877.19**	**1970.161**	**2066.428**	**2162.003**	**2266.877**	**2366.339**	**-9.802**	**-9.789**	**-9.785**	**-9.780**	**-9.796**	**-9.800**
1-pentyl alcohol	**-1145.286**	**1712.397**	**1803.524**	**1897.996**	**1952.117**	**2028.373**	**2074.778**	**-7.271**	**-7.317**	**-7.369**	**-7.322**	**-7.329**	**-7.269**
n-hexane	**-1779.298**	**1782.987**	**1871.049**	**1962.348**	**2055.375**	**2150.031**	**2231.128**	**-9.064**	**-9.058**	**-9.060**	**-9.065**	**-9.075**	**-9.053**
n-heptane	**-2340.487**	**1684.511**	**1757.597**	**1856.145**	**1986.243**	**2081.892**	**2179.682**	**-10.242**	**-10.169**	**-10.161**	**-10.229**	**-10.213**	**-10.204**
n-octane	**-2407.647**	**1532.556**	**1623.828**	**1694.884**	**1844.202**	**1925.856**	**2022.75**	**-10.026**	**-10.004**	**-9.933**	**-10.052**	**-10.008**	**-10.001**
n-nonane	**-2823.129**	**1378.364**	**1480.73**	**1618.886**	**1718.626**	**1810.499**	**1907.356**	**-10.691**	**-10.680**	**-10.755**	**-10.737**	**-10.701**	**-10.678**

Table-3: Adsorption enthalpy, ΔHa (cal/mol) with alcohols and alkanes for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN) with alcohols and alkanes.

(a)

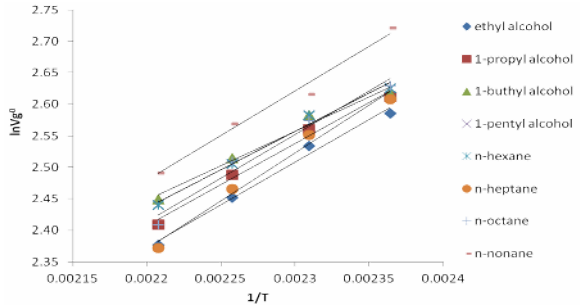
	ΔHa (cal/mol)
Probe / T (K)	
Ethyl Alcohol	**3173.217**
1-Propyl Alcohol	**3934.347**
1-Buthyl Alcohol	**2977.032**
1-Pentyl Alcohol	**395.19**
n-Hexane	**954.506**
n-Heptane	**1373.596**
n-Octane	**708.721**
n-Nonane	**-1158.337**

(b)

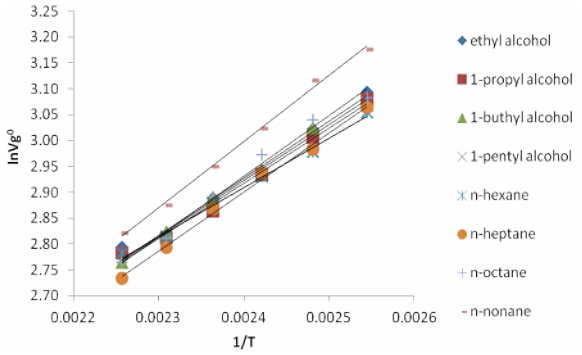
	ΔHa (cal/mol)
Probe / T (K)	
Ethyl Alcohol	**3009.154**
1-Propyl Alcohol	**2419.849**
1-Buthyl Alcohol	**386.756**
1-Pentyl Alcohol	**-3381.458**
n-Hexane	**-1427.341**
n-Heptane	**-616.182**
n-Octane	**-229.871**
n-Nonane	**-2981.31**

(c)

Probe / T (K)	ΔHa (cal/mol)
Ethyl Alcohol	**3566.694**
1-Propyl Alcohol	**3769.827**
1-Buthyl Alcohol	**1778.778**
1-Pentyl Alcohol	**-1882.955**
n-Hexane	**1293.18**
n-Heptane	**1250.663**
n-Octane	**648.854**
n-Nonane	**-1504.286**



(a)



