

## The ratio of crystallinity and thermodynamical interactions of polycaprolactone with some aliphatic esters and aromatic solvents by inverse gas chromatography

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### Summary

The retention diagrams of benzene, toluene, ethyl benzene, chloro benzene, n-propyl benzene, isopropyl benzene, methyl acetate, ethyl acetate, n-propyl acetate, n-butyl acetate and isoamyl acetate on the polycaprolactone were plotted at temperatures between 70 and 140°C by inverse gas chromatography technique. Percent crystallinity of polycaprolactone were obtained at temperatures below melting point from the retention diagrams of benzene, toluene and ethyl benzene. It was concluded that the data obtained by inverse gas chromatography were comparable those of obtained by differential scanning calorimetry. Specific retention volume,  $V_g^o$ , Flory-Huggins polymer-solvent interaction parameters,  $\chi_{12}^\infty$ , the weight fraction activity coefficients of the solvents at infinite dilution,  $\Omega_1^\infty$ , effective exchange energy parameters,  $X_{\text{eff}}$  were determined. Later, the partial molar heat of sorption,  $\Delta H_{1,\text{sorp}}$  and the partial molar heat of mixing,  $\Delta H_1^\infty$  were obtained from the slope of the logarithm of specific retention volume,  $\ln V_g^o$  versus  $1/T$  plot and from the slope of the logarithm of the weight fraction activity coefficients,  $\Omega_1^\infty$  versus  $1/T$  plot, respectively.

### Introduction

Polycaprolactone (PCL) is a biodegradable and semicrystalline thermoplastic polymer derived from the chemical synthesis of crude oil [1-4]. Although it is not produced from renewable raw materials, it is completely biodegradable. PCL has good water, oil, solvent and chlorine resistance. It has a low melting point (58-60°C) and low viscosity, and it is easy to process. The low melting-point makes the material suited for composting as a means of disposal, due to the temperature obtained during composting routinely exceeding 60°C. Degradation time is very short. PCL is often mixed with starch to obtain a good biodegradable material at a low price. It is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopedic splints and fully biodegradable compostable bags, sutures, and fibres.

Determination of percent crystallinity of polymer is very important, because polymers' usage and solubility properties depend on their crystallinity ratio. Inverse gas chromatography (IGC) is a novel technique for the determination of crystallinity ratio of polymers [5].

In this study, percent crystallinity of PCL were obtained by using benzene, toluene and ethyl benzene as probes by IGC. There is no any other data in literature related to the determination of percent crystallinity of PCL by IGC. In earlier studies, percent crystallinity of PCL was determined by DSC, which needs some data about the crystallinity enthalpy of the 100% crystalline polymer determined by another way. If someone can not find any data in literature or can not measure it, the percent crystallinity can not be determined. However, there is no need any other data to determine the percent crystallinity in IGC technique. It was determined the crystallinity ratio of PCL by IGC and was compared to the data determined by DSC to confirm the reliability of the new technique. We have determined the Flory-Huggins polymer-solvent interaction parameter,  $\chi_{12}^{\infty}$  of PCL with some esters and some aromatic solvents [6-9] at temperature range of 70 and 140°C by using IGC. Then, it was found the effective exchange energy parameter,  $X_{\text{eff}}$  in the equation of state theory which is assumed to be independent of temperature and composition of the mixture [10-12]. However, it has been observed that the parameter,  $X_{\text{eff}}$  is dependent on temperature for some polymer-solvent systems because of enthalpy and entropy contributions [13]. In this study, we also investigated the dependence of  $X_{\text{eff}}$  parameters on temperature.

### Theoretical background

The specific retention volume,  $V_g^{\circ}$  is determined experimentally from IGC measurements as follows [14-17],

$$V_g^{\circ} = Q (t_R - t_A) J 273.2 / (T_r w) \quad (1)$$

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 extrapolation of the straight line above melting point,  $T_m$  to the temperatures below the  $T_m$  makes possible to estimate the specific retention volumes that would correspond to the hypothetical amorphous state of the entire polymer in this temperature range. By applying this approach on the PCL retention diagram, one can calculate the percentage of crystallinity PCL by the equation in the following [5]

$$\text{Percent Crystallinity} = 100 (1 - V_g^{\circ} / V_g^{\circ'}) \quad (2)$$

where  $V_g^{\circ'}$  and  $V_g^{\circ}$  are extrapolated and measured values of the retention volumes at a given temperature, respectively.

