Macromol. Symp. **2004**, *217,* 301-306

Determination of Rate of Crystallinity and Thermodynamical Interaction Parameters of Polycaprolactone with Some Solvents by Gas Chromatography

Ayfer Saraç, Özlem Cankurtaran, Ferdane Yilmaz*

Yýldýz Technical University, Department of Chemistry, Davutpasa Campus, 34010 Esenler, Istanbul, Turkey
E-mail: kurtaran@yildiz.edu.tr

Summary: The retention diagram of polycaprolactone for tert-butyl acetate was obtained by inverse gas chromatography method in the temperature range of 40-140 °C. Rate of crystallinity was determined between 45.0 percent and 37.1 percent in the temperatures at 40 and 53 °C, respectively. Thermodynamic interaction parameters were determined for cyclopentane, cyclohexane, tetrahydrofuran and 1,4-dioxane with polycaprolactone between 70 and 130 °C. Specific retention volumes, V_g^o, Flory Huggins polymer-solvent interaction parameters, χ_{12}^{∞}, equation of state polymer-solvent interaction parameters, χ_{12}^{*}, weight fraction activity coefficients of the solvents at infinite dilution, Ω_1^{∞}, effective exchange energy parameters, $\overline{X}_{12}$were determined.

Keywords: chromatography; crystallinity ratio; polycaprolactone; polyesters; thermodynamic interactions

Introduction

Polycaprolactone (PCL) that is a semicrystalline and biodegradable aliphatic polyester is prefered due to lack of toxicity, low cost, hydrolyzability in the human body as well as in natural circumstances and slower rate of degradation than other biodegradable polyesters.[1-4] Thermodynamic interactions of PCL with solvents are important to use it to be a polymeric biomaterial such as a coating material for tablets or capsules.[5] Inverse gas chromatography (IGC) is a very useful technique for the determination of some thermodynamic interaction parameters of a polymer with solvents [6-9] and degree of crystallinity of a polymer.[10] The advantage of IGC method is that it does not need any other data determined by another way like differential scanning calorimetry to determine the ratio of crystallinity.

DOI: 10.1002/masy.200451326

Experimental

Tert butyl acetate (tBA), cyclopentane (c-P), cyclohexane (c-H), tetrahydrofurane (THF) and dioxane (DO) were analytical reagent grade produced by Merck AG., PCL was a product of Polysciences Inc, with a number average molecular weight of 33 000 g mol^{-1}. Chromosorb W (AW-DMCS- treated, 80/100 mesh) which was a Merck AG. product was used as a support material. A Hewlett-Packard 5890 model, series II gas chromatograph with a thermal conductivity detector was used in this study. HP-3365 software was used for data acquisition and analysis.

Theory

The specific retention volume, V_g^o is experimentally determined from IGC measurements as follows [11-13].

$$V_g^o = 273.2\, Q\, (t_R - t_A)\, J\, (w\, T_r)^{-1} \qquad (1)$$

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

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

$$\mathrm{Ln}\, \Omega_1^\infty = \mathrm{Ln}\, [\, 273.2\, R\, /\, (V_g^o\, p_1^o\, M_1)] - p_1^o\, (B_{11} - V_1^o)\, (RT)^{-1} \qquad (2)$$

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

According to Flory-Huggins and equation of state theory, polymer-solvent interaction parameters, χ is defined in the Eq.3 and Eq.4, respectively:

$$\chi_{12}^{\infty} = \mathrm{Ln}\,[273.2\,R\,v_2 / (p_1^{o}\,V_g^{o}\,V_1^{o})] - 1 - p_1^{o}\,(B_{11} - V_1^{o})\,(RT)^{-1} \qquad (3)$$

$$\chi_{12}^{*} = \mathrm{Ln}\,[273.2\,R\,v_2^{*} / (p_1^{o}\,V_g^{o}\,V_1^{*})] - 1 - p_1^{o}\,(B_{11} - V_1^{o})\,(RT)^{-1} \qquad (4)$$

where v_2 and v_2^{*} are specific volume and specific hard-core volume of the polymer, respectively and V_1^{*} is molar hard-core volume of the solvent.

