Solubility behaviour of polystyrene: thermodynamic studies using gas chromatography

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Studies of thermodynamic parameters and solution properties of polystyrene with various solvents have been performed by gas–liquid chromatography (g.l.c.). A range of solvents has been selected for this purpose. Experiments were performed at 162.31°C, 171.84°C, 219.77°C and 229.43°C. From the chromatographic retention data obtained at these temperatures, the solubility behaviour of polystyrene with each of the solvents selected has been observed and the Flory–Huggins interaction parameters, infinite dilution activity coefficients and heats of solution were determined. The glass transition temperature of polystyrene was determined experimentally.

INTRODUCTION

The purpose of this study[1] was to investigate the solubility behaviour of an industrially important polymer, polystyrene, by g.l.c. The study of polymers by inverse gas chromatography has gained momentum in the past decade. This technique is preferred to static techniques because it is simple, economical, practical and requires only small amounts of polymer and solvent[2,3,4].

The thermodynamic parameters under consideration here are the infinite dilution activity coefficient, the Flory–Huggins interaction parameter and the heat of solution. These parameters describe the solubility behaviour for a specific polymer–solvent pair and are useful for solvent selection and equipment design in the polymer processing industry, e.g. for chemical reactors, separators, dryers etc. The application of g.l.c. to the determination of glass transition curves is also a recent technique[5–7].

EXPERIMENTAL

Equipment

The major equipment used was a Varian Aerograph Moduline 2800 Gas Chromatograph with a TCD and Varian A-25 Recorder. A Hewlett Packard Quartz Thermometer 2801 A with a precision of ±0.01°C was used to measure the temperature of the chromatograph oven. The column inlet pressure was read by a mercury manometer with a precision of ±1.0 mm Hg. Helium was used as the carrier gas. Before entering the chromatograph, the carrier gas was cleaned by a column of molecular sieves. A soap bubble flowmeter was used for measuring the gas flow rate at the outlet of column. The experimental set-up is given elsewhere[3].

Column preparation

Stainless steel tubing, 1/8 in outside diameter and 111.8 cm in length, was filled with inert Fluoropak-80† (40/60 mesh) coated by polystyrene with a coverage ratio of 11.1%. This was the maximum possible coverage ratio that could be used because, above this coverage ratio, it was observed that serious sticking problems occurred. The reasons for selecting Fluoropak-80 as the inert support have been explained elsewhere[8,9]. Polystyrene was obtained from Petkim, Petrokimya A.S., Yarimca, Turkey, with a product code of PS K-500. PS K-500 was obtained by a suspension process[10]. Its number average molecular weight ($\bar{M}_n$) has been determined as 20 000 ± 5000 by gel permeation chromatography[11].

Polymer and support were weighed in a beaker and polymer was dissolved in chloroform. The whole system was continuously stirred and simultaneously heated at about 50°–70°C, until all of the solvent was evaporated. The preparation was dried in an oven at 50°C for three days. The polymer coated support was filled into the previously prepared stainless steel tubing. Silane-treated glasswool was used to plug the ends of the chromatographic column to prevent leaking of the solid particles out of the column.

Carrier gas flow rate

Flow rate is an important factor affecting the retention data, and therefore was held almost constant during experiments. The flow rate was adjusted to a value between 5.0–7.0 ml min^{-1}. The reason for selecting such a low gas flow rate is to lessen any effect of flow rate on retention data. Lower values of flow rate were tried, but, because of control problems, 5 ml min^{-1} was chosen.

Injection technique

For injections, a 1 μl Hamilton syringe was used. 0.1 μl of solvent was taken into the syringe and flushed into the air. The residual solvent was diluted by taking 0.1 μl of air into the syringe. The dilute sample of solvent was injected

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† Fluoropak (powdered Teflon) is a registered trademark of E. I. du Pont de Nemours and Co., Inc.

