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Secondary transitions and thermodynamic interaction parameters of poly (phenyl sulfone) by gas chromatography

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Summary

Trace amount of solvents such as n-octane, n-nonane, n-decane, isopropyl acetate, tert-butyl acetate and isoamyl acetate were passed through the column of a gas chromatograph, which stationary phase is poly (phenyl sulfone) trademarked as Radel®R. The retention diagrams were obtained by plotting the logarithm of the specific retention volumes of the solvents against reciprocal of the absolute column temperature between 50 and 280 °C. The slope changes on the diagram were assigned as secondary transitions. Three secondary transition temperatures were established at 140, 110 and 80 °C below glass transition temperature, 210 °C. Weight fraction activity coefficients of the solvents at infinite dilution, Ω_1^∞ and hard-core polymer solvent interaction parameters χ_t^∞ were given for the studied solvents at 250 °C. The values of the parameters Ω_1^∞ and χ_t^∞ suggest that n-alkanes are very poor whereas esters studied are moderately poor solvents for poly (phenyl sulfone) at 250 °C.

Introduction

Poly (phenyl sulfone) (PPSf) is an amorphous polymer with high thermal capability, exceptional toughness and high impact strength. In addition, there was a large endothermic peak between room and glass transition temperatures on the differential scanning calorimeter traces of PPSf [1]. These properties imply that some energy absorbing molecular motions should exist in the polymer below glass transition i.e, β - transition, γ - transition and so on. The values of these secondary transitions design the use of a polymer as a material absorbing heat, noise and impact shock.

Inverse gas chromatography (igc) [2] 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. In the igc technique, a known volatile substance was passed through a gas chromatographic column by means of an inert carrier gas. The column was packed with a polymer as a stationary phase on an inert support. The difference is that the polymer in the column was examined instead of volatile substance in the igc technique although the experimental procedure is completely same with common analytical gas chromatography.

Several investigators have observed that bisphenol A polysulfone (BAPSf) exhibits multiple secondary transitions. Dangayach and Bonner [3] have reported the existence of two intermediate secondary transition temperatures in the BAPSf at 120 and 140 °C below the glass transition temperature (190 °C) by using igc technique. Fried and Kalkanoglu [4] have reported also two secondary transitions occurring at –100 and 60 °C below the glass transition temperature of BAPSf (202 °C) by dynamic mechanical analysis.

In this study, we aimed to observe the secondary transitions of PPSf, which is another polysulfone, trademarked as Radel®-R, by igc in order to establish the reliability of the method in determination of secondary transition temperatures. In addition, weight fraction activity coefficient of the solvents at infinite dilution, Ω_1^∞ and hard-core polymer solvent interaction parameter, χ_t^∞ related to solubility of the polymer were determined at 250 °C.

Theoretical Background

As the temperature of a polymer is lowered, the glass transition is called as α- and successively lower temperatures are customary called as β-, γ-, δ- transition temperatures [5]. The transitions are caused by rotations of side groups around an axis which is perpendicular to the chain, by the motion of sequences of 3 - 5 methylenic groups (Schatzki's crankshaft effect) or by motions of chain portions in polymers containing heteroatoms in the main chain [2]. Such transitions may be demonstrated by igc [2, 3, 5]. The mechanism of these transitions observed on the retention diagrams is not yet clear.

In order to obtain a retention diagram of a solvent on a polymer loaded in the column as a stationary phase, one needs specific retention volume, V_g^o of the solvent on the polymer, defined by Littlewood [6] as

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

where Q is volume flow rate measured at column outlet at room temperature, T_r; J is pressure drop correction factor which equals to $[3(p_i/p_o)^2-1] / [2(p_i/p_o)^3-1]$ where p_i and p_o are column inlet and outlet pressures, respectively; t_R and t_A are retention times of the solvent and air, respectively and w is total mass of the polymer in the column. Thus, specific retention volume of a solvent is the volume of the carrier gas, measured at 273.2 K and corrected for column pressure drop, which will elute the vapor from the column containing 1 g of the polymer as a stationary phase.

The magnitude of an activity coefficient of a solvent reflects the extent of the thermodynamic interactions of the components in the mixture. Patterson *et al.*[7] defined weight fraction activity coefficient of a solvent at infinite dilution, Ω_1^∞ as

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

where R is universal gas constant; T is absolute column temperature; M_1, p_1^O, V_1 and B_{11} are molecular weight, saturated vapor pressure, liquid molar volume and second virial coefficient of the solvent, respectively. The equation given above is derived from the fundamental physicochemical concepts thus Ω_1^∞ does not include any uncertainty arising from assumptions of any theoretical model of polymer solutions.

