Thermophysical properties of polymer–probe pairs by gas chromatography

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The chromatographic technique of measuring thermophysical parameters at infinite dilution is applied for polyisobutylene (PIB), antishock polystyrene (high-impact polystyrene) and styrene–butadiene rubber (SBR) using benzene, cyclohexane, n-hexane and n-pentane as probes. The experiments were performed for antishock polystyrene in the temperature range of 313.3 to 402.3 K, for SBR in the temperature range of 343.3 to 363.2 K and for PIB at 313.1 and 323.1 K. The chromatographic retention data obtained at these temperatures were used to determine the Flory–Huggins interaction parameter, weight fraction infinite dilution activity coefficient and diffusion coefficient. In addition, the glass transition temperature of antishock polystyrene was estimated.

(Keywords: polymer–probe pairs; inverse gas chromatography; diffusion coefficients; glass transition temperature; Flory–Huggins parameter; Van Deemter curves)

INTRODUCTION

The main purpose of this study[1] was to obtain certain thermophysical parameters of industrially important polymers, namely polyisobutylene (PIB), antishock polystyrene and styrene–butadiene rubber (SBR), with different probes by using inverse gas chromatography. This technique is preferred to static techniques because it is simple, economical, practical and requires very small amounts of polymer and solvent[2–6].

EXPERIMENTAL

Equipment

The gas chromatograph used was a Shimadzu Moduline GC-8APT with a thermal conductivity detector, Shimadzu R-111 recorder and Shimadzu C-R1B data processor. Column oven temperature was measured within ±0.1°C by use of the Meter Digital Thermometer (model D96M). The inlet pressure of the column was read by a mercury manometer with a precision of ±1 mmHg (up to 1 atm). At high pressures, the mercury manometer could not be used and the pressure was directly read on the apparatus with a precision of $\pm 0.25\ \mathrm{kg\ cm^{-2}}$. Helium was used as the carrier gas and its flow rates, in the range of $10\text{–}150\ \mathrm{ml\ min^{-1}}$, were measured at room temperature by a soap-film flowmeter. The retention times were obtained by using the data processor. The experimental set-up is given elsewhere[1].

Column preparation

The stationary phases were coated onto Chromosorb P, AW-DMCS by dissolution in benzene by gentle mixing and slow evaporation. When constant weight was attained, the coated Chromosorb was then filled in to a 100 cm long and 0.3175 cm i.d. stainless-steel tube with the aid of a mechanical vibrator and vacuum pump. Loadings of approximately 10% by weight were used for all of the three kinds of polymers studied.

Antishock polystyrene and SBR were supplied by Petkim Petrokimya A.S. Yarimca, Turkey. SBR contains approximately 25% styrene and 75% butadiene[7]. Antishock polystyrene represents the class of rubber-modified styrene polymers and it is a high-impact polystyrene. It contains about 5–10% polybutadiene[7]. The number average molecular weights of the antishock polystyrene, SBR and PIB were determined as 73 000 ± 1000, 170 000 ± 3000 and 860 000 ± 2000, respectively, by a membrane osmometer in the Physical Chemistry Laboratories of Professor Dr Bahattin Baysal in I.T.U.

Other experimental details are given in the literature[1,5].

DATA ANALYSIS

The specific retention volume (V_g^0) corrected to 0°C can be obtained as the volume per unit weight of the polymer, from the following expression[5,8,9]:

$$V_g^0 = Q(t_R - t_A)\left(\frac{273.2}{T_{rm}}\right)\left(\frac{f_p}{m_2}\right) \quad (1)$$

where Q is the carrier gas flow rate at room temperature, t_R is the retention time of solute, t_A is the retention time of air, f_p is the pressure correction factor[8], T_{rm} is room temperature and m_2 is the amount of polymer loaded into the column. Here, air is a reference gas not taking part in any retention mechanism with the stationary phase in the column.