The weight fraction activity coefficient of each solvent  $\Omega_1^{\infty}$  is defined by the following equation,

$$\text{Ln}\Omega_1^{\infty} = \text{Ln}(273.2 R / V_g^{\circ} p_1^{\circ} M_1) - p_1^{\circ} (B_{11} - V_1^{\circ}) / RT \quad (3)$$

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 Flory-Huggins and equation-of-state theory, interaction parameters,  $\chi$  are defined in the Eq.(4) and Eq.(5), respectively:

$$\chi_{12}^\infty = \text{Ln} (273.2 R v_2 / p_1^0 V_g^0 V_1^0) - 1 - p_1^0 (B_{11} - V_1^0) / R T \quad (4)$$

where  $v_2$  is specific volume of polymer.

$$\chi_{12}^* = \text{Ln} (273.2 R v_2^* / p_1^0 V_g^0 V_1^*) - 1 - p_1^0 (B_{11} - V_1^0) / R T \quad (5)$$

In the equation of state theory,  $v_r$ ,  $T_r$ , and  $p_r$  which are reduced volume, temperature and pressure, respectively, of the system, are ratios of the actual  $v$ ,  $T$  and  $P$  to characteristic parameters,  $v^*$ ,  $T^*$  and  $p^*$  which can be evaluated from the thermal expansion and pressure coefficients as follows:

$$v_r^{1/3} = (V/V^*)^{1/3} = [(\alpha T/3)/(1+\alpha T)] + 1 \quad (6)$$

$$T_r = T/T^* = (v_r^{1/3} - 1) / v_r^{4/3} \quad (7)$$

$$p^* = \gamma T v_r^2 \quad (8)$$

where  $\alpha$  is the thermal expansion coefficient defined as:

$$\alpha = (1/V) (\partial V / \partial T)_{p=0} \quad (9)$$

and  $\gamma$  is the thermal pressure coefficient defined as:

$$\gamma = (\partial p / \partial T)_v \quad (10)$$

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

$$RT \chi_{12}^* = p_1^* V_1^* \{ 3 T_{1r} \text{Ln} [(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)] + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}} V_1^* v_{2r}^{-1} \} \quad (11)$$

The partial molar heat of sorption,  $\Delta H_{1,\text{sorp}}$  and the partial molar heat of mixing,  $\Delta H_1^\infty$  are calculated from Eq.(12) and Eq.(13), respectively.

$$\Delta H_{1,\text{sorp}} = -R [\partial (\text{Ln } V g^0) / \partial (1/T)] \quad (12)$$

$$\Delta H_1^\infty = R [\partial (\text{Ln } \Omega_1^\infty) / \partial (1/T)] \quad (13)$$

Molar heat of vaporization,  $\Delta H_v$  is related to  $\Delta H_{1,\text{sorp}}$  and  $\Delta H_1^\infty$  as follows:

$$\Delta H_v = \Delta H_1^\infty - \Delta H_{1,\text{sorp}} \quad (14)$$

### Experimental

Benzene (B), toluene (T), ethyl benzene (EB), chloro benzene (CB), n-propyl benzene (nPB), isopropyl benzene (IPB), methyl acetate (MA), ethyl acetate (EA), n-propyl acetate (nPA), n-butyl acetate (nBA), isoamyl acetate (IAA) were Merck AG. Inc. products. Acid washed and dimethyl dichlorosilane treated Chromosorb W (AW-DMCS, 80/100 mesh) was also supplied from Merck AG. Inc. as a support material. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc. PCL was a product of Polysciences Inc, with a number average molecular weight of 33,000 g/mol.

A Hewlett-Packard 5890 Model, series II gas chromatography with a thermal conductivity detector was used in this study. HP-3365 software was used for data acquisition and analysis. The flow rate of the carrier gas was kept below 6 cm<sup>3</sup>/minute. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length. The polymer was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb W in the polymer solution. The loading of the coated polymer on the support was determined as 8.69% by calcination.

