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ESTIMATION OF SOLUBILITY PARAMETERS OF POLY(METHYL METHACRYLATE) AND DERIVATIVES BY INVERSE GAS CHROMATOGRAPHY

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SUMMARY

Flory - Huggins polymer-solute interaction (χ_{12}) parameters have been determined by inverse gas chromatography (i.g.c.) at 453-463 K for alkanes, alcohol, acetates, ketones and O - Xylene in PMMA. PEMA, PIBMA and Pt-BMA to estimate the polymer solubility parameters (δ_2) Partial molar free energies of mixing (ΔG_1^∞) and weight fraction activity coefficients of solute probes at infinite dilution (Ω_1^∞) were calculated at temperature range 453-463 K.

Keywords : solubility parameters, inverse gas chromatography,

INTRODUCTION

The solubility parameter concept has been used extensively in practical applications of polymers. Dipaola-Baranyi and Guillet[1] have recently shown that inverse gas chromatography, using a polymer as the stationary phase, can be a simple and convenient method for estimating solubility parameters for polymers. The method is based on the principle that the Flory-Huggins(χ) parameter can be readily determined from retention data on various small molecule probes and that χ can be related to solubility parameters by Hildebrand-Scathard theory[2] combined with Flory theory[3]. In the usual experiment, χ is determined under conditions approximating infinite dilution of the probe in the polymer and hence the value of δ_2 is more correctly designated δ_2^∞, since it is also an infinite dilution quantity. For reasons outlined previonsly this quantity may have more fundamental significance than the value of δ_2 measured at finite solute concentrations by classical methods such as swelling or solubility measurements[4].

The method has been succesfully applied to estimate consistent δ_2^∞ values for polystyrene at 193°C, poly(methyl acrylate) at 100°C, poly(vinyl acetate) at 135°C and poly (p-chlorostyrene) using a variety of standard hydrocarbon solutes of different δ_1 values [5-7].

DATA REDUCTION

The probe specific retention volumes V_g° corrected to 0°C were calculated from the standard chromatographic relation.[8]

$$V_g^{\circ} = \Delta t F J \times 273.2/W\ T(K) \qquad (1)$$

Where $\Delta t = t_p - t_m$ is the difference between the retention times of the probe tp and marker tm. F is the flow rate of the carrier gas T is the column temperature. w is the mass of the polymeric stationary phase and J is a correction factor for gas compressibility, defined by the following relation:

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

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

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

$$\chi_{12} = \ln(273.2 R v_2 / V_g^{\circ}\ P_1^{\circ} V_1) - 1 - P_1^{\circ}/RT(B_{11} - V_1) \qquad (3)$$

Where R has the usual meaning as the gas constant, v_2 is the specific volume of polymer (ml gr^{-1}) V_1 is the molar volume of the solute. P_1° is the vapour pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. V_1, P_1° and B_{11} were calculated at the column temperature.

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

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

Where t is the temperature (in°C) and the constants A.B and C.[9] Second virial coefficients B_{11}, were computed using the following equation:[10]

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

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 using:[9]

For $0.2 \leq Tr \leq 0.8$

$$Vr^{(0)} = 0.33593 - 0.33953Tr + 1.51941Tr^2 - 2.02512Tr^3 + 1.11422Tr^4 \qquad (6)$$

For $0.8 < Tr < 1.0$

$$Vr^{(0)} = 1.0 + 1.3(Tr)\log(1 - Tr) - 0.50879(1 - Tr) - 0.91534(1 - Tr)^2 \qquad (7)$$

For $0.2 < Tr < 1.0$

$$\Gamma = 0.29607 - 0.09045Tr - 0.04842Tr^2 \qquad (8)$$

$$V_1/V^R = Vr^{(0)}(Tr)[1 - w\Gamma(Tr)]/Vr^{(0)}(Tr^R)[1 - w\Gamma(Tr^R)] \qquad (9)$$

Where $Vr^{(0)}$ and Γ are functions of reduced temperature, and W is the acentric factor, Tr is reduced temperature and $V^R = M/d$, M and d are the molecular weight of the solute and density and Tr^R is reduced reference temperature.