The weight fraction infinite dilution activity coefficient (Ω_1^∞) is calculated by the relation[2]:

$$\ln \Omega_1^\infty = \ln\left(\frac{273.2R}{P_1^s V_g^0 M_1}\right) - \frac{P_1^s}{RT}(B_{11} - V_1) \quad (2)$$

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Table 1 Comparison of χ^* values[a] of PIB with those in the literature[17]

T (K)	Probe	V_g^0 (ml g^{-1})	Ω_1^∞	χ^* This work	χ^* Lit.
313.1	Benzene	191.18	6.35	0.93	0.96
	Cyclohexane	229.48	4.90	0.53	0.54
	n-Pentane	39.04	7.46	0.77	0.801
323.1	Benzene	131.40	6.96	0.91	0.92
	Cyclohexane	157.97	4.90	0.52	0.53
	n-Pentane	29.19	7.42	0.76	0.797

[a] Based on hard-core volumes

Table 2 Specific retention volumes, weight fraction infinite dilution activity coefficients and Flory–Huggins interaction parameters of benzene, cyclohexane and n-hexane with SBR at various temperatures

Probe	Temp. (K)	V_g^0 (ml g^{-1})	Ω_1^∞	χ
Benzene	343.3	95.94	4.23	0.33
	353.3	74.44	4.04	0.27
	358.3	63.92	4.03	0.26
	363.2	55.01	4.02	0.25
Cyclohexane	343.3	58.06	6.58	0.66
	353.1	43.60	6.48	0.63
	358.3	37.94	6.43	0.61
	363.2	32.57	6.43	0.60
n-Hexane	343.3	26.46	10.34	0.94
	353.1	19.98	10.09	0.90
	358.3	16.35	9.24	0.80
	363.2	14.41	9.03	0.77

where P_1^s is the vapour pressure of the probe, M_1 is the molecular weight of the probe molecule, B_{11} is the probe vapour second virial coefficient and V_1 is the probe molar volume. The solvent volatility at large polymer concentrations is related to the infinite dilution activity coefficient. It also provides a convenient measure of comparing polymer–probe interactions for a series of probes with a given polymer[2].

The Flory–Huggins interaction parameter (χ) can be obtained from the following expression[10]:

$$\chi=\ln\left(\frac{273.2RV_{2sp}}{V_g^0P_1^sV_1}\right)-\left(1-\frac{V_1}{\bar{M}_nV_{2sp}}\right)-\frac{P_1^s}{RT}(B_{11}-V_1) \quad (3)$$

where V_{2sp} is the liquid polymer specific volume and $\bar{M}_n$ is the number average molecular weight of the polymer.

Van Deemter *et al.*[11] related peak broadening to column properties through the relation:

$$H=A+(B/u)+Cu \quad (4)$$

where H is the plate height, u is the linear velocity of the carrier gas, and A, B, C are constants independent of flow rate. The constant C is given as[12,13]:

$$C=(8/\pi^2)(d_f^2/D_1)[k/(1+k)^2] \quad (5)$$

where d_f is the thickness of the stationary phase, D_1 is the diffusion coefficient of the vapour in the stationary phase and k is the partition coefficient ratio, which is defined as:

$$k=(t_R-t_A)/t_A \quad (6)$$

The generalized retention diagram of the logarithm of the specific retention volume *versus* reciprocal of the absolute temperature is a linear plot in the absence of any transitions. A Z-shaped curve is indicative of a glass transition. From such a diagram, the glass transition temperature of antishock polystyrene was estimated[14–16].

RESULTS AND DISCUSSION

Experimental data were obtained for PIB with three probes at two different temperatures (313.1 and 323.1 K) for comparison with data reported in the literature. The values of χ^* obtained for PIB by using hard-core volumes (V_1^* for V_1 and V_{2sp}^* for V_{2sp} in equation (3)) for 10% loading are given in *Table 1*. The χ^* values of this study are compared with those given in the literature[17,18]. During the calculation[10] of χ^*, the V_1^* and V_{2sp}^* values were used as given by Bonner and Prausnitz[19].

