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Determination of secondary transitions and thermodynamic interaction parameters of poly (ether imide) by inverse gas chromatography

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Summary

The retention diagrams of poly(ether imide) for ethyl benzene, n-propyl benzene, isopropyl benzene, chloro benzene, n-butyl acetate, tert-butyl acetate, isoamyl acetate, n-nonane, n-decane, n-undecane, n-dodecane and n-tridecane were obtained by inverse gas chromatography technique. In this work, the slope changes on the diagram were assigned as secondary transitions. The secondary transition temperatures obtained by inverse gas chromatography technique are in good agreement with the ones obtained by thermally stimulated depolarization current in the literature. Specific retention volume, V_g^0, the weight fraction activity coefficients of the solvents at infinite solution, Ω_1^∞, Flory-Huggins polymer-solvent interaction parameters, χ_{12}^∞, equation-of-state polymer-solvent interaction parameters, χ_{12}^*, effective exchange energy parameters, X_{eff} were determined. Later, the partial molar heat of sorption, $\Delta\bar{H}_{1,sorp}$ and the partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ were obtained. The solubility parameter of poly(ether imide), δ_2 was determined as 10.7 (cal/cm^3)$^{1/2}$ by extrapolation of the δ_2 values obtained by considering the free volume effects from studied temperature range to room temperature.

Introduction

Aromatic polyimides are an important class of engineering thermoplastics possessing useful physical properties such as superior thermal stability, high modulus, toughness, and chemical resistance [1-4]. These polymers are used in a variety of applications such as coatings, adhesives, composites and moulded components. In many cases, polyimides are subjected to severe environments including exposure to ultraviolet radiation. One of the successful approaches to increase solubility and moldability of polyimides is the introduction of flexible linkages into polymer backbone. An important commercialized example, which contains flexible ether (–O–) and isopropylidene [–C(CH$_3$)$_2$–] groups is Ultem. Ultem is an amorphous thermoplastic polymer with the structure as shown in Figure 1.

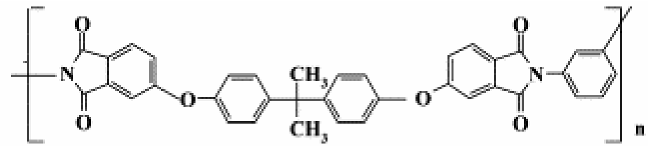

Figure 1. The chemical structure of Ultem.

Although inverse gas chromatography method (IGC) has been widely used to investigate the interactions of polymeric materials with various solvents [5-7], it is a new method determination of the secondary transitions of the polymers and there is only a few study in the literature [8-11]. IGC is a very fast and inexpensive technique to determine the secondary transition temperatures of a polymer, in comparison to dynamic mechanical and dielectric analysis techniques and etc. Therefore, the method needs lots of studies to confirm the reliability of it. Belena et al. [12] have observed that Ultem exhibits multiple secondary transitions by using thermally stimulated depolarization current (TSDC) measurements. Belena et al. have reported four and one secondary transition temperatures below and above the glass transition temperature, respectively. In this study, we aimed to observe the secondary transitions of Ultem, by IGC in order to establish the reliability of the method in determination of secondary transition temperatures. In addition, thermodynamical interactions of Ultem with studied solvents were determined at temperature range of 260 and 285°C by using IGC. Later, the partial molar heat of sorption, $\Delta\overline{H}_{1,sorp}$ and the partial molar heat of mixing, $\Delta\overline{H}_1^\infty$ and the solubility parameter of Ultem, δ_2 were obtained.

Theoretical Background

The specific retention volume, V_g^0 is determined experimentally from inverse gas chromatography measurements as follows [13-17]

$$V_g^0 = Q\left(t_R - t_A\right) J\ 273.2/\left(T_r\ w\right) \tag{1}$$

where Q is carrier gas flow rate measured at the room temperature T_r, t_R and t_A are retention times of the solute probe and air, respectively, J is pressure correction factor, w is weight of polymer in the column.