Weight fraction activity coefficient of the solute probe at infinite dilution (Ω_1^{∞}) is calculated according to the following equation: [10]

$$\Omega_1^{\infty} = 273.2R/V_g^{\circ} P_1^{\circ} M_1\ \exp[-P_1^{\circ}(B_{11} - V_1)/RT] \qquad (10)$$

Where P_1°, V_1 and B_{11} were defined in equation(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 of the solute as follows:

$$\Delta G_1^{\infty}=RT\ln\Omega_1^{\infty} \qquad (11)$$

Solubility Parameter Theory: Solubility Parameters (δ_1) were calculated for the various solutes (probes) from the relation

$$\delta_1=[(\Delta Hv-RT)/V_1]^{½} \qquad (12)$$

Where R is the universal gas constant and V_1 is the solute molar volume corresponding to temperature, T(K) and ΔHv is the molar enthalpy of vaporization for the solute at temperature T. The molar enthalpy ΔHv is calculated according to the followings equations: [9]

$$\Delta H_v=\Delta H_{vb}\ Tr/T_{br}\ x+x^q/1+x^p \qquad (13)$$

$$X=Tbr/Tr\ 1-Tr/1-T_{br} \qquad (14)$$

Where ΔHvb is the molar enthalpy of vaporization at the boiling temperature, Tbr=Tb/Tc, Tbr, Tb and Tc is reduced boiling temperature, boiling temperature and critical temperature, respectively, and X is temperature function, and the constants q and P are also taken from C.R. *Reid et al. compilation.*[9]

EXPERIMENTAL

Materials

Eleven polar and non-polar probes were used in this study. Octane, nonane, decane, undecane and dodecane were supplied from Aldrich chemical Co.and methanol, acetone, ethyl methyl ketone, o-xylene, methyl acetate and ethyl acetate were supplied from Merck Chemical Co. as chromatographic grade. Poly(methyl methacrylate), Poly (ethyl methacrylate), Poly (isobuthyl methacrylate) and Poly (t-buthyl methacrylate) were supplied by Aldrich Chemical Co. in powder from. PMMA is (Mw=120.000) and its density d:1.190 (reflective index n_D^{20}:(1.4893). Molecular weigth of PEMA was estimated from intrinsic viscosity η) =0.46 dl gr^{-1} in 2-butanone at room temperature,(its density d=1.110 and refrective index, n_D^{20}:1.4850) to be 215.000 using published Chinai and Samuels constants [11](a=0.79, K=$2.83.10^{-3}$ $mlgr^{-1}$). Density and reflective index of PIBMA is d:1.090, n_D^{20}=1.4770 respectively. Density and reflective index, of Pt-BMA is d:1.022, n_D^{20}=1.4638 respectively. Chromosorb W(45-60 mesh) was supplied from Sigma Chemical Co.

Instrumentation and procedure

A Shimadzu GC-14A model gas chromatography equipped with a dual flame ionization dedector, FID was used in the analysis. Dried nitrogen gas was used as a carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at inlet at outlet of the column, read from a mercury manometer(mm Hg) 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 measured at room temperature.

The spiral glass columns were washed with methanol and were annealed prior to use.The polymers were first dissolved in a suitable solvent and deposited onto an inert chromatographic support by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for ca. 72 h, with slight heating the chromatographic support was packed with the aid of a

Table 1. Stationary phase and column description

Column	Solvent	Polymer Loading(%,W/W)	Mass of Polymer (g)	Mass of Support(g)	Column length(cm)
PMMA	Benzene	9.55	0.53600	6.15731	210
PEMA	N,N Dimethyl acetamide	10.00	0.60000	6.60000	210
PIBMA	"	10.00	0.58595	5.85948	210
Pt-BMA	"	7.43	0.43108	5.80108	210

Table 2. Thermodynamic parameters of some probes at the temperature range 453-463K