Retention volumes, weight fraction activity coefficients and Flory–Huggins interaction parameters obtained for three solvents with antishock polystyrene and SBR are shown in *Tables 2–4*. As can be seen from these tables, benzene appears to have the lowest values of χ and Ω_1^∞, and hence it is the most suitable solvent for both antishock polystyrene and SBR.

Plots of χ against temperature for antishock polystyrene using n-hexane, benzene and cyclohexane are shown in *Figure 1*. It is evident that all systems exhibit a

Table 3 Specific retention volumes, weight fraction infinite dilution activity coefficients and Flory–Huggins parameters of n-hexane with antishock polystyrene at various temperatures

Temp. (K)	V_g^0 (ml g^{-1})	Ω_1^∞	χ
313.3	46.96	15.36	1.41
323.2	33.43	15.16	1.38
328.3	28.09	15.01	1.36
333.1	24.74	14.82	1.34
343.3	18.5	14.78	1.32
353.1	13.92	14.50	1.28
363.2	12.48	11.87	1.06
373.3	11.73	9.84	0.85
382.3	9.37	9.67	0.81
390.3	7.70	10.34	0.87
394.1	6.81	11.04	0.92
402.3	5.47	11.26	0.93

Table 4 Specific retention volumes, weight fraction infinite dilution activity coefficients and Flory–Huggins interaction parameters of benzene and cyclohexane with antishock polystyrene at various temperatures

Probe	Temp. (K)	V_g^0 (ml g^{-1})	Ω_1^∞	χ
Benzene	363.3	48.24	4.58	0.40
	373.3	44.24	3.73	0.18
	385.2	34.77	3.72	0.16
	388.2	30.57	3.86	0.19
	396.6	24.98	4.19	0.26
Cyclohexane	363.3	25.46	8.24	0.87
	373.3	24.52	6.48	0.62
	385.2	19.32	6.30	0.57
	388.2	16.62	6.84	0.65
	396.6	14.1	7.18	0.69

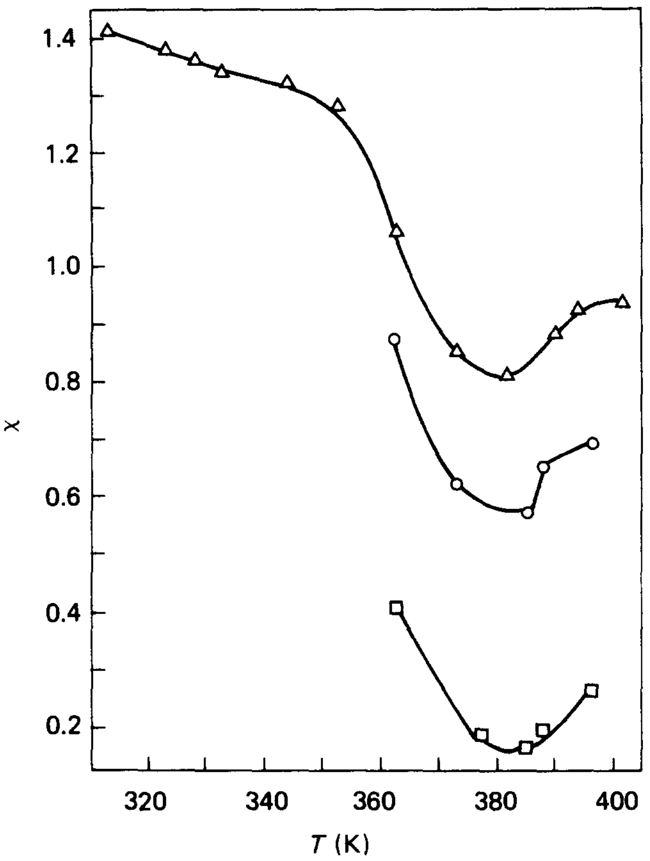

Figure 1 Plots of χ against temperature for probe–antishock polystyrene binary systems: △, n-hexane; ○, cyclohexane; □, benzene