The weight fraction activity coefficient of solvents at infinite dilution Ω_1^∞, is defined by the following equation,

$$Ln\Omega_1^\infty = Ln\left(273.2\,R/V_g^0\ p_1^0\ M_1\right) - p_1^0\left(B_{11} - V_1^0\right)/RT \tag{2}$$

where R is the universal gas constant; p_1^0, M_1, B_{11} and V_1^0 are saturated vapour pressure, molecular weight, gaseous state second virial coefficient and molar volume of the solvent at temperature T, respectively.

According to the theories of Flory-Huggins and equation-of-state, interaction parameters, χ_{12}^∞ and χ_{12}^* are defined in the Eq.3 and Eq.4, respectively:

$$\chi_{12}^{\infty} = Ln\left(273.2\, R\, v_2 / p_1^0\, V_g^0\, V_1^0\right) - 1 - p_1^0\left(B_{11} - V_1^0\right)/R\,T \qquad (3)$$

where v_2 is specific volume of polymer.

$$\chi_{12}^{*} = Ln\left(273.2\, R\, v_2^* / p_1^0\, V_g^0\, V_1^*\right) - 1 - p_1^0\left(B_{11} - V_1^0\right)/R\,T \qquad (4)$$

where v_2^* is specific hard-core volume of polymer and V_1^* is molar hard-core volume of solvent.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$R\,T\chi_{12}^{*} = p_1^*\, V_1^* \left\{ 3T_{1r}\, Ln\left[\left(v_{1r}^{1/3} - 1\right)\Big/\left(v_{2r}^{1/3} - 1\right)\right] + v_{1r}^{-1} - v_{2r}^{-1} + X_{eff}/P_1^*\, v_{2r} \right\} \qquad (5)$$

where p_1^* is characteristic pressure, v_{1r} and v_{2r} are reduced volume of solvent and polymer, respectively. T_{1r} is reduced temperature of solvent.

The partial molar heat of sorption, $\Delta\overline{H}_{1,sorp}$ and the partial molar heat of mixing, $\Delta\overline{H}_1^{\infty}$ are calculated from Eq.(6) and Eq.(7)

$$\Delta\overline{H}_{1,sorp} = -R\left[\partial\left(Ln\, V_g^0\right)/\partial\left(1/T\right)\right] \qquad (6)$$

$$\Delta\overline{H}_1^{\infty} = R\left[\partial\left(Ln\, \Omega_1^{\infty}\right)/\partial\left(1/T\right)\right] \qquad (7)$$

Molar heat of vaporization is related to $\Delta\overline{H}_{1,sorp}$ and $\Delta\overline{H}_1^{\infty}$ as follows:

$$\Delta\overline{H}_V = \Delta\overline{H}_1^{\infty} - \Delta\overline{H}_{1,sorp} \qquad (8)$$

The solubility parameter of the polymer, δ_2 is found by combining of the theories Flory-Huggins and Hildebrand-Scathard [5-6]

$$\left(\delta_1^2/R\,T - \chi_{12}^{\infty}/V_1^0\right) = \left(2\delta_2\, \delta_1/RT\right) - \left(\delta_2^2/R\,T\right) \qquad (9)$$

Experimental

Ultem was a product of General Electric Corporation. Ethyl benzene (EB), n-propyl benzene (nPB), isopropyl benzene (IPB),chloro benzene (CB) tert-butyl acetate (tBA), n-butyl acetate (nBA), isobutyl acetate (IBA), isoamyl acetate (IAA), n-nonane(N), n-decane(D), n-undecane (UD), n-dodecane (DD) and n-tridecane (TD) were Merck AG. Inc. products, analytical reagent grade and used without further purification. The solvents and support material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc., respectively. A Hewlett-Packard 5890 Model, series II gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents in this study. Data acquisition and analysis were performed by means of HP-3365 software. The column was stainless steel tubing with 3.2 mm o.d. and 1 m in length. The polymer was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb-W in the polymer solution.