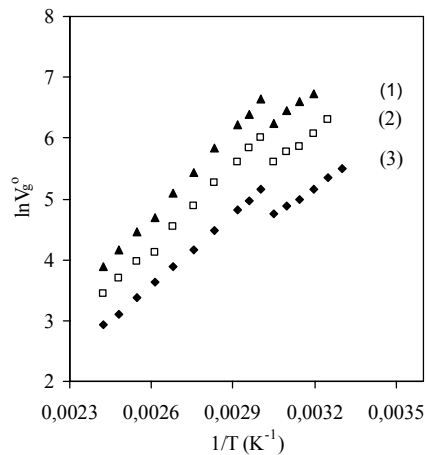
### Results and discussion

The specific retention volumes,  $V_g^0$  of the aliphatic esters and aromatic solvents were obtained experimentally from IGC measurements using Eq.(1). Numeric results and graphical results were given in Table 1 and Fig.1 for B, T and EB between 30 and 140°C, as well as in Fig.2 for CB, nPB, IPB and in Fig.3 for MA, EA, nPA, nBA IAA between 70 and 140°C, respectively.

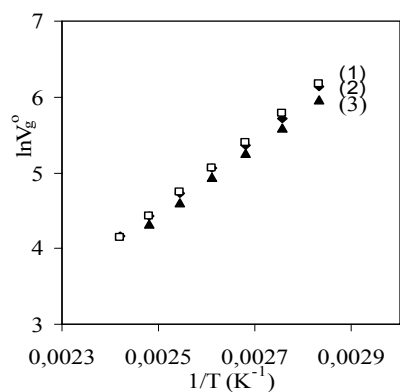
**Table 1.** The specific retention volumes,  $V_g^0$  of the aliphatic esters and aromatic solvents on PCL.

t(°C)	70	80	90	100	110	120	130	140
B	124.72	88.40	64.74	48.45	37.63	29.45	22.32	18.64
T	270.37	191.88	131.14	94.70	61.55	53.25	40.28	31.44
EB	502.77	343.64	228.64	163.09	109.28	86.96	64.20	48.71
CB	---	459.66	301.45	213.67	157.14	113.60	84.25	63.86
nPB	---	---	390.68	268.84	193.08	138.51	99.92	74.80
IPB	---	477.47	324.41	220.37	158.98	115.34	84.13	63.14
MA	45.26	35.98	25.12	19.20	15.14	13.22	9.24	7.99
EA	72.77	52.89	39.09	29.23	22.27	18.25	13.94	11.08
nPA	147.31	103.60	73.83	53.42	39.18	31.84	23.55	18.07
nBA	305.18	209.28	145.85	101.77	73.77	57.24	41.45	30.15
IAA	471.24	313.49	209.25	146.06	103.69	77.34	56.86	41.21

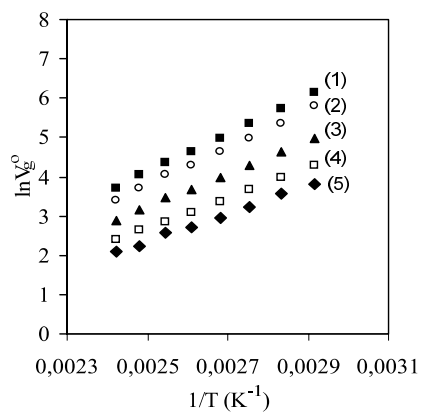
**Figure 1.** The retention diagrams of the ethyl benzene (1), toluene (2) and benzene (3).



**Figure 2.** The retention diagrams of the isopropyl benzene (1), n-propyl benzene (2) and chloro benzene (3).



**Figure 3.** The retention diagrams of the isoamyl acetate (1), n-butyl acetate (2), n-propyl acetate (3), ethyl acetate (4) and methyl acetate (5).



The percent crystallinities of the PCL determined from Eq.(2) and were given in Table 2. The crystallinity of PCL calculated as 55.5% from injection of benzene at 30°C are in agreement with those supplied as 59.1% by differential scanning calorimetry (DSC) [18] at 25°C. This suggest that IGC is a useful tool to determine the crystallinity ratio of a polymer. We reported somewhat lower crystallinity ratio of 45% at 40°C for the same PCL sample determined using tert-butyl acetate, earlier [19]. This can be explained that highly branched solvent (tBA) can not be entirely absorbed by the melted polymer at high temperatures. Therefore, it can be stated that small and unbranched solvent molecules would be better in the determination of percent crystallinity of a polymer.