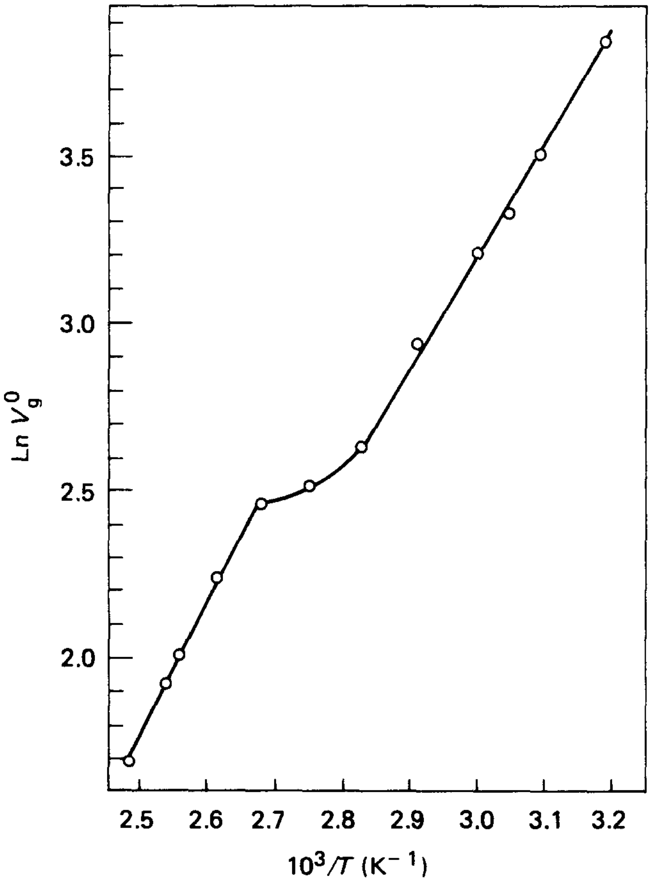

Figure 2 Glass transition curve of antishock polystyrene using n-hexane

similar type of behaviour. In particular, all plots show a positive minimum and curvature which remains positive throughout the range of temperatures investigated. A partial explanation of the exhibition of minima in χ vs. T plots is given by Patterson and Kuwahara[20]. They expressed χ as follows:

$$\chi = -(U/RT)v^2 + (C_p/2R)\tau^2 \qquad (7)$$

where $-U$ is the energy of vaporization of the solvent, C_p is the configurational heat capacity, and R is the gas constant. The parameter v is related to the difference of cohesive energy and size between the solvent molecule and polymer segments. The parameter τ reflects the free volume change which occurs on mixing the dense polymer with the solvent. The variation of the two terms on the right-hand side of equation (7) with temperature were discussed by Patterson[20] and Kuwahara[21] who concluded that the first term, which represents the contact energy dissimilarity and is positive, should decrease with an increase in temperature, while the second term, reflecting the free volume dissimilarity, should increase without limit. This situation would clearly explain why plots of χ vs. T show a minimum.

Ln V_g^0 vs. $1/T$ was plotted for antishock polystyrene to estimate its glass transition temperature. n-Hexane was injected into the column at 12 different temperatures selected in the temperature range of 313.3 to 402.3 K. It is reported[22] that heterogeneous polymer systems such as high-impact polystyrene (antishock polystyrene) exhibit glass transitions for each of the individual polymers present, although some shifting and broadening are almost always observed as well. Therefore, antishock polystyrene reveals its heterogeneous nature by showing the two distinct damping peaks, i.e. the rubber peak at −80°C to −95°C and the polystyrene peak at about 80°C to 90°C. As seen from *Figure 2*, the glass transition is at about 80±5°C. The reason for selecting n-hexane as a probe was based on the study of Braun and Guillet[23]. They have shown that both solvent and non-solvent probes should be appropriate for such experiments.