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Table 1 Infinite dilution activity coefficients, Flory–Huggins interaction parameters and specific retention volumes of 42 solvents with polystyrene at 162.31°C

Solvent	Ω_1^∞	χ	V_g^0 (ml g^{-1})
Acetic acid	36.52	3.00	3.08
Acetone	16.77	1.30	2.05
Acetonitrile	32.39	2.02	2.75
n-Amyl alcohol	24.42	1.75	5.49
Aniline	8.93	1.11	50.54
Benzaldehyde	8.75	1.22	39.25
Benzene	8.01	0.66	5.70
Benzyl alcohol	14.13	1.42	60.17
n-Butyl acetate	10.91	1.01	7.55
n-Butyl alcohol	19.56	1.47	4.38
i-Butyl alcohol	25.05	1.71	2.93
Carbon tetrachloride	5.73	0.90	3.94
Chlorobenzene	6.11	0.68	16.30
Chloroform	4.29	0.43	4.39
Cyclohexane	14.16	1.11	3.21
Cyclohexanone	9.66	1.08	20.90
1,2-Dichloroethane	6.22	0.85	5.59
Dichloromethane	5.98	0.62	2.86
Diethyl ether	13.17	0.78	1.51
Diisopropyl ether	22.05	1.42	1.30
1,4-Dioxane	8.10	0.95	7.29
Ethyl acetate	12.95	1.14	2.77
Ethyl alcohol	28.56	1.80	1.57
Ethylene glycol	142.80	3.77	11.15
Formamide	144.01	4.11	13.68
n-Heptane	20.73	1.33	2.64
n-Hexane	22.53	1.35	1.57
Methyl alcohol	40.40	2.19	1.12
Methyl ethyl ketone	14.67	1.16	3.16
Nitrobenzene	9.04	1.18	82.24
n-Octane	45.99	2.19	1.89
i-Octane	29.14	1.72	1.76
n-Octyl alcohol	17.35	1.41	29.02
n-Pentane	20.30	1.12	1.11
n-Propyl alcohol	25.16	1.71	2.41
i-Propyl alcohol	27.55	1.74	1.47
Pyridine	10.54	1.02	9.02
Tetrahydrofuran	7.92	0.70	4.53
Toluene	7.90	0.67	9.52
Trichloroethylene	4.98	0.69	6.46
Water	250.98	4.40	0.96
o-Xylene	8.20	0.72	15.27

through a silicone rubber septum of the injection port of the chromatograph. The dilution procedure was repeated at least three times, until no further peak could be observed on the recorder paper. The reason for applying such a dilution procedure was to obtain data at infinite dilution conditions.

DATA ANALYSIS

Retention volume

The specific retention volume (V_g^0), corrected to 0°C, can be obtained from the following expression[3,12,13]:

$$V_g^0 = Q(t_g - t_r)\left(\frac{273.15}{T_r}\right)\left(\frac{f_p}{m_2}\right) \qquad (1)$$

where Q is the carrier gas flow rate at room temperature, t_g is the retention time of solute, t_r is the retention time of air, f_p is a pressure correction factor[12], T_r is the 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.

Weight fraction infinite dilution activity coefficient

The weight fraction infinite dilution activity coefficient (Ω_1^∞) is given by the relation[14]:

$$\ln \Omega_1^\infty = \ln\left(\frac{273.15\,R}{P_1^s V_g^0 M_1}\right) - \frac{P_1^s}{RT}(B_{11} - v_1) \qquad (2)$$

where M_1 is the molecular weight of solvent. The activity coefficient Ω_1^∞, a fundamental thermodynamic quantity, provides a useful function for relating thermodynamic behaviour to intermolecular forces. It can also be related to the solvent volatility at infinite solvent concentration[14].

Flory–Huggins interaction parameter

The Flory–Huggins interaction parameter (χ) is a measure of the strength of interaction between polymer and solvent. The χ-parameter can be determined from experimental g.l.c. data by the relation[15]:

$$\chi = \ln\left(\frac{273.15\,Rv_{2sp}}{V_g^0 P_1^s v_1}\right) - \left(1 - \frac{v_1}{\bar{M}_n v_{2sp}}\right) - \frac{P_1^s}{RT}(B_{11} - v_1) \qquad (3)$$

where v_2 is the liquid polymer molar volume, v_{2sp} is the specific volume of polymer, v_1 is the solvent molar volume, B_{11} is the solvent vapour second virial coefficient and P_1^s is the vapour pressure of the solvent. If χ is less than 0.5, favourable interactions result between the solvent and polymer, and the solvent dissolves the polymer[16].