	V_1(cm^3 mol^{-1})		ΔH_v(k.cal mol^{-1})		δ_1(cal.cm^{-3})$^{1/2}$		P_1°	
Probes/T(K)	453	463	453	463	453	463	453	463
Methanol	60.53	61.76	5.39	5.00	8.61	8.12	9.93	10.10
Acetone	111.64	113.92	4.30	3.96	5.52	5.17	9.60	9.77
E.M.K.	135.93	138.72	5.36	5.08	5.73	5.48	9.03	9.21
Met.Acet.	120.40	122.98	4.42	4.06	5.40	5.06	9.57	9.73
Et.Acet.	148.04	151.17	5.26	4.94	5.43	5.15	9.10	9.28
O-xylene	183.39	187.30	8.17	7.97	6.29	6.14	7.49	7.70
n-Octane	245.54	250.53	6.94	6.67	4.96	4.79	7.93	8.13
n-Nonane	269.24	274.90	8.12	7.81	5.18	5.01	7.34	7.56
n-Decane	293.25	299.61	9.24	8.98	5.33	5.19	6.78	7.02
n-Undec.	316.77	323.39	10.34	10.08	5.46	5.32	5.68	5.96
n-Dodec.	341.38	348.42	11.45	11.18	5.56	5.43	6.22	6.48

mechanical vibrator into 3.2 mm I.D. spiral glass columns. Columns parameters are described in Table 1. The prepared columns was conditioned at 80°C and fast carrier gas flow rate for 24 h prior to use. The probes were injected onto the column with 1μl Hamilton syringes. Three consecutive injections (0.3 μl) were made for each probe at each set of measurements. The retention times of the probes were measured by using chromatopac CR 6A, Shimadzu. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide.

RESULTS and DISCUSSION

Weigth fraction activity coefficient (Ω_1^{∞}) and the Flory-Huggins parameter polymer-solute interaction parameters (χ_{12}), solubility parameters and molar volumes V_1 of probes and partial molar free energy of mixing, ΔG_1^{∞} were determined for alkanes, acetates, ketones, alcohol and o-xylene in PMMA, PEMA, PIBMA and Pt-BMA by measuring the retention volumes over the temperature range 453-463K and the results are given in Tables 3. and Table 4.

A third approach is to combine the Flory treatment with Hildebrand -Scatchard theory to give the following relationship for the interaction parameter, χ[5,12]

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \qquad (15)$$

Table 3. Thermodynamic parameters of selected probes in PMMA and PEMA at the temperature range 453 -463K

	PMMA								PEMA							
	χ_{12}		Ω_1^{∞}		ΔG_1^{∞} (k.cal mole^{-1})		V_g°		χ_{12}		Ω_1^{∞}		ΔG_1^{∞} (k.cal mole^{-1})		V_g°	
Probes/(T)	453	463	453	463	453	463	453	463	453	463	453	463	453	463	453	463
Methanol	0.213	0.032	5.67	4.95	1.56	1.47	5.45	5.21	0.854	0.680	9.96	8.83	2.07	2.00	3.08	2.92
Acetone	0.119	0.274	4.54	4.13	1.36	1.31	5.50	5.26	0.394	0.253	7.07	6.51	1.76	1.72	3.53	3.33
E.M.K.	0.211	0.051	5.77	5.18	1.58	1.51	5.89	5.63	0.567	0.462	7.69	7.28	1.84	1.83	4.42	4.00
Met.Acet.	0.033	0.177	3.68	3.38	1.17	1.12	5.55	5.30	0.183	0.048	5.86	5.42	1.59	1.56	3.48	3.30
Et.Acetat.	0.051	0.099	4.71	4.23	1.40	1.33	5.62	5.38	0.369	0.236	6.57	6.08	1.69	1.66	4.03	3.74
O-xylene	0.767	0.799	8.33	8.82	1.91	2.00	11.76	9.12	0.841	0.710	8.36	7.53	1.91	1.86	11.71	10.68
n-Octane	0.849	0.777	10.12	9.82	2.08	2.10	6.13	5.28	1.230	1.080	13.82	12.41	2.36	2.32	4.49	4.18
n-Nonane	1.297	1.176	14.54	13.33	2.41	2.38	6.57	5.85	1.474	1.340	16.19	14.65	2.51	2.47	5.90	5.32
n-Decane	1.491	1.446	16.66	16.34	2.53	2.57	8.79	7.14	1.554	1.398	16.54	14.53	2.53	2.46	8.85	8.03
n-Undecane	1.733	1.569	20.30	17.61	2.71	2.64	11.24	10.10	1.787	1.681	20.00	18.38	2.70	2.69	11.41	9.68
n-Dodecane	2.272	2.088	33.78	28.57	3.17	3.08	10.48	9.44	1.864	1.802	20.95	20.01	2.74	2.76	16.90	13.48