Results and discussion

The specific retention volumes, V_g^0 of the solvents were obtained experimentally from IGC measurements using Eq.1. Results were given in Fig.2, for some acetates and aromatic solvents between 40 and 285°C, respectively and were given in Table 1 for some acetates, aromatic solvents and n-alkanes between 260 and 285°C, respectively. The glass transition temperature T_g (α-) of Ultem was determined as 220°C in Fig.2. The first deviated point from linearity at lower temperature side of the diagram was accepted as a secondary transition temperature of the polymer. These transition are usually labeled with Greek letters, α, β, γ and so on. More clearly, five β- below α- and one ρ- above α- temperatures of the polymer were accepted as 170, 150, 120, 90, 60 and 245°C, respectively from the first point of deviation from linearity towards to higher temperatures in the retention diagrams of the solvents on Ultem (Fig. 2). The point exhibited by most of the probes was accepted as secondary transition temperature.

Table 1. The specific retention volumes, V_g^0 (cm^3/g) of the solvents on Ultem

t(°C)	260	265	270	275	280	285
EB	2.559	2.392	2.177	1.991	1.891	1.743
nPB	2.987	2.852	2.651	2.545	2.397	2.277
IPB	2.916	2.728	2.523	2.337	2.148	1.978
CB	3.332	3.154	2.949	2.782	2.604	2.496
nBA	1.714	1.710	1.581	1.523	1.341	1.181
IAA	2.165	1.981	1.881	1.747	1.548	1.495
N	2.605	2.525	2.501	2.339	2.219	2.116
D	3.141	2.957	2.819	2.728	2.700	2.662
UD	2.781	2.671	2.523	2.390	2.238	2.146
DD	3.022	2.811	2.757	2.688	2.475	2.331
TD	3.366	3.235	3.102	3.018	2.857	2.642

The three of our values obtained in this study are comparable to those given β-ransitions by Belena et al. as seen in Table 2. We determined an additional two β-transitions at 170 and 120 °C. The all transition temperatures observed in this study are comparable with the value given by Belena et al. This study suggests that IGC is more sensitive and reliable than TCDC technique to observe secondary transitions of a polymer.