The effective exchange energy parameter, $\overline{X}_{12}$ in the equation of state theory is given in the following relation,

$$RT\chi_{12}^{*} = p_1^{*}V_1^{*}\{3T_{1r}\,\mathrm{Ln}\,[(v_{1r}^{1/3}-1)/(v_{2r}^{1/3}-1)] + v_{1r}^{-1} - v_{2r}^{-1}\} + \overline{X}_{12}V_1^{*}v_{2r}^{-1} \qquad (5)$$

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

Results and Discussion

The specific retention volumes of the solvents, V_g^{o} were obtained from IGC measurements according to Eq.1. Fig.1 represents the retention diagram of tBA on PCL between 40 and 140 °C. Determination of crystallinity of a polymeric stationary phase is based on the different solubilities of the solvent in the crystalline and amorphous regions.[10] By assuming as the crystalline regions do not participate in the retention of the molecules of the solvent in the range below melting point, T_m, it is possible to estimate the degree of crystallinity of the polymer. The extrapolation of the line above T_m into the temperature range below T_m makes possible to estimate the retention volume that would correspond to the hypothetical amorphous state of the entire polymer at temperatures below T_m. By applying this on the retention diagram in the Fig.1, one can calculate the percentage of crystallinity of PCL by Eq.6,

$$\text{Percent Crystallinity} = 100\,(1 - V_g^{o} / V_g^{o'}) \qquad (6)$$

where $V_g^{o'}$ and V_g^{o} are extrapolated and measured values of the retention volumes at a given temperature, respectively. From injection of tBA, the crystallinity of PCL was calculated as 45 % and 37 % at 40°C and 53°C, respectively.

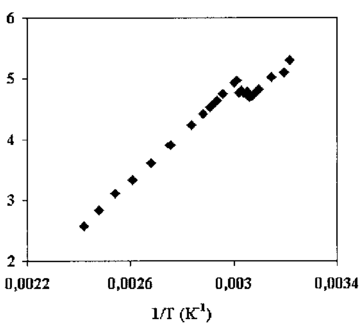

Fig. 1. The retention diagram of tBA on PCL.

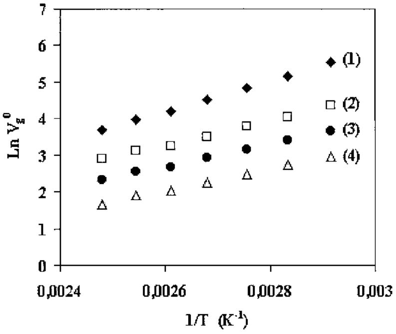

Fig. 2. The retention diagrams of DO (1), THF(2), c-H (3) and c-P (4) on PCL.

Fig.2. represents the retention diagrams of c-P, c-H, THF and DO on PCL between 70 and 130 °C. The parameters Ω_1^∞ and χ_{12}^∞ determined according to Eq. 2 and Eq.3 were given in Table 1.

Table 1. Weight fraction activity coefficients at infinite dilution of the solvents, Ω_1^∞ and Flory-Huggins polymer-solvent interaction parameters, χ_{12}^∞ for PCL.

	c-P		c-H		THF		DO	
T(° C)	Ω_1^∞	χ_{12}^∞	Ω_1^∞	χ_{12}^∞	Ω_1^∞	χ_{12}^∞	Ω_1^∞	χ_{12}^∞
70	9.26	0.82	9.79	0.92	3.66	0.15	2.91	0.00
80	8.83	0.76	9.31	0.86	3.69	0.15	2.98	0.02
90	9.12	0.78	9.22	0.84	3.64	0.13	2.97	0.01
100	9.09	0.76	8.72	0.79	3.70	0.14	2.95	-0.01
110	9.04	0.74	8.78	0.79	3.76	0.14	3.11	0.04
120	8.56	0.68	7.92	0.68	3.48	0.05	2.95	-0.03
130	9.06	0.72	8.13	0.70	3.53	0.05	2.99	-0.02

If Ω_1^∞ and χ_{12}^∞ are lower than 5 and 0.5, respectively, the solvent is good for the polymer, however, if they are higher than 10 and 0.5, it is poor solvent for the polymer.[14] The values of

Ω_1^{∞} and χ_{12}^{∞} suggest that c-P and c-H were moderately poor solvents for PCL which has ester groups in the backbone but THF and DO with their etheric oxygen derivatives were good solvents. It seems that introduction of etheric oxygen into the aliphatic hydrocarbon create some favorable interactions between etheric oxygens of the solvents and ester group of the PCL. Polymer-solvent interaction parameters, χ_{12}^{*} and effective exchange energy parameters in the equation of state theory, $\overline{X}_{12}$ were calculated from Eq. 4 and Eq.5, respectively. Results were given in Table 2.