Table 4. Thermodynamic parameters of selected probes in PIBMA and Pt-BMA at the temperature range 453-463K

	PIBMA								Pt-BMA							
	χ_{12}		Ω_1^{∞}		ΔG_1^{∞} (k.cal.mol^{-1})		V_g°		χ_{12}		Ω_1^{∞}		ΔG_1^{∞} (k.cal.mol^{-1})		V_g°	
Probes/T(K)	453	463	453	463	453	463	453	463	453	463	453	463	453	463	453	463
Methanol	0.797	0.668	9.24	8.57	2.00	1.98	3.32	3.01	0.703	0.473	7.88	6.61	1.86	1.74	3.89	3.90
Acetone	0.357	0.253	6.69	6.39	1.71	1.71	3.73	3.39	0.379	0.178	6.42	5.56	1.67	1.58	3.89	3.90
E.M.K.	0.604	0.514	7.83	7.52	1.85	1.85	4.34	3.87	0.796	0.557	8.90	7.37	1.97	1.84	3.82	3.95
Met.Acet.	0.113	0.021	5.37	5.18	1.51	1.51	3.80	3.45	0.201	0.019	5.50	4.85	1.54	1.45	3.71	3.69
Et.Acetat.	0.358	0.244	6.38	6.01	1.67	1.65	4.15	3.78	0.535	0.321	7.13	6.09	1.77	1.66	3.71	3.73
O-xylene	1.028	1.009	9.90	9.96	2.06	2.12	9.89	8.07	2.000	1.668	24.54	18.07	2.88	2.66	3.99	4.45
n-Octane	1.099	1.038	11.91	11.68	2.23	2.26	5.21	4.44	1.511	1.245	16.86	13.47	2.54	2.39	3.68	3.85
n-Nonane	1.377	1.302	14.42	13.85	2.40	2.42	6.62	5.63	1.779	1.560	20.23	16.80	2.71	2.60	4.72	4.64
n-Decane	1.559	1.513	16.32	16.00	2.51	2.55	8.97	7.29	2.168	1.911	28.15	22.35	3.00	2.86	5.20	5.22
n-Undecane	1.702	1.682	18.04	18.06	2.60	2.66	12.65	9.85	2.531	2.298	38.74	31.38	3.29	3.17	5.89	5.67
n-Dodecane	1.799	1.769	19.26	19.00	2.66	2.71	18.38	14.19	2.935	2.606	56.28	41.18	3.63	3.42	6.29	5.55

Table 5. Nature of Selected Solvents

Polymer	Good	Moderate	Bad
PMMA	Acetates,Ketones	Methanol	Alkanes,O-xylene
PEMA	-	Acetates,Ketones	Alkanes,o-xylene Methanol
PIBMA	Acetates	Ketones	Alkanes,O-xylene Methanol
Pt-BMA	Methyl acetates	Ketones,Methanol Ethyl acetates	Alkanes,O-xylene