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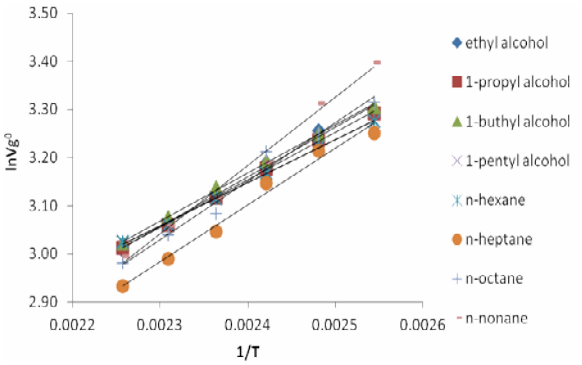
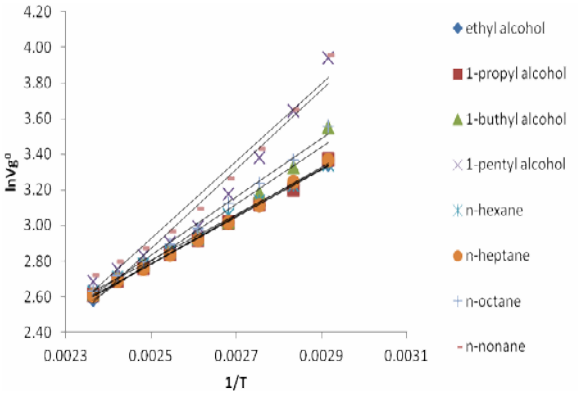


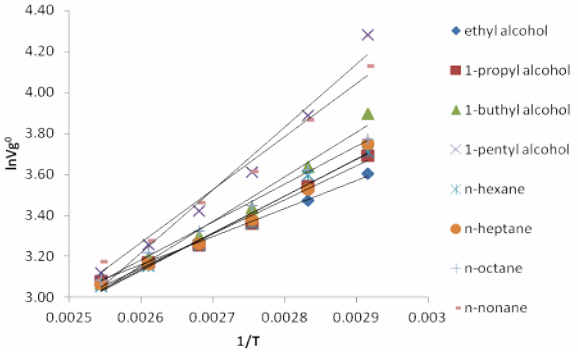
(c)

Fig. 2: Variation of logarithm of specific retention volumes, Vg^0 (ml/g) of alcohols and alkanes with reciprocal of absolute column temperature for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN) for ΔH_1^s (cal/mol).

ΔH_a and ΔH_1^S values of poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN)] -probe systems were calculated by plotting ln V_g^0 against $1/T(K^{-1})$ using Eqs.(5) and (2), respectively. Table-2 (a), (b) and (c) show the experimentally obtained sorption enthalpy, ΔH_1^S, in the temperature range of 423-453 K for poly(ABM) and 393-443 K for poly(ABM%41-coAN)-poly(ABM%71-co-AN). Table-3 (a), (b) and (c) shows experimentally obtained adsorption enthalpy ΔH_a in the temperature range of 343-423 K for poly(ABM) and 343-393 K for poly(ABM%41-coAN)-poly(ABM%71-co-AN), respectively. The ΔH_a values of the probes that were determined from the slopes of straight lines in Fig.3. When the ΔH_a values of polymers are evaluated in general, the interactions of probes under Tg with poly(ABM) and poly(ABM%41-co-AN) are poor but with poly(ABM%71-co-AN) are higher.



(a)



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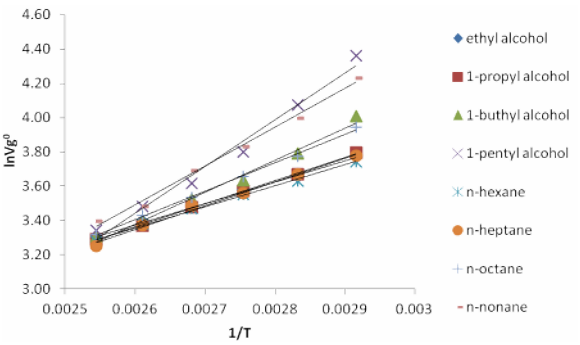


(c)

Fig. 3: Variation of logarithm of specific retention volumes, Vg^0 (ml/g) of alcohols and alkanes with reciprocal of absolute column temperature for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN), for ΔHa (cal/mol).