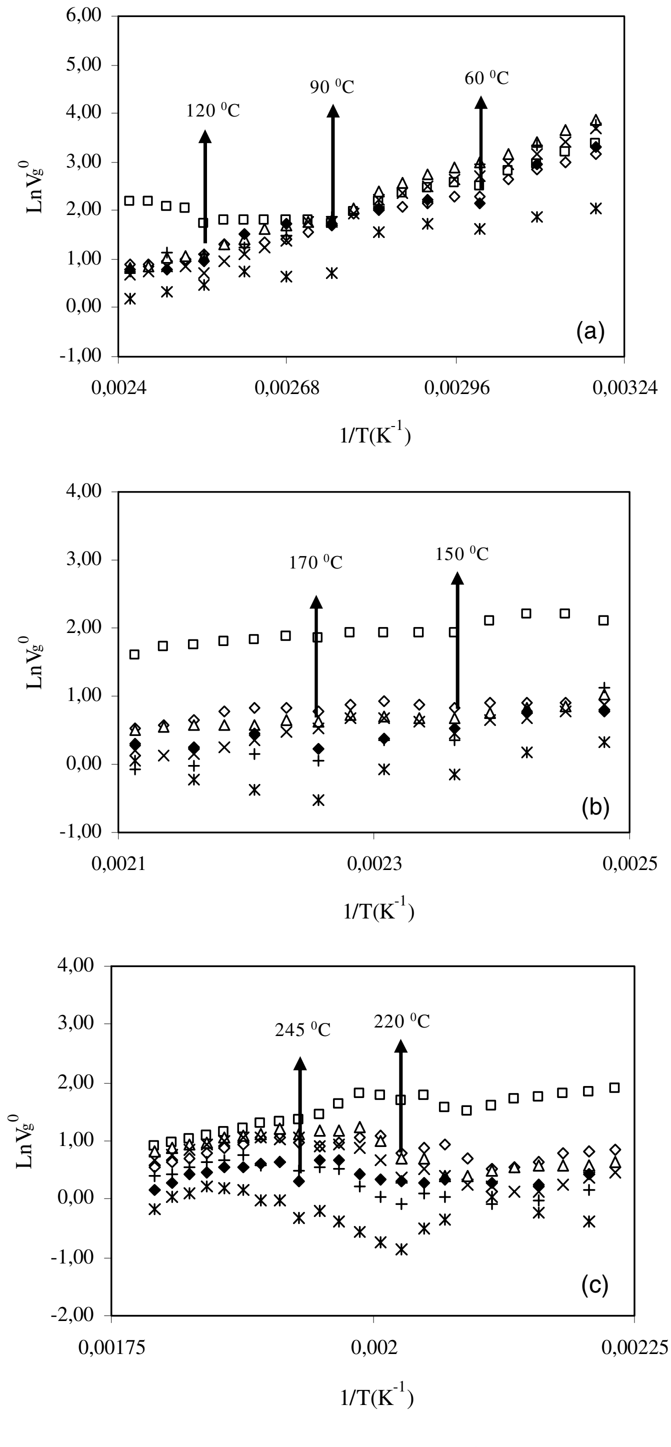

Figure 2. Retention diagrams of nPB (Δ), IPB (×), CB (□), EB (◊), nBA (♦), tBA (⁎) and IAA (+) on Ultem at low (a), medium (b) and high (c) temperature ranges.

Table 2. Comparison of the secondary transitions determined in this study with literature

Secondary transitions	IGC t(°C)	Literature [12] t(°C)
γ	-	-123
β_5	60	70
β_4	90	90
β_3	120	-
β_2	150	152
β_1	170	-
α	220	225
ρ	245	244

The weight fraction activity coefficients of the studied solvents at infinite dilution, Ω_1^∞ were determined from Eq. 2. Results were given in Table 3 for all of the studied solvents. According to Guillet [5], the solvent is good if Ω_1^∞ is lower than 5 and poor it is higher than 10, respectively. The values between 5 and 10 indicate moderately solubility. The values in the Table 3 suggest CB is good solvent as EB, nPB and IPB are poor solvents for the Ultem. In the case of aromatic hydrocarbons, the solvent quality of EB and IPB decrease but it increases in nPB with temperature, respectively. The solvent quality of CB does not change with temperature. According to the values of Ω_1^∞ belonging to n-alkanes, N and D are moderately good solvents but UD, DD and TD are poor solvents. It is shown that solubility is decreasing as the alkane chain length is increased. The solubility of the polymer tends to increase with temperature in all alkanes used in this study. nBA is poor while IAA is moderately good solvent of Ultem and the solvent quality of nBA and IAA decrease with temperature.

Table 3. The weight fraction activity coefficients of the solvents at infinite dilution, Ω_1^∞ with Ultem

T(°C)	260	265	270	275	280	285
EB	9.0	9.1	9.4	9.7	9.7	10.0
nPB	10.1	9.9	9.9	9.7	9.7	9.6
IPB	9.1	9.1	9.2	9.4	9.6	9.9
CB	5.9	5.9	5.9	5.9	6.0	5.9
nBA	9.9	9.4	9.6	9.5	10.2	11.1
IAA	8.0	8.3	8.1	8.2	8.8	8.6
N	9.9	9.7	9.2	9.3	9.2	9.2
D	10.6	10.5	10.3	9.9	9.4	9.0
UD	15.4	15.3	15.0	14.7	14.6	14.2
DD	19.6	19.3	18.1	17.1	17.1	16.8
TD	23.6	22.3	21.3	20.0	19.4	19.2

The polymer-solvent interaction parameters, χ_{12}^∞ and χ_{12}^* determined from Eq. 3 and Eq. 4. Results were given in Tables 4 and 5. If the χ_{12}^∞ is lower than 0.5, the solvent is good solvent for the polymer, however, if it is higher than 0.5, the solvent is poor solvent for the polymer. The values of them confirm the former discussion on the solubility behavior of Ultem.