Heat of solution

From g.l.c., the heat of solution (ΔH_s) is determined by using the approximate relation[9]:

$$\Delta H_s = -R\,\frac{\mathrm{d}\ln V_g^0}{\mathrm{d}(1/T)} \qquad (4)$$

Glass transition behaviour

The g.l.c. technique can also be applied to determine the glass transition curve. Cross-plotting of the natural logarithm of the specific retention volume taken at different temperatures (in a range including glass transition temperature of a specific polymer), against $1/T$ gives a z-shaped diagram. From this diagram, the glass transition temperature can be estimated[5–7].

RESULTS AND DISCUSSION

Experimental retention volumes for 42 solvents at four different temperatures (162.31°C, 171.84°C, 219.77°C and 229.43°C) are shown in *Tables 1–4*. Heats of solution are shown in *Table 5*.

If the Flory–Huggins parameters and infinite dilution activity coefficients in *Tables 1–4* are examined, chloroform appears to have the minimum values of χ and Ω_1^∞. Hence, chloroform is the most suitable solvent for polystyrene. Among 42 solvents, halogenated compounds in general have better solubility characteristics with polystyrene, because their Flory–Huggins parameters and infinite dilution activity coefficients have smaller values than those

Table 2 Infinite dilution activity coefficients, Flory–Huggins interaction parameters and specific retention volumes of 42 solvents with polystyrene at 171.84°C

Solvent	Ω_1^∞	χ	V_g^0 (ml g^{-1})
Acetic acid	31.81	2.85	2.84
Acetone	15.32	1.18	1.94
Acetonitrile	26.45	1.79	2.81
n-Amyl alcohol	22.27	1.64	4.90
Aniline	8.72	1.08	39.51
Benzaldehyde	8.39	1.16	31.86
Benzene	7.83	0.61	4.94
Benzyl alcohol	12.67	1.30	47.37
n-Butyl acetate	9.92	0.90	6.80
n-Butyl alcohol	19.92	1.48	3.58
i-Butyl alcohol	21.99	1.55	2.68
Carbon tetrachloride	5.34	0.81	3.60
Chlorobenzene	5.75	0.61	14.15
Chloroform	4.40	0.44	3.78
Cyclohexane	13.43	1.04	2.88
Cyclohexanone	8.75	0.97	18.13
1,2-Dichloroethane	5.71	0.74	5.14
Dichloromethane	5.49	0.51	2.72
Diethyl ether	13.13	0.71	1.35
Diisopropyl ether	15.53	1.03	1.60
1,4-Dioxane	7.50	0.86	6.56
Ethyl acetate	11.20	0.96	2.70
Ethyl alcohol	22.67	1.54	1.63
Ethylene glycol	135.85	3.70	7.57
Formamide	130.31	4.00	11.16
n-Heptane	17.62	1.15	2.62
n-Hexane	17.93	1.09	1.71
Methyl alcohol	33.80	1.98	1.12
Methyl ethyl ketone	13.08	1.02	3.02
Nitrobenzene	8.19	1.07	67.33
n-Octane	36.18	1.93	1.99
i-Octane	22.55	1.44	1.93
n-Octyl alcohol	14.68	1.23	24.76
n-Pentane	16.20	0.83	1.25
n-Propyl alcohol	19.75	1.45	2.49
i-Propyl alcohol	20.68	1.42	1.62
Pyridine	7.42	0.65	10.54
Tetrahydrofuran	7.39	0.61	4.17
Toluene	7.28	0.57	8.60
Trichloroethylene	4.68	0.60	5.84
Water	180.19	4.05	1.07
o-Xylene	7.96	0.68	12.77

of other solvents. χ-parameters tabulated show that benzene, toluene and xylene have relatively good solubility characteristics with polystyrene. Benzene, with its favourable π-interactions and its small molecular size, can penetrate the polymer matrix, and thus dissolve polystyrene. On the other hand, as the relatively high χ-parameters indicate, polar solvents such as acetonitrile, and hydrogen bonding solvents such as acetic acid, water and alcohols have poor solubility characteristics with polystyrene. Bench-scale laboratory experiments, performed at 25°C with various solvents, justified the solubility characteristics of solvents for polystyrene as indicated by their tabulated χ-parameters.