Table 2. Polymer-solvent interaction parameters, χ_{12}^{*} and effective exchange energy parameters, $\overline{X}_{12}$(J/cm^3) of the equation of state theory, for PCL.

	c-P		c-H		THF		DO	
T(° C)	χ_{12}^{*}	$\overline{X}_{12}$	χ_{12}^{*}	$\overline{X}_{12}$	χ_{12}^{*}	$\overline{X}_{12}$	χ_{12}^{*}	$\overline{X}_{12}$
70	0.98	28.09	1.04	29.95	0.30	-4.78	0.11	-9.40
80	0.93	26.99	0.97	30.72	0.31	-5.11	0.14	-10.12
90	0.97	28.84	0.95	31.91	0.29	-3.50	0.12	-8.74
100	0.96	30.30	0.88	31.04	0.30	-3.04	0.12	-10.5
110	0.96	30.90	0.87	32.95	0.32	-2.08	0.16	-5.98
120	0.88	30.25	0.76	29.58	0.25	-9.08	0.11	-9.90
130	0.94	34.18	0.76	31.48	0.26	-7.51	0.13	-10.23

The values of $\overline{X}_{12}$ of the cyclic hydrocarbons are approximately fourty times higher than those of their etheric oxygen derivatives. In conclusion, small values of $\overline{X}_{12}$ denote specific favorable interactions between polymer and solvent. This study suggests that the values of $\overline{X}_{12}$ are a better indicator than the values of weight fraction activity coefficents of the solvents and interaction parameters to reflect favorable interactions between polymer and solvent, consequently solvent quality.

Acknowledgement

This study was supported by the Scientific Research Projects Coordination Center of the Yildiz Technical University.

[1] S. H. Rhee, J.Y. Choi and H. Kim, Biomaterials **2002**, 33, 24, 4915.
[2] F. Kawai , Adv. Biochem Eng Biotechnol **1995**, 52, 151.
[3] W.J. Lin and C.H. Lu, Journal of Membrane Science **2002**, 198, 1, 109.
[4] C.G. Pitt, T.A. Marks and A. Schindler, "Biodegradable Drug Delivery Systems Based Upon Aliphatic Polyesters: Application to Contraceptives and Narcotic Antagonists", In: R. Baker, Editor, Academic Press, New York **1980**, 232.
[5] G. Seretoudi, D.Bikiaris and C. Panayiotou, Polymer **2002**, 43, 20, 5405.
[6] D.G. Gray, "Gas Chromatographic Measurements of Polymer Structure and Interactions", In: A.D. Jenkins, Editor, in Progress in Polymer Science **1977**, 5, Pergamon Press, Oxford, 1.
[7] V.G. Berezkin, I.B. Alishoyev, I.B. Nemirovskaya, "Gas Chromatography", Elsevier Scientific Pub Co Amsterdam **1977**, 195.
[8] J.S. Aspler, "Theory and Applications of Inverse GC" in "Chromatographic Science", In: S.A.Liebman and E.J. Levy, Editor, 29, Marcel Dekker, New York **1985**, 399.
[9] R. Vilcu , M. Leca , Studies in Polymer Science, 4, Amsterdam: Elsevier, Editura Academiei Romane **1990**, 132.
[10] J.E. Guillet, "Study of Polymer Structure and Interactions by Inverse Gas Chromatography", in: New Development in Gas Chromatography, J.H. Purnel Ed Wiley-Interscience, New York, **1973**.
[11] B.E. Eichinger and P.J. Flory, Trans Faraday Soc. **1968** ,64, 2035.
[12] B.E. Eichinger and P.J. Flory, Trans Faraday Soc. **1968**, 64, 2053.
[13] B.E. Eichinger and P.J. Flory, Trans Faraday Soc. **1968**, 64, 2061.
[14] J.E. Guillet and J.H. Purnell, "Advances in Analytical Chemistry and Instrumentation Gas Chromatography", John Wiley and Sons, New York, **1973**.