Table 4. Flory-Huggins polymer-solvent interaction parameters of the solvents, χ_{12}^{∞}, with Ultem

t(°C)	260	265	270	275	280	285
EB	0.657	0.651	0.672	0.690	0.672	0.684
nPB	0.790	0.758	0.754	0.719	0.705	0.684
IPB	0.671	0.662	0.666	0.669	0.682	0.694
CB	0.498	0.480	0.476	0.464	0.461	0.436
nBA	0.658	0.583	0.584	0.543	0.592	0.640
IAA	0.529	0.538	0.511	0.508	0.553	0.513
N	0.502	0.455	0.388	0.378	0.355	0.327
D	0.620	0.596	0.561	0.513	0.443	0.378
UD	1.042	1.024	0.992	0.960	0.941	0.900
DD	1.134	1.289	1.214	1.146	1.138	1.109
TD	1.534	1.470	1.411	1.339	1.298	1.281

Table 5. Equation-of-state polymer-solvent interaction parameters of solvents, χ_{12}^{*}, with Ultem

t(°C)	260	265	270	275	280	285
EB	0.966	0.971	0.999	1.026	1.019	1.045
nPB	1.069	1.044	1.048	1.020	1.016	1.003
IPB	0.962	0.955	0.982	0.979	1.005	1.025
CB	0.783	0.770	0.776	0.774	0.779	0.766
nBA	1.067	1.006	1.020	0.995	1.060	1.126
IAA	0.892	0.910	0.894	0.905	0.961	0.934
N	0.865	0.831	0.775	0.780	0.770	0.758
D	0.944	0.930	0.906	0.865	0.807	0.753
UD	1.330	1.319	1.294	1.273	1.261	1.227
DD	1.577	1.558	1.490	1.430	1.428	1.408
TD	1.774	1.716	1.662	1.596	1.561	1.553

The effective exchange energy parameters, X_{eff} in the equation of state theory of studied solvents were calculated from Eq. 5 and results were given in Table 6. It was determined that X_{eff} of Ultem in EB, IPB, nBA and IAA increased with temperature while those of D, DD and TD decreased with temperature. X_{eff} of Ultem in nPB, CB, N, UD were independent on temperature.

$\Delta\overline{H}_{1,sorp}$ and $\Delta\overline{H}_1^{\infty}$ were calculated from the slopes of the plots of LnV_g^0 versus $1/T$ and $Ln\Omega_1^{\infty}$ versus $1/T$ in the temperature range 260-285°C using Eq. 6 and Eq. 7, respectively. The values of $\Delta\overline{H}_V$ obtained from Eq. 8 were compared to the values of $\Delta\overline{H}_V$ calculated according to the Reference [18]. All results were given in Table 7 with the boiling temperature of the solvents. The agreement is good for the solvents that boiling temperature is close to the average of the studied column temperatures [19].

Table 6. Effective exchange energy parameters of solvents, X_{eff} (J/cm^3), with Ultem

t(°C)	260	265	270	275	280	285
EB	28.9	29.6	32.0	34.2	34.5	36.7
nPB	28.9	28.1	28.7	27.9	28.0	27.9
IPB	23.8	24.3	24.8	26.3	27.8	29.4
CB	24.0	24.0	24.6	24.9	25.9	25.4
nBA	28.9	27.1	29.3	29.6	34.7	40.0
IAA	16.7	18.4	18.5	19.9	23.5	23.4
N	12.4	11.7	10.3	11.2	11.7	12.2
D	12.4	12.2	11.7	10.9	9.4	8.2
UD	22.8	22.8	22.5	22.0	22.0	21.4
DD	27.9	27.7	26.0	24.6	24.8	24.5
TD	31.5	30.3	29.1	27.7	27.0	26.9