The diffusion coefficients obtained in this study are given in *Tables 5* and *6*. The numerical values of the partition ratio k and slope of curve C were also included in the tables at all temperatures. The results of a series of experiments to measure the amount of peak spreading as a function of flow rate are shown in *Figure 3*. When sufficiently slow flow rates are employed, the plate heights can be seen to pass through a minimum, as shown in

Table 5 Diffusion coefficients of benzene, cyclohexane and n-hexane in SBR at various temperatures

Probe	Temp. (K)	Van Deemter C term ($\mathrm{s} \times 10^3$)	k	D_1 ($\mathrm{cm^2\,s^{-1}} \times 10^7$)
Benzene	343.3	4.7±0.1	7.0	4.2
	353.1	4.2±0.9	4.9	6.1
	363.1	2.9±0.1	4.0	9.8
Cyclohexane	243.3	9.8±0.9	4.2	2.9
	353.1	10.5±1.0	3.2	3.2
	363.1	14.5±0.1	2.7	3.7
n-Hexane	343.3	18.9±0.1	1.8	2.2
	353.1	18.3±0.2	1.4	2.4
	363.1	16.0±0.1	1.3	2.8

Table 6 Diffusion coefficients of benzene, cyclohexane and n-hexane in antishock polystyrene at various temperatures

Probe	Temp. (K)	Van Deemter C term ($s \times 10^3$)	k	D_1 ($cm^2 s^{-1} \times 10^8$
Benzene	382.3	59 ± 0.2	2.3	6.4
	394.1	53 ± 2.0	2.0	7.7
	402.3	49 ± 1.0	1.6	8.8
Cyclohexane	382.3	77 ± 1.0	1.3	5.7
	394.1	76 ± 3.0	1.2	6.0
	402.3	66 ± 1.0	1.0	6.9
n-Hexane	382.3	81 ± 0.6	0.6	5.3
	394.1	69 ± 0.5	0.5	5.9
	402.3	60 ± 2.0	0.4	6.2

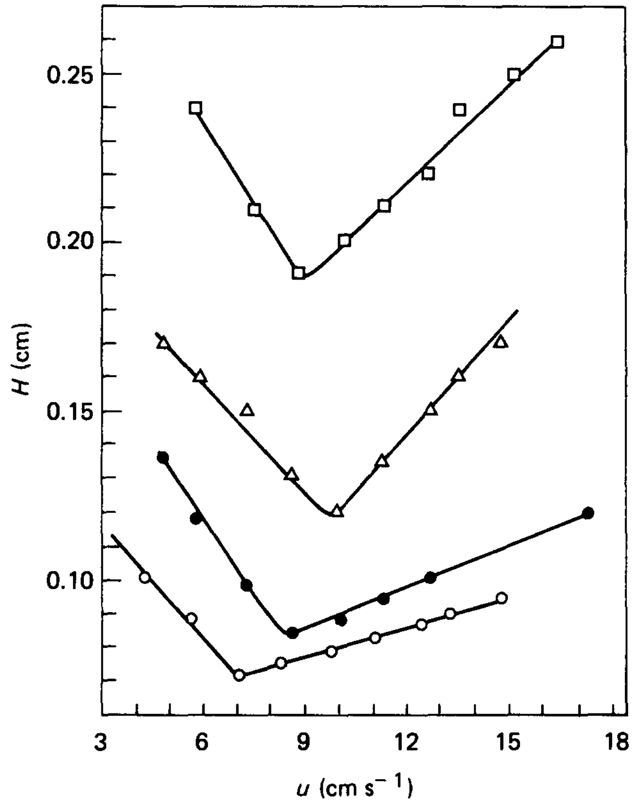

Figure 3 Van Deemter curves for SBR–probe systems where probes are: □, cyclohexane, 70°C; △, cyclohexane, 80°C; ●, benzene, 80°C; ○, benzene, 90°C

equation (4). At higher flow rates, H increases linearly with u, with a gradient C given by the Van Deemter expression.

In conclusion, weight fraction infinite dilution activity coefficients, Flory–Huggins parameters and diffusion coefficients of various polymer–probe pairs at different temperatures were obtained by gas chromatography. Such thermophysical properties are useful not only for theoretical reasons but also in applications. PIB–probe data obtained in this study for χ^* agree quite well with those in the literature, showing that the gas chromatographic procedure followed in this study is quite dependable.

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