**Table 2.** Comparison of percent crystallinities of PCL determined by IGC and DSC\*.

t(°C)	B	T	EB
25	59.1*	----	----
30	55.5	----	----
40	51.5	54.1	54.9
45	50.5	52.5	49.5
50	45.8	47.5	45.5
55	43.4	45.0	45.4

The weight fraction activity coefficients at infinite dilution of solvent,  $\Omega_1^\infty$  were determined from Eq.(3) and were given in Table 3. According to Guillet [6], the solvent is good if  $\Omega_1^\infty$  is lower than 5 and is poor if  $\Omega_1^\infty$  is higher than 10. The values between 5 and 10 indicate moderately poor solubility. The parameter  $\Omega_1^\infty$  derived from fundamental relations of physical chemistry does not include any uncertainty coming from theoretical assumptions. The values of  $\Omega_1^\infty$  found in this study suggest that all aromatic solvents and aliphatic esters are good solvents for PCL.

**Table 3.** The weight fraction activity coefficients of the solvents at infinite dilution,  $\Omega_1^\infty$  of PCL with some aromatic solvents and aliphatic esters.

t(°C)	70	80	90	100	110	120	130	140
B	3.29	3.40	3.46	3.54	3.54	3.58	3.79	3.69
T	3.43	3.40	3.58	3.65	4.21	3.73	3.82	3.88
EB	3.82	3.79	3.94	3.94	4.27	3.98	4.07	4.13
CB	---	2.27	2.42	2.45	2.44	2.52	2.59	2.63
nPB	---	---	4.31	4.31	4.24	4.26	4.34	4.35
IPB	---	3.84	3.84	3.96	3.93	3.96	4.05	4.10
MA	4.60	4.31	4.72	4.76	4.81	4.43	5.17	4.96
EA	4.63	4.62	4.66	4.72	4.78	4.60	4.82	4.93
nPA	4.53	4.48	4.48	4.52	4.60	4.32	4.52	4.65
nBA	4.19	4.42	4.37	4.43	4.42	4.22	4.39	4.64
IAA	4.86	4.74	4.74	4.64	4.59	4.41	4.39	4.54

The parameters  $\chi_{12}^\infty$  determined from Eq.(4) were compared with Tian and Munk [20] and Riedl [21] results in Table 4. The parameters,  $\chi_{12}^\infty$  reported by Lezcano [22]

were considerably higher values than those of ours, such as 1.117 for EA, 0.964 for nPA and 0.864 for nBA with PCL at 190°C and they were not included in Table 4.

**Table 4.** Comparison of the  $\chi_{12}^{\infty}$  parameters obtained in this study with literature.

t (°C)	70	80	90	100	110	120	130	140
B	-0.04	-0.02	-0.01	0.00	-0.01	-0.00	0.04	0.01
B[20]	0.03	0.04	0.05	0.07	0.08	---	---	---
T	-0.01	-0.03	0.02	0.03	0.17	0.04	0.06	0.07
T[20]	0.06	0.07	0.07	0.10	0.11	---	---	---
EB	0.10	0.08	0.12	0.11	0.19	0.11	0.13	0.14
EB[20]	0.16	0.16	0.16	0.18	0.19	---	---	---
CB	---	-0.18	-0.12	-0.11	-0.12	0.10	0.08	-0.06
nPB	---	---	0.20	0.20	0.18	0.18	0.20	0.19
IPB	---	0.10	0.10	0.12	0.10	0.11	0.12	0.13
MA	0.35	0.26	0.34	0.34	0.33	0.23	0.37	0.32
MA[20]	0.39	0.39	0.41	0.42	0.42	---	---	---
EA	0.32	0.30	0.29	0.29	0.30	0.31	0.28	0.29
EA[20]	0.36	0.36	0.38	0.39	0.39	---	---	---
EA[21]	---	---	---	---	---	0.42	---	---
nPA	0.29	0.26	0.25	0.25	0.26	0.18	0.22	0.24
nPA[20]	0.34	0.34	0.35	0.35	0.34	---	---	---
nBA	0.21	0.26	0.24	0.25	0.24	0.18	0.21	0.26
nBA[20]	0.31	0.32	0.32	0.33	0.32	---	---	---
IAA	0.40	0.37	0.36	0.33	0.31	0.26	0.25	0.28

The number in the first column indicates the reference number.

The equation of state parameters  $V^*$ ,  $P^*$ ,  $T^*$  were calculated between 70 and 140°C using Equations (6) - (10) and the values at 110 °C were collected in Table 5.