The heats of solution for polystyrene obtained in this work are compared with those obtained by Covitz and King[17] in *Table 5*. The absolute values of heats of solution of Covitz and King are higher than those obtained in this work. The heats of solution of our work are reported over a narrow temperature range of 162.31–171.84°C. The reason for the use of such a narrow temperature range is the use of the slope of the ln V_g^0 *versus* $1/T$ curve in the calculation of heats of solution as given by equation (4). The temperature range of heats of solution reported by Covitz and King is relatively large (133.32–171.23–210.48°C). In addition, the infinite dilution activity coefficients and χ-parameters reported in our study do not agree with Covitz and King, as seen in *Tables 6* and *7*. These results indicate that the gas chromatographic retention data, and thus the heats of solution data of the two studies, disagree.

The infinite dilution activity coefficients of polystyrene obtained by us at 171.84°C are compared with those in the literature in *Table 6*. There is some variation in the reported values of activity coefficients. This is due mainly to the differences in coverage ratios or film thicknesses, types of polystyrene and support used, and experimental procedures. The polymer film on the support should be thin enough to assure equilibrium with solvent vapour, but thick enough to avoid adsorption effects. Newman and Prausnitz[8] pointed out that the activity coefficients were independent of coverage, for coverage ratios above 20%. In our work, the maximum coverage ratio achieved was 11.1% due to sticking problems encountered with the Fluoropak support. Lipatov and Nesterov[18] observed that, at a particular temperature, an increase in film thickness increased the infinite

Table 3 Infinite dilution activity coefficients, Flory–Huggins interaction parameters and specific retention volumes of 42 solvents with polystyrene at 219.77°C

Solvent	Ω_1^∞	χ	V_g^0 (ml g^{-1})
Acetic acid	16.32	2.08	2.20
Acetone	11.26	0.60	1.45
Acetonitrile	20.22	1.37	1.82
n-Amyl alcohol	13.89	1.06	2.73
Aniline	7.08	0.81	15.07
Benzaldehyde	6.67	0.85	13.92
Benzene	7.57	0.46	2.58
Benzyl alcohol	7.89	0.76	17.87
n-Butyl acetate	11.39	0.93	2.54
n-Butyl alcohol	16.88	1.18	1.64
i-Butyl alcohol	18.04	1.21	1.34
Carbon tetrachloride	4.75	0.56	2.09
Chlorobenzene	5.24	0.44	6.56
Chloroform	4.41	0.28	2.02
Cyclohexane	11.89	0.78	1.67
Cyclohexanone	6.68	0.62	8.57
1,2-Dichloroethane	4.56	0.39	3.15
Dichloromethane	4.30	0.03	2.02
Diethyl ether	13.13	0.71	1.13
Diisopropyl ether	11.32	0.41	1.25
1,4-Dioxane	7.94	0.81	2.84
Ethyl acetate	12.46	0.87	1.24
Ethyl alcohol	14.58	0.88	1.15
Ethylene glycol	48.05	2.59	3.66
Formamide	85.25	3.53	4.84
n-Heptane	21.85	1.21	1.04
n-Hexane	11.89	0.42	1.44
Methyl alcohol	15.89	0.97	1.13
Methyl ethyl ketone	9.49	0.54	2.11
Nitrobenzene	6.54	0.79	23.65
n-Octane	20.73	1.26	1.53
i-Octane	14.71	0.87	1.49
n-Octyl alcohol	9.46	0.70	9.78
n-Pentane	16.20	0.83	0.98
n-Propyl alcohol	12.00	0.78	1.73
i-Propyl alcohol	10.73	0.50	1.44
Pyridine	6.46	0.43	5.27
Tetrahydrofuran	6.50	0.33	2.49
Toluene	6.50	0.36	4.41
Trichloroethylene	4.12	0.36	3.31
Water	76.84	3.13	0.97
o-Xylene	8.09	0.61	5.17

Table 4 Infinite dilution activity coefficients, Flory–Huggins interaction parameters and specific retention volumes of 42 solvents with polystyrene at 229.43°C