ΔG_1^S and ΔS_1^S values of [poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN)] -probe systems were calculated from Eqs.(3) and (4), respectively, and are given in Table-2 (a), (b) and (c). The ΔS_1^S values of probes were found from the slope of straight lines in Fig. 2. The ΔS_1^S and ΔH_1^S values were negative, and the ΔG_1^S values were positive. These values are expected values for polymer-nonsolvent systems [19].

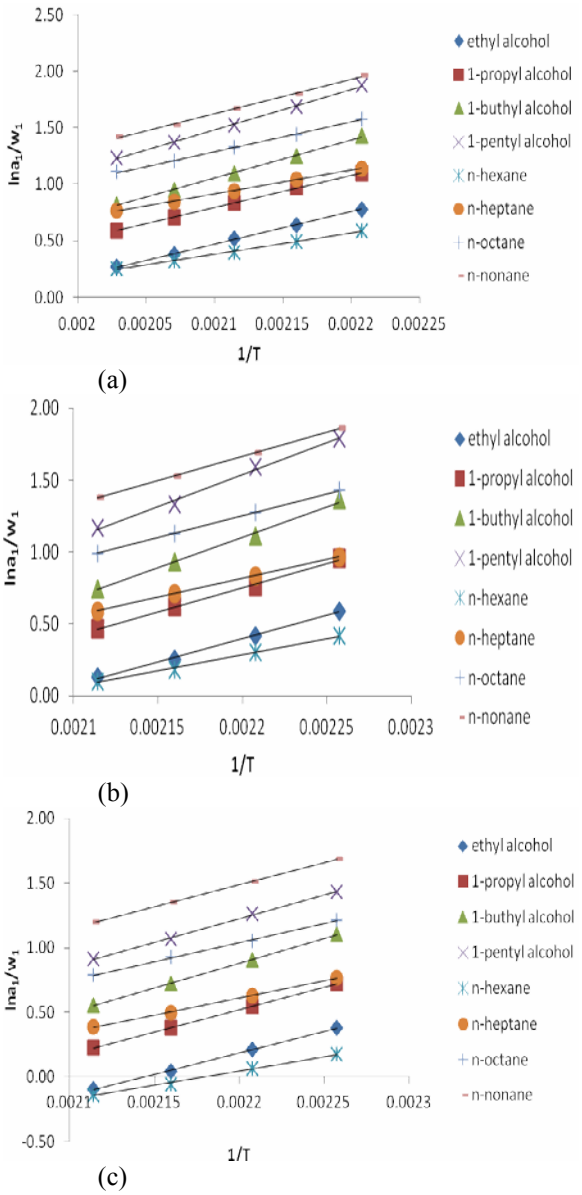
The partial molar heats of mixing at infinite solute dilution, $\Delta H_{1,}^{\infty}$ of the polymers-probe system were calculated by plotting $\ln(a_1/w_1)$ against $1/T(K^{-1})$ (Fig. 4.) using Eq (6). The $\Delta H_{1,}^{\infty}$ values were positive, and correspond with the expected values for polymer-nonsolvent systems(14).

The values of Ω_1^{∞} and χ_{12}^{∞} obtained using equations (8) and (9), respectively, and are presented in Tables 5-6.

Furthermore Ω_1^{∞} values greater than 5 have been considered to indicate poor polymer-solute systems, while lower values have been considered to indicate good solubility for such systems. The following rules have been formulated by Guillet [20].

$\Omega_1^{\infty} < 5$	good solvents
$5 < \Omega_1^{\infty} < 10$	moderat solvents
$\Omega_1^{\infty} > 10$	poor solvents

Here, χ_{12}^{∞} values greater than 0.5 represent unfavorable polymer-solvent interactions, while values lower than 0.5 indicate favorable interactions in dilute polymer solutions [21]. Based on these values (in Tables 5, 6) and according to the Ω_1^{∞} and χ_{12}^{∞}, all of the probes under T_g are poor solvent for polymers. When the probes are above the T_g according to their $\Omega_1^{\infty}$and χ_{12}^{∞} values, they can dissolve the polymers. The χ_{12}^{∞} and Ω_1^{∞} values did not depend on the number of carbons in the series. However, the χ_{12}^{∞} and Ω_1^{∞} values decreased in all of the series as the column temperature increased [22].



(a)

(b)

(c)

Fig. 4: The weight fraction activity coefficiency of solute probes at infinite dilution Ω_1^{∞} with reciprocal of absolute column temperature for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN) with alcohols and alkanes.