Table 7. The partial molar heat of sorption, $\Delta\overline{H}_{1,sorp}$(kcal/mol), the partial molar heat of mixing, $\Delta\overline{H}_1^{\infty}$ (kcal/mol), molar heat of vaporization, $\Delta\overline{H}_V$ (kcal/mol) obtained by Eq. 8 in the temperature range 260-285°C and molar heat of vaporization, $\Delta\overline{H}_V$ [18] (kcal/mol) at normal boiling temperature T_b (°C)

solvents	$\Delta\overline{H}_{1,sorp}$	$\Delta\overline{H}_1^{\infty}$	$\Delta\overline{H}_V$	$\Delta\overline{H}_V$ [18]	T_b
EB	9.1	-2.4	6.8	8.5	136
nPB	6.5	1.1	7.5	9.1	159
IPB	9.2	-2.1	7.2	9.0	153
CB	7.0	-0.2	6.8	8.7	132
nBA	8.8	-2.8	6.1	8.6	126
IAA	9.0	-2.2	6.8	9.0	142
N	5.0	1.7	6.7	8.8	150
D	3.8	4.0	7.8	9.4	174
UD	6.9	1.9	8.8	9.9	195
DD	5.7	3.9	9.7	10.4	216
TD	5.4	5.1	10.5	10.9	235

The solubility parameter of Ultem, δ_2 was determined as a mean value obtained from the slope and intercept of the plots drawn according to Eq. 9. According to Kong et al. [20], δ_2 is determined lower than real δ_2 at high temperatures because of free volume differences between the solvent and the polymer. Kong et al. developed a new model to determine the δ_2 by using inverse gas chromatography method at high temperature. According to this model, Eq. 10 is obtained instead of Eq. 9 by using equation of state parameters at high temperatures as follows:

$$\frac{\delta_{1,0}^2}{RT} - \frac{\chi_{12}^*}{V_1^*} = \left(\frac{2\delta_{2,0}}{RT}\right)\delta_{1,0} - \frac{\delta_{2,0}^2}{RT} \qquad (10)$$

$$\delta_i^2 = \tilde{\rho}_i \delta_{i,0}^2 = \frac{1}{\tilde{V}} \delta_{i,0}^2 \tag{11}$$

where $\delta_{1,0}$ and $\delta_{2,0}$ are the hard-core solubility parameters of the solvent and the polymer, respectively. $\tilde{\rho}_i$ is the reduced density.

The magnitudes of δ_2 was found as a mean value at studied temperatures like in the former procedure [21]. In Figure 3, the solubility parameter of the Ultem, δ_2 at room temperature was estimated approximately as 11.3 (cal/cm^3) $^{1/2}$ and 10.7 (cal/cm^3) $^{1/2}$ from Eq. 9 and Eq. 10, respectively by extrapolating the average values of the δ_2 to 25°C. On the other hand, since χ_{12}^{∞} varies linearly with 1/T, χ_{12}^{∞} values at studied temperatures can be extrapolated to 25°C. By means of Eq. 9, δ_2 was obtained as 10.9 (cal/cm^3) $^{1/2}$ using χ_{12}^{∞} values at 25°C. It is comparable with the values, 11.3 (cal/cm^3) $^{1/2}$ and 10.7(cal/cm^3) $^{1/2}$ calculated from the slope and intercept of the plots drawn according to Eq. 9 and Eq. 10 at 25°C.

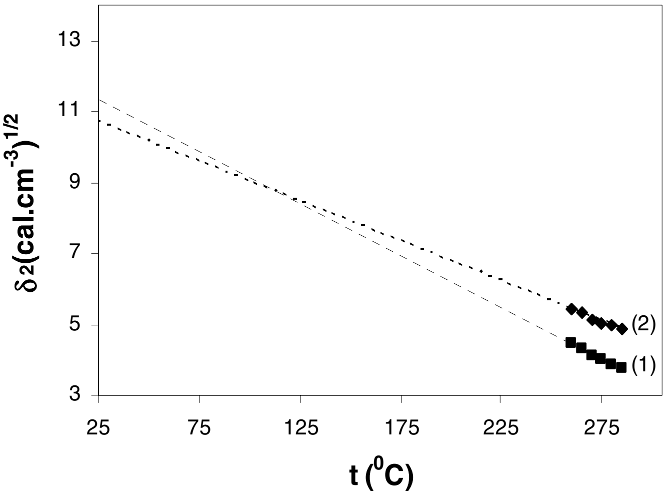

Figure 3. (1) and (2) are extrapolation of δ_2 of Ultem from studied temperatures to 25°C from Eq. 9 and Eq. 10, respectively.

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