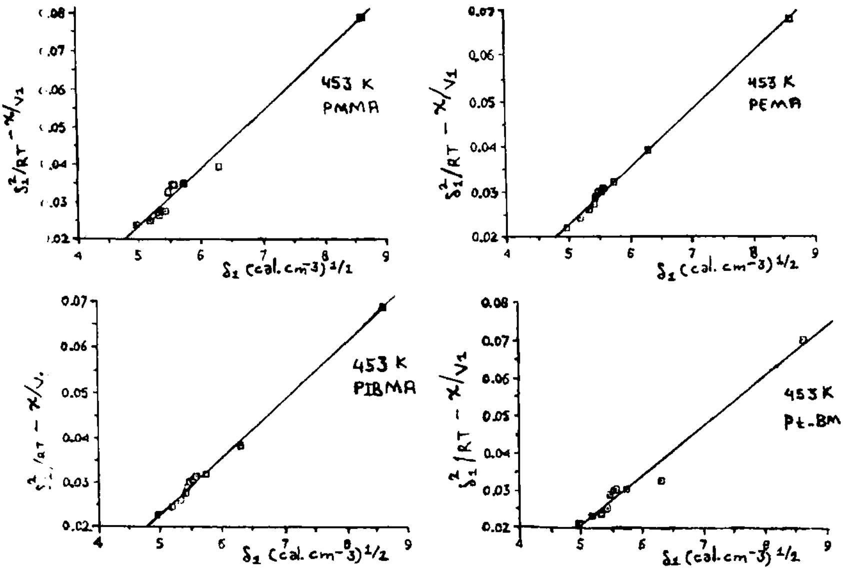

Figure 1.Estimation of solubility parameters (δ_2) of PMMA, PEMA, PIBMA and Pt-BMA from solubility parameters of the probes (δ_1) and Flory-Huggins interaction parameters χ_{12} at 453K

Equation (15) can be rewritten as

$$(\delta_1^2/RT-\chi/V_1)=(2\delta_2/RT)\,\delta_1-\delta_2^2/RT \qquad (16)$$

Therefore a plot of $[(\delta_1^2/RT)-(\chi/V_1)]$ vs. δ_1 of probe should yield a straight line with a slope of $2\delta_2/RT$ and an intercept of $-(\delta_2^2)/RT$.[1] Polymer solubility parameters should be obtained from eq. 16 for PMMA, PEMA, PIBMA and Pt-BMA at the temperature range 453 -463K. The values of selected probes have been given in Table 2. Polymer-solute interactions are given in Table 5.according to results in Table 3. and 4.

Table 6. Estimated solubility parameters of PMMA, PEMA, PIBMA, and Pt-BMA at the temperature 453-463K

				δ_2 from eq.16				δ_2 from eq.17	
	T(K)	slope	intercpt.	cal.from slope	cal.from intercpt.	slope	intercpt.	cal.from slope	cal.from intercpt
PMMA	453	0.0152	-0.0522	6.84	6.85	9.0099	-28.9764	4.51	5.38
	463	0.0146	-0.0487	6.72	6.69	8.4411	-26.1526	4.24	5.11
PEMA	453	0.0126	-0.0398	5.67	5.99	7.1987	-20.3037	3.60	4.51
	463	0.0119	-0.0361	5.47	5.76	6.6437	-17.8141	3.32	4.22
PIBMA	453	0.0127	-0.0402	5.72	6.02	7.3494	-20.9023	3.67	4.57
	463	0.0119	-0.0359	5.47	5.75	6.6414	-17.8305	3.32	4.22
PtBMA	453	0.0134	-0.0462	6.03	6.45	8.0958	-26.3947	4.04	5.14
	463	0.0129	-0.0425	5.93	6.25	7.5811	-23.3195	3.79	4.83