Solvent	Ω_1^∞	χ	V_g^0 (ml g^{-1})
Acetic acid	17.95	2.15	1.70
Acetone	12.35	0.56	1.21
Acetonitrile	13.59	0.93	2.39
n-Amyl alcohol	11.69	0.86	2.73
Aniline	6.30	0.68	13.83
Benzaldehyde	6.48	0.80	11.93
Benzene	5.62	0.13	3.10
Benzyl alcohol	7.11	0.65	15.61
n-Butyl acetate	7.25	0.45	3.46
n-Butyl alcohol	12.07	0.82	1.98
i-Butyl alcohol	12.58	0.81	1.67
Carbon tetrachloride	3.62	0.26	2.47
Chlorobenzene	4.56	0.28	6.48
Chloroform	3.41	–0.01	2.36
Cyclohexane	8.97	0.46	1.99
Cyclohexanone	6.03	0.49	8.02
1,2-Dichloroethane	3.97	0.22	3.21
Dichloromethane	3.74	–0.21	2.15
Diethyl ether	13.13	0.71	1.17
Diisopropyl ether	11.32	0.41	1.19
1,4-Dioxane	5.52	0.42	3.57
Ethyl acetate	7.90	0.35	1.76
Ethyl alcohol	10.04	0.43	1.48
Ethylene glycol	34.05	2.23	3.85
Formamide	59.60	3.16	5.54
n-Heptane	8.78	0.25	2.32
n-Hexane	8.54	–0.03	1.85
Methyl alcohol	10.28	0.44	1.55
Methyl ethyl ketone	8.33	0.36	2.15
Nitrobenzene	6.18	0.72	20.15
n-Octane	13.57	0.80	2.05
i-Octane	9.10	0.35	2.15
n-Octyl alcohol	8.25	0.55	8.93
n-Pentane	16.20	0.83	0.93
n-Propyl alcohol	7.52	0.27	2.39
i-Propyl alcohol	6.28	–0.15	2.20
Pyridine	5.39	0.23	5.49
Tetrahydrofuran	4.15	–0.16	3.51
Toluene	4.84	0.04	5.19
Trichloroethylene	3.35	0.12	3.62
Water	76.58	3.10	0.82
o-Xylene	5.86	0.26	6.13

Table 5 Heats of solution of solvents with polystyrene

Solvent	$-\Delta H_s$ (kcal mol^{-1}) This work[a]	Ref 17[b]
Acetic acid	3.23	
Acetone	2.24	
Acetonitrile	–0.89	
n-Amyl alcohol	6.08	
Aniline	10.08	
Benzaldehyde	8.41	
Benzene	5.60	6.62 ± 0.11
Benzyl alcohol	9.40	
n-Butyl acetate	4.26	
n-Butyl alcohol	9.87	
i-Butyl alcohol	3.42	
Carbon tetrachloride	3.47	5.65 ± 0.11
Chlorobenzene	5.70	
Chloroform	7.29	
Cyclohexane	4.26	
Cyclohexanone	5.75	
1,2-Dichloroethane	3.41	
Dichloromethane	1.98	
Diethyl ether	4.51	
Diisopropyl ether	–8.41	
1,4-Dioxane	4.29	7.37 ± 0.12
Ethyl acetate	0.93	
Ethyl alcohol	–1.54	
Ethylene glycol	15.03	
Formamide	7.91	
n-Heptane	0.27	
n-Hexane	–3.39	
Methyl alcohol	0.13	
Methyl ethyl ketone	1.90	6.42
Nitrobenzene	8.05	
n-Octane	–1.92	
i-Octane	12.17	
n-Octyl alcohol	6.42	
n-Pentane	–4.55	
n-Propyl alcohol	–1.37	
i-Propyl alcohol	–3.89	
Pyridine	–6.34	
Tetrahydrofuran	3.38	
Toluene	4.15	7.58 ± 0.18
Trichloroethylene	4.12	
Water	–4.52	
o-Xylene	7.25	8.52 ± 0.13

[a] Temperature range 162.31°–171.84°C

[b] Data at 133.32°C, 171.23°C and 210.48°C used

dilution activity coefficient. If the polymer film is too thick, the probe molecules cannot diffuse through the entire coating thickness during the time of passage of the peak, and, therefore, the specific retention volume is greatly reduced. However, the effects of the support may not be apparent; but use of a support that gives asymmetric peaks will affect the retention data. In addition, the porosity of the support affects the film thickness, due to polymer penetration into pores.

The success of gas–liquid chromatography in predicting the activity coefficients or any thermodynamic property depends on the fact that the retention volumes should be independent both of sample size and flow rate. If any variation is observed, then the values of retention volumes should be extrapolated to zero flow rate and sample size[3].

The Flory–Huggins interaction parameters (χ) of polystyrene obtained in this work at 162.31°C were compared with those in the literature. There is some variation in the values of χ-parameters reported by various workers. The differences in the values of χ can be explained by the same reasons given earlier for the differences in infinite dilution activity coefficients.