Table-4: Partial molar enthalpy of solute probes at infinite dilution, ΔH_1^{∞} (cal/mol) with alcohols and alkanes systems for **(a)** poly(ABM), (b) poly(ABM%71-co-AN) and (c) poly(ABM%41-co-AN) with alcohols and alkanes.

(a)

	ΔH1∞ (cal/mol)
Probe / T (K)	
Ethyl Alcohol	**5651.822**
1-Propyl Alcohol	**5643.874**
1-Buthyl Alcohol	**6734.34**
1-Pentyl Alcohol	**7077.097**
n-Hexane	**3755.231**
n-Heptane	**4151.24**
n-Octane	**5165.802**
n-Nonane	**6046.838**

(b)

	ΔH1∞ (cal/mol)
Probe / T (K)	
Ethyl Alcohol	**6436.886**
1-Propyl Alcohol	**6699.965**
1-Buthyl Alcohol	**8448.922**
1-Pentyl Alcohol	**8836.387**
n-Hexane	**4446.112**
n-Heptane	**5205.94**
n-Octane	**6042.665**
n-Nonane	**6700.958**

(c)

	ΔH1∞ (cal/mol)
Probe / T (K)	
Ethyl Alcohol	**6651.085**
1-Propyl Alcohol	**6946.353**
1-Buthyl Alcohol	**7627.894**
1-Pentyl Alcohol	**7268.446**
n-Hexane	**4404.384**
n-Heptane	**5288.797**
n-Octane	**5881.321**
n-Nonane	**6801.699**

Table-5: (a) Weight fraction activity coefficient Ω_1^{∞} of with alcohols and alkanes systems for poly (ABM).

	Ω_1^{∞}				
Probe / T (K)	**453**	**463**	**473**	**483**	**493**
Ethyl Alcohol	**2.179**	**1.896**	**1.673**	**1.463**	**1.312**
1-Propyl Alcohol	**2.983**	**2.651**	**2.302**	**2.031**	**1.803**
1-Buthyl Alcohol	**4.149**	**3.497**	**2.992**	**2.59**	**2.27**
1-Pentyl Alcohol	**6.501**	**5.419**	**4.572**	**3.939**	**3.438**
n-Hexane	**1.803**	**1.64**	**1.493**	**1.377**	**1.29**
n-Heptane	**3.123**	**2.84**	**2.565**	**2.337**	**2.157**
n-Octane	**4.825**	**4.216**	**3.75**	**3.336**	**3.028**
n-Nonane	**7.106**	**6.037**	**5.29**	**4.641**	**4.124**

Table-5: (b) Weight fraction activity coefficient Ω_1^{∞} of with alcohols and alkanes systems for poly(ABM%71-co-AN).

	Ω_1^{∞}			
Probes/T(K)	**443**	**453**	**463**	**473**
Ethyl alcohol	**1.809**	**1.517**	**1.287**	**1.142**
1-propyl alcohol	**2.593**	**2.134**	**1.858**	**1.588**
1-buthyl alcohol	**3.907**	**3.046**	**2.539**	**2.112**
1-pentyl alcohol	**5.595**	**4.933**	**3.796**	**3.209**
n-hexane	**1.515**	**1.355**	**1.203**	**1.106**
n-heptane	**2.63**	**2.302**	**2.031**	**1.807**
n-octane	**4.174**	**3.567**	**3.101**	**2.696**
n-nonane	**6.436**	**5.419**	**4.618**	**3.97**

Table-5: (c) Weight fraction activity coefficient Ω_1^{∞} of with alcohols and alkanes systems for poly(ABM%41-co-AN).

	Ω_1^{∞}			
Probes/T(K)	**443**	**453**	**463**	**473**
Ethyl alcohol	**1.49**	**1.237**	**1.048**	**0.906**
1-propyl alcohol	**2.06**	**1.728**	**1.46**	**1.249**
1-buthyl alcohol	**3.019**	**2.469**	**2.054**	**1.743**
1-pentyl alcohol	**4.17**	**3.539**	**2.912**	**2.486**
n-hexane	**1.19**	**1.065**	**0.946**	**0.87**
n-heptane	**2.157**	**1.871**	**1.64**	**1.476**
n-octane	**3.366**	**2.871**	**2.519**	**2.196**
n-nonane	**5.414**	**4.549**	**3.853**	**3.32**

Table-6: (a) Interaction parameters, χ_{12}^{∞}, of poly(ABM) with alcohols and alkanes systems.