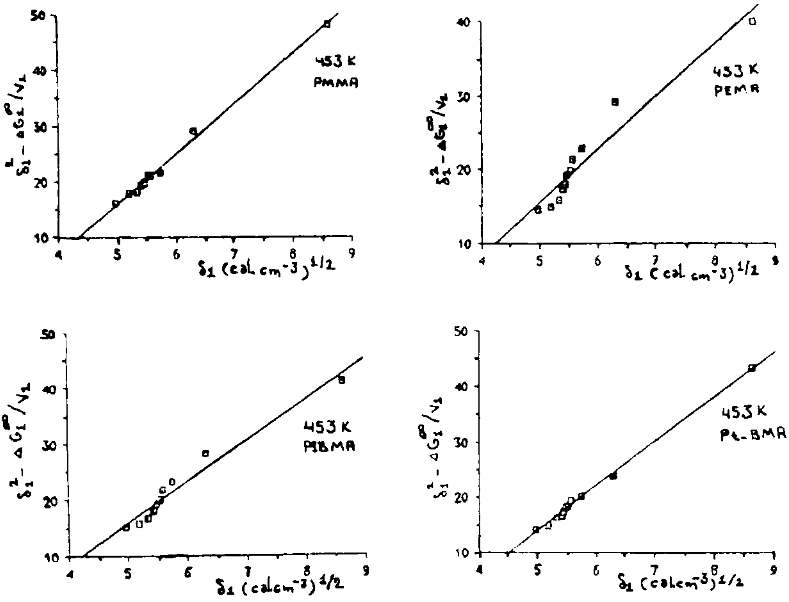

Figure 2. Estimation of solibility parameters (δ_2) of PMMA, PEMA, PIBMA and Pt-BMA from solubility parameters of the probes (δ_1) and free energies of mixing ΔG_1^∞ at 453K

The following rules have been formulated by Guillet.[13]

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

The results are illustrated in Figure 1.An excellent linear correlation is found (11 data points each for polymers at the temperature range 453-463K in PMMA, PEMA,PIBMA and Pt-BMA).Slopes and intercepts were obtained from a linear least-squares analysis. Derived values of δ_2 for the polymers are listed in Table 6.

On the other hand, solubility parameters of polymers,δ_2 can be estimated by using the following relation :

$$\delta_1^2-(\Delta G_1^{\infty}/V_1) = (2\delta_2)\,\delta_1-\delta_2^2 \qquad (17)$$

Results are graphically illustrated in Figure 2. These plots show extra scatter of experimental points, especially for the heat of mixing data (Figure 2). Results of a least-squares analysis of such plots are also summerized in Table 5.

The solubility parameter of PMMA, PEMA, PIBMA and Pt-BMA were evaluated from the slope and intercept of Figure 1 as 6.84, 6.85; 5.67 5.99; 5.72, 6.02; 6.03, 6.45; (cal $cm^{-3})^{1/2}$ at 453K.respectively. The reported experimental values for PMMA, PEMA, PIBMA, Pt-BMA 9.3, 8.95 8.65, 8.65 at 298 K, respectively [14]. For a polymer one expects the variation of δ_2 to be smaller than for δ_1, because of the relatively small coefficient of thermal expension of the polymer.

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REFERENCES

1- G. Di Paola-Baranyi and J.E.Guillet, Macromolecules,11,228,(1978)
2- G. Di Paola-Baranyi, J.E.Guillet, J.Klein and H.E.Jeberien, J.Chromatopr.,166, 349 (1978)
3- J.H.Hildebrand and R.L.Scott,"The Solubility of Nonelectrolytes", 3rd. ed., Reinhold, New York (1950)
4- H.Ito and J.E. Guillet, Macromolecules, 21, 1163, 1979
5- D. Patterson, Rubber Chem. Technol.,40, 1 (1967)
6- R.L. Scott and M. Magat, J. Chem. Phys., 13, 172 (1945)
7- I.Yılmaz,Ö.G.Cankurtaran,and B.M.Baysal,Polymer,33,4563,(1992)
8- A.B.Littlewood,C.S.G.Phillips and D.T.Price,J.Chem.Soc.1480,(1955)
9- C. R. Reid, J. M. Prausnitz and T. K. Sherwood," The Properties of Gases and Liquids",3 rd.ed.Mc.Graw -Hill Book Com., New York (1977)
10- C.Chein -Tai and Z.Y.Al -Saigh,Polymer,31,1170,(1990)
11- S.N.Chinai and R.J.Samuels,J.Polm.Sci.19,463,(1956)
12- G.DiPaola-Baranyi and J.E.Guillet,Macromolecules,11,228,(1978)
13- J.E.Guillet and J.H.Purnell,Advances in Analytical Chemistry and Instrumentation, Gas chromatography,John Wiley and sons, New York (1973)
14- J.Brandrup and E.H.Immergut "Polymer Handbook" second Ed.(1975)