In the equation of state theory, Flory and co-workers [8] have defined a different interaction parameter, χ, from the one in the Flory-Huggins theory. In this definition, molar and specific hard-core volumes of the components were used instead of their molar and specific volumes and segment fraction of the polymer was used instead of its volume fraction. We have used the interaction parameter defined in the equation of state theory with the symbol of χ_t^∞. The reason of infinitive superscript is that the polymer concentration is very high since trace amount solvent is used during igc measurements. Therefore, the parameter χ_t^∞ obtained by igc quantifies the interaction between polymer and solvent at infinite dilution of the solvent in the mixture. The parameter χ_t^∞ is obtained by the following equation [7],

$$\chi_t^\infty = \mathrm{Ln}\,(273.2\,R\,v_2^* / p_1^o\,V_g^o\,V_1^*) - (1 - V_1^* / M_2 v_2^*) - p_1^o (B_{11} - V_1) / RT \qquad (3)$$

where V_1^* is characteristic liquid molar hard-core volume of the solvent; v_2^* and M_2 are characteristic specific hard-core volume and molecular weight of the polymer, respectively. The characteristic volumes are calculated by using the following equations from the thermal expansion coefficients, α of the pure components as follows

$$v_r^{1/3} = (V/V^*)^{1/3} = [(\alpha T / 3) / (1 + \alpha T)] + 1 \qquad (4)$$

$$\alpha = (1 / V)\,(\partial V / \partial T)_{p=0} \qquad (5)$$

where v_r is reduced volume of the pure component.

Experimental

PPSf trademarked as Radel®R was a product of Amoco Corp. with a number-average molecular weight of 2.8×10^4. n- Oktane (nO), n- nonane (nN), n- dekane (nD), isoamyl acetate (IAA) and chloroform were analytical reagent grade produced by Merck AG and were used without further purification. Chromosorb - W (AW - DMCS treated, 80/100 mesh) was also supplied from Merck AG. Inc. and was used as a support material in the column. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

A Hewlett - Packard 5890 Model, series II gas chromatograph with a thermal conductivity detector was used in this study. Data acquisition and analysis was performed by means of HP - 3365 software.

The flow rate of the carrier gas (He) was kept below 6 cm^3 per minute measured by a soap bubble flow meter. Before the experiments, it was determined that the retention volume does not depend on the flow rate of the carrier gas below this flow rate. The polymer was coated on support by slowly evaporation of chloroform as stirring the Chromosorb W in the polymer solution. The proportion of polymer on the support was determined as 7.24 % by calcination. The column was stainless steel tubing with 3.2 mm o.d. and 1 m in length. Trace amount of solvent was injected into the column.

Results and discussion

The specific retention volumes of the solvents on PPSf were determined by using eqn. 1. The percent error in V_g^0 was calculated as less than 1 by using three or four successive measurements of each datum. The slope changes in the retention diagrams, i.e., Ln V_g^0 versus 1/T plots were assigned as secondary transition temperatures of the polymer. More clearly, the first deviated point from linearity at lower temperature side of the diagram was accepted as a secondary transition temperature of the polymer. The α-(glass-), β-, γ- and δ- transition temperatures of the polymer were accepted as 210, 140, 110 and 80 °C, respectively, from change of the slope in the retention diagrams of the solvents on the PPSf, by considering both of the plots given in Figure 1 and 2.

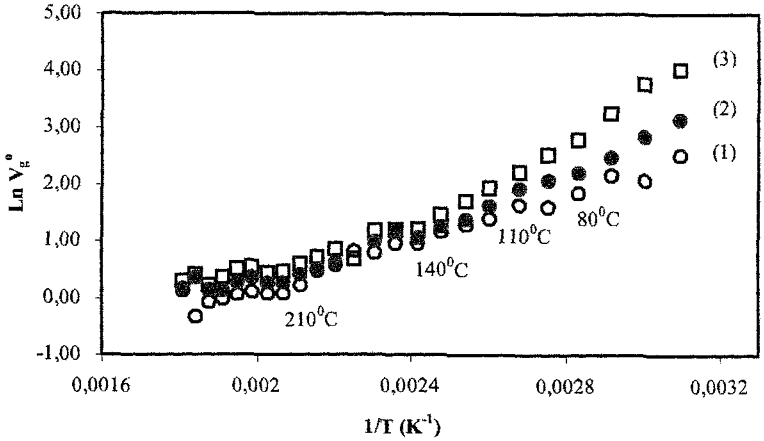

Figure 1. Retention diagrams of n - octane (1), n - nonane (2) and n - decane (3) on PPSf