	χ_{12}^{∞}				
Probes/T(K)	**453**	**463**	**473**	**483**	**493**
Ethyl alcohol	**-0.625**	**-0.758**	**-0.873**	**-0.994**	**-1.087**
1-propyl alcohol	**-0.313**	**-0.43**	**-0.567**	**-0.687**	**-0.798**
1-buthyl alcohol	**0.034**	**-0.14**	**-0.294**	**-0.434**	**-0.559**
1-pentyl alcohol	**0.486**	**0.301**	**0.128**	**-0.021**	**-0.157**
n-hexane	**-0.907**	**-1.001**	**-1.091**	**-1.17**	**-1.231**
n-heptane	**-0.352**	**-0.445**	**-0.546**	**-0.637**	**-0.715**
n-octane	**0.082**	**-0.052**	**-0.168**	**-0.284**	**-0.379**
n-nonane	**0.448**	**0.284**	**0.15**	**0.019**	**-0.099**

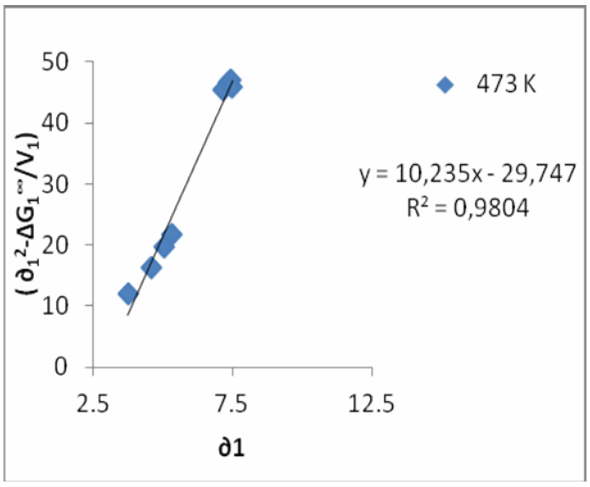
Table-6: (b) Interaction parameters, χ_{12}^{∞}, of poly(ABM%71-co-AN) with alcohols and alkanes systems.

	χ_{12}^{∞}			
Probes/T(K)	**443**	**453**	**463**	**473**
Ethyl alcohol	**-0.815**	**-0.988**	**-1.145**	**-1.255**
1-propyl alcohol	**-0.453**	**-0.648**	**-0.784**	**-0.939**
1-buthyl alcohol	**-0.029**	**-0.278**	**-0.46**	**-0.642**
1-pentyl alcohol	**0.404**	**0.21**	**-0.054**	**-0.224**
n-hexane	**-1.083**	**-1.193**	**-1.31**	**-1.393**
n-heptane	**-0.525**	**-0.657**	**-0.781**	**-0.896**
n-octane	**-0.061**	**-0.218**	**-0.358**	**-0.499**
n-nonane	**0.352**	**0.177**	**0.016**	**-0.136**

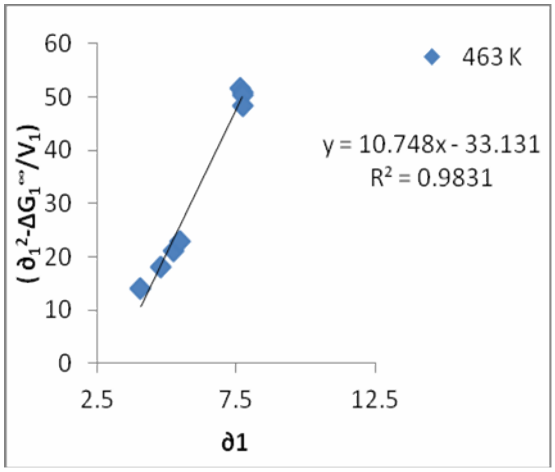
Table-6: (c) Interaction parameters, χ_{12}^{∞}, of poly(ABM%41-co-AN) with alcohols and alkanes systems.