**Table 5.** Equation of state parameters of solutes and PCL at 110°C.

t (°C)	$V^*$ (cm <sup>3</sup> /mol)	$P^*$ (J/cm <sup>3</sup> )	$T^*$ (K)
B	72.17	548	4986
T	89.23	492	5507
EB	103.23	476	5663
CB	83.35	613	5371
nPB	116.88	474	5643
IPB	114.16	481	5349
MA	61.48	623	4411
EA	76.89	559	4548
nPA	91.32	525	4724
nBA	103.69	508	4867
IAA	113.51	490	4994
PCL	91.68	---	---

The parameters  $X_{\text{eff}}$  calculated from Eq.(11) were given in Table 6. It was determined that  $X_{\text{eff}}$  of PCL in B, T, EB, CB, nPB, IPB, MA, EA, nPA and nBA increased with temperature by increasing with decreasing molecular weight of the solvent, but  $X_{\text{eff}}$  of PCL in IAA was almost independent on temperature.

**Table 6.** Effective exchange energy parameters of the equation-of-state theory,  $X_{\text{eff}}$  ( $\text{J}/\text{cm}^3$ ), of PCL with some aromatic solvents and aliphatic esters.

T ( $^{\circ}\text{C}$ )	70	80	90	100	110	120	130	140
B	-20.42	-16.51	-11.23	-8.60	-5.47	-4.05	0.04	0.19
T	-9.66	-8.79	-3.87	-2.34	5.74	-0.08	2.35	3.45
EB	-3.80	-2.98	0.72	1.33	5.88	3.66	4.96	6.14
CB	---	-12.29	-8.95	-7.91	-9.22	-8.77	-6.79	-6.71
nPB	---	---	2.63	3.47	4.37	5.62	6.59	6.97
IPB	---	-0.46	-0.82	0.17	0.32	0.39	1.07	1.44
MA	-13.78	-12.70	-2.80	2.06	5.63	3.32	15.78	15.17
EA	-13.81	-9.29	-4.96	-0.88	2.75	6.92	7.82	10.69
nPA	-11.06	-7.91	-4.78	-1.63	1.45	0.68	4.41	7.04
nBA	-0.48	0.98	0.49	0.94	0.97	-0.62	1.21	3.79
IAA	6.26	5.29	5.19	4.55	4.28	3.02	3.12	4.57

$\Delta H_{1,\text{sorp}}$  and  $\Delta H_1^{\infty}$  were calculated from the slopes of the plots of  $\text{Ln } V_{\text{g}}^{\circ}$  versus  $1/T$  and  $\text{Ln } \Omega_1^{\infty}$  versus  $1/T$  using Eq.(12) and Eq.(13), respectively. The values of  $\Delta H_{\text{v}}$  obtained from Eq. (14) were compared to the values of  $\Delta H_{\text{v}}$  calculated according to the Reference 17. All results were given in Table 7. According to the values of  $\Delta H_1^{\infty}$ , the solubility of PCL in B, T, EB, CB, nPB, IPB, MA, EA, nPA and nBA are slightly exothermic but it is endothermic in IAA.

**Table 7.** The partial molar heat of sorption,  $\Delta H_{1,\text{sorp}}$  (cal/mol) the partial molar heat of mixing,  $\Delta H_1^{\infty}$  (cal/mol), molar heat of vaporization,  $\Delta H_{\text{v}}$  obtained Eq. (9) and molar heat of vaporization,  $\Delta H_{\text{v}}[17]$  (kcal/mol) of solvents.

solvents	$-\Delta H_1^{\infty}$	$-\Delta H_{1,\text{sorp}}$	$\Delta H_{\text{v}}$	$\Delta H_{\text{v}}[17]$
B	0.49	7.7	7.2	7.3
T	0.59	8.7	8.1	7.9
EB	0.35	9.5	9.1	8.5
CB	0.63	9.4	8.8	8.7
nPB	0.062	9.8	9.7	9.1
IPB	0.32	9.7	9.4	9.0
MA	0.42	7.1	6.7	7.2
EA	0.28	7.6	7.3	7.7
nPA	0.041	8.4	8.4	8.2
nBA	0.19	9.4	9.2	8.6
IAA	-0.37	9.7	10.1	9.0



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