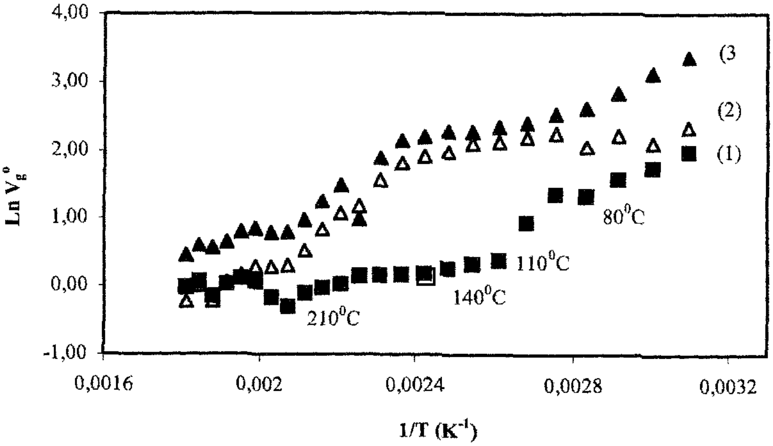

Figure 2. Retention diagrams of tert - butyl acetate (1), isopropyl acetate (2) and isoamyl acetate (3) on PPSf.

It seems that n-alkanes do not reflect obviously the transitions at lower temperatures however esters especially tert-butyl acetate indicates them more evidently. This suggests that branched solvents are better to reveal the secondary thermal transitions of a polymer by igc. The β - transition temperature (140°C) observed in this study is the same with that of given by Dangayach and Bonner for BAPSf. The γ - transition temperature (110 °C) observed in this study is comparable with the value (120 °C) given by the same authors. The δ - transition temperature (80 °C) is also comparable with the value (60 °C) given by Fried and Kalkanoglu. The deviations may arise from the different structures of the polymers used in these studies. The repeating units of BAPSf and PPSf are $\text{-(-O-Ø-SO}_2\text{-Ø-O-Ø-C(CH}_3)_2\text{-Ø-)}_n\text{-}$ and $\text{-(-O-Ø-SO}_2\text{-Ø-O-Ø-Ø-)}_n\text{-}$, respectively, where Ø indicates phenylene group. The values obtained in this study are compared to those in the literature in Table 1 by calling δ- and ε-transitions instead of β- and γ- transitions named by Fried and Kalkanoglu.

Table 1. Comparison of the transition temperatures obtained in this study with literature.

Reference Polymer	Fried-Kalkanoglu[4] (BAPSf)	Dangayach-Bonner[3] (BAPSf)	This study (PPSf)
Transition		Temperature(°C)	
α - (T_g)	202[a]	appr. 190[b]	210
β -	--	140[b]	140
γ -		120[b]	110
δ -	60[a]	--	80
ε -	-100[a]	--	--

[a]: from Ref [4]
[b]: from Ref [3]

There is no any study related to the secondary transitions of PPSf in the literature. The closeness of the secondary transition temperatures of BAPSf and PPSf suggests that similar thermal relaxation mechanisms are valid in the polymers belonging to the polysulfone family. The transition at 140 °C may arise from the motion of $-\text{SO}_2-$ group in the backbone since the group presents in the same position in both polymer.

There is only a few study related to determination of the secondary transitions of the polymers in the literature [2, 3, 5]. Therefore the method needs lots of studies to confirm the reliability of the method and this study exhibits its reliability.

The magnitude of activity coefficient of a solvent reflects the solubility properties of the polymer in the solvent. According to Guillet, [9] the solvent is good if Ω_1^∞ is lower than 5 and is poor if Ω_1^∞ is higher than 10. The values between 5 and 10 indicate moderately poor solubility. The values of the parameters Ω_1^∞ and χ_t^∞ found by Eqns. 2 and 3, respectively, are given in Table 2.

Table 2. Weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^∞ and hard - core polymer solvent interaction parameters χ_t^∞ at 250 °C

Solvent	nO	nN	nD	IPA	tBA	IAA
Ω_1^∞	22.3	25.4	26.9	11.3	9.0	10.2
χ_t^∞	1.56	1.71	1.78	0.58	0.49	0.72

The values of the parameters suggest that n - alkanes are very poor however esters are slightly poor solvents for PPSf.

In conclusion, this study suggests that igc is a very useful and reliable technique to observe secondary transitions of a polymer if a branched solvent is used. In addition, this technique is fast as well as cheap since small amount of the polymer and solvents are sufficient. The gas chromatograph used is also available almost in every research laboratory.

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