	χ_{12}^{∞}			
Probes/T(K)	**443**	**453**	**463**	**473**
Ethyl alcohol	**-1.029**	**-1.192**	**-1.351**	**-1.487**
1-propyl alcohol	**-0.683**	**-0.859**	**-1.025**	**-1.178**
1-buthyl alcohol	**-0.286**	**-0.489**	**-0.672**	**-0.834**
1-pentyl alcohol	**0.046**	**-0.121**	**-0.319**	**-0.479**
n-hexane	**-1.325**	**-1.434**	**-1.551**	**-1.633**
n-heptane	**-0.723**	**-0.864**	**-0.995**	**-1.098**
n-octane	**-0.276**	**-0.436**	**-0.567**	**-0.703**
n-nonane	**0.179**	**0.002**	**-0.165**	**-0.315**

The solubility parameter of a polymer, δ_2, can be determined from either the slope or the intercept of a straight line obtained by plotting the left-hand side of equation (11)/9-15/ against δ_1. These values are shown in Table-7. The solubility parameter of poly(ABM) was evaluated from either the slope or intercepts shown in Fig. 5 (a) and (b) 5.117 $(cal/cm^3)^{0.5}$ or 5.454 $(cal/cm^3)^{0.5}$ at 473 K, respectively. The solubility parameter of poly(ABM%71-co-AN) was evaluated from either slope or intercepts of Fig. 5 (c) and (d) 5.388 $(cal/cm^3)^{0.5}$ or 5.54 $(cal/cm^3)^{0.5}$ at 473 K, respectively. The solubility parameter of poly(ABM%41-co-AN) was evaluated from either slope or intercepts of Fig. 5 (e) and (f) 5.544 $(cal/cm^3)^{0.5}$ or 5.578 $(cal/cm^3)^{0.5}$ at 473 K, respectively. As shown in Table-7 (a), (b) and (c), at 463 and 473 K, the solubility parameters of the three polymers are similar. When comparing the solubility values of poly(ABM), poly(ABM%41-co-AN) and poly(ABM%71-co-AN) at different temperatures, the solubility parameters decreased with increasing temperature [23].

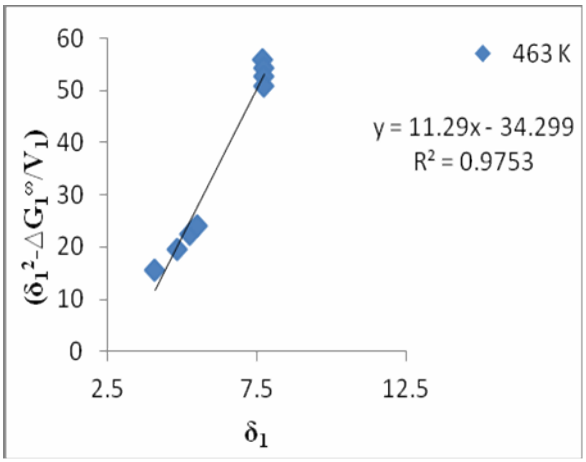


(a)

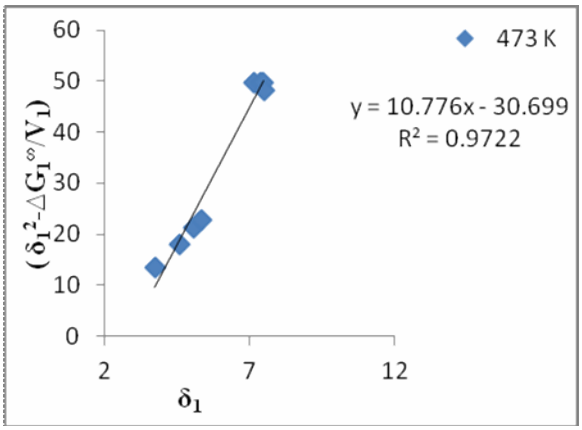


(b)

Fig. 5: Variation of term $(\delta_1^2-\Delta G_1^{\infty}/V_1)$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at temperatures (a) 473 K and (b) 463 K for. Poly(ABM).

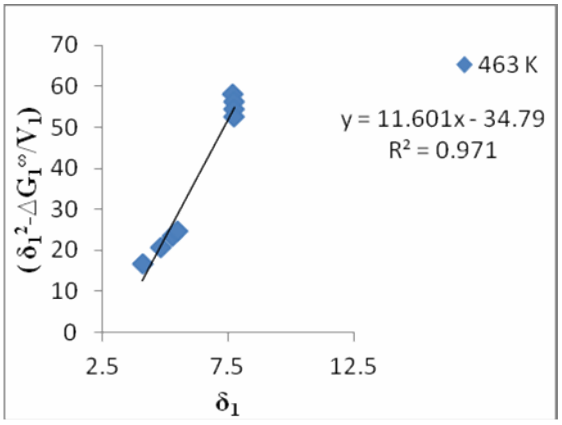


(c)

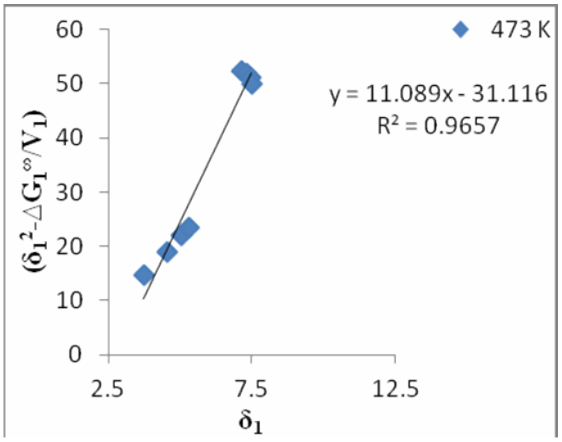


(d)

Fig. 5: Variation of term $(\delta_1^2-\Delta G_1^{\infty}/V_1)$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at temperatures (c) 473 K and (d) 463 K for oly(ABM%71-co-AN).



(e)



(f)

Fig. 5: Variation of term $(\delta_1^2-\Delta G_1^{\infty}/V_1)$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at temperatures (e) 473 K and (f) 463 K for poly(ABM%41-co-AN).

Table-7: (a) The solubility parameter, δ_2 $(cal/cm^3)^{0.5}$ of poly(ABM) at 473 and 463 K.

T(K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
473	10.235	29.747	5.117	5.454	0.98
463	10.748	33.131	5.374	5.755	0.983

Table-7: (b) The solubility parameter, δ_2 $(cal/cm^3)^{0.5}$ of poly(ABM%71-co-AN) at 473 and 463 K.

T(K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
473	10.776	30.699	5.388	5.54	0.972
463	11.29	34.299	5.645	5.856	0.975

Table-7: (c) The solubility parameter, δ_2 $(cal/cm^3)^{0.5}$ of poly(ABM%41-co-AN) at 473 and 463 K.

T(K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
473	11.089	31.116	5.544	5.578	0.965
463	11.601	34.79	5.8	5.898	0.971

Conclusion

Inverse gas chromatography (IGC) is simple, fast and economical technique that provides valuable thermodynamic and physical information for characterization of polymeric materials. In this study, IGC was successfully applied to determine certain thermodynamic and pyhsical properties of poly(ABM), poly(ABM0.41-co-AN) and poly(ABM0.71-co-AN), such as the glass transition temperature, Tg; the sorption enthalpy, $\Delta H_1^{S,}$ sorption free energy, ΔG_1^S; sorption entropy, ΔS_1^S; the weight fraction activity coefficients, Ω_1^∞; partial molar free energy of mixing, ΔG_1^∞; partial molar heat of mixing, ΔH_1^∞; and the Flory-Huggins interaction parameters, χ_{12}^∞, at infinite dilution. The T_g, was approximately 423 K for poly(ABM), 393 K for poly(ABM%71-co-AN) and poly(ABM%41-co-AN). According to the Ω_1^∞ and χ_{12}^∞ values, the probes solvated all three polymers at Tg. In addition, the solubility parameter values of poly(ABM), δ_2, were determined to be 5.117 $(cal/cm^3)^{0.5}$ and 5.454 $(cal/cm^3)^{0.5}$ at 473K, the solubility parameter values of poly(ABM%71-co-AN) were determined as 5.388 $(cal/cm^3)^{0.5}$, 5.54 $(cal/cm^3)^{0.5}$ respectively at 473K and the solubility parameter values of poly(ABM%41-co-AN) were determined to equal 5.544 $(cal/cm^3)^{0.5}$and 5.578 $(cal/cm^3)^{0.5}$, respectively, at 473K from slope and intercept, of the straight line obtained by plotting the left-hand side of equation (11) versus δ_1 values of probes.

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