Table 6 Comparison of weight fraction activity coefficients for polystyrene–solvent systems at infinite dilution obtained in this work with others

Solvent	Ω_1^∞ Ref 8[a]	Ref 17[b]	Ref 18[c]	This work[d]
Acetonitrile	19.8			26.45
Benzene	5.67	3.98	6.44	7.83
Chlorobenzene	3.85			5.75
Cyclohexane	10.5			13.43
Cyclohexanone	6.14			8.75
1,2-Dichloroethane	4.83			5.71
1,4-Dioxane	5.41	4.15		7.50
n-Heptane			18.4[e]	17.62
Methyl ethyl ketone	9.30			13.08
Toluene	5.29	4.24	6.88	7.28
o-Xylene		4.15		7.96

[a] At 175°C, $\overline{M}_n$ = 97000

[b] At 174.3°C; M_n = 96200

[c] At 175°C; M_{av} = 190000; film thickness = 570–3430 μm

[d] From *Table 2*. At 171.84°C; M_n = 20000

[e] Film thickness = 1000 μm

Table 7 Comparison of Flory–Huggins interaction parameters for polystyrene–solvent systems at infinite dilution obtained in this work with others

	χ			
Solvent	Ref 17[a]	Ref 18[b]	Ref 19[c]	This work[d]
Benzene	0.322	0.552		0.66
Carbon tetrachloride	0.483			0.90
1,4-Dioxane	0.516			0.95
n-Heptane		1.327[e]		1.33
Methyl ethyl ketone	0.796		0.582	1.16
Tetrahydrofuran			0.709	0.70
Toluene	0.324	0.615	0.723	0.67
o-Xylene	0.375			0.72

[a] At 133.32°C; $\bar{M}_n$ = 97 200; coverage ratio = 10.53%
[b] At 150°C; M_{av} = 190 000; film thickness = 570–3430 μm
[c] At 145.5°C; coverage ratio = 4.7%
[d] From *Table 1*. At 162.31°C; $\bar{M}_n$ = 20 000; coverage ratio = 11.1%
[e] Film thickness = 1000 μm

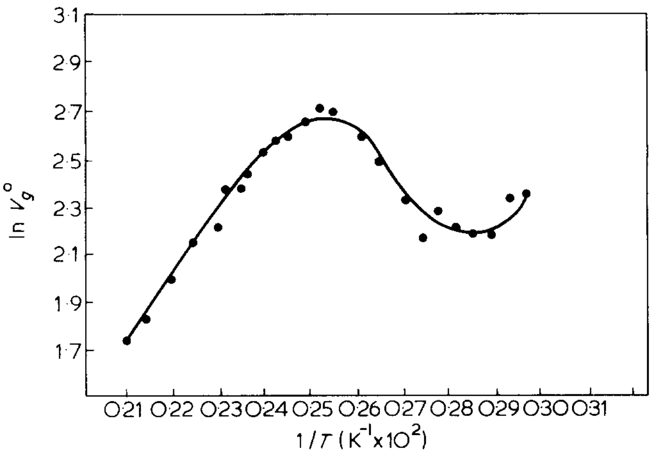

Figure 1 Retention diagram of polystyrene obtained by injection of toluene

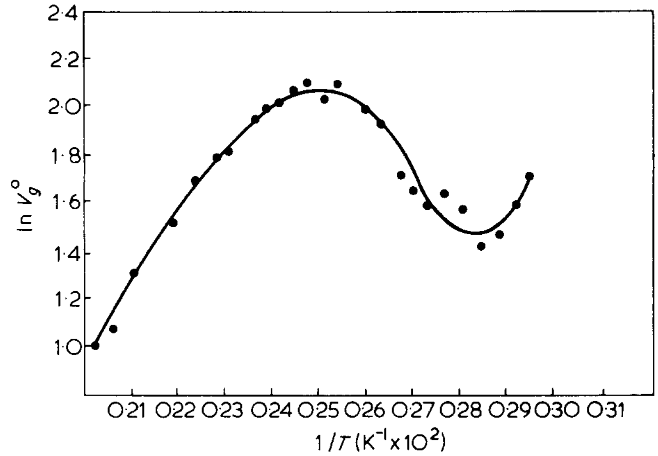

Figure 2 Retention diagram of polystyrene obtained by injection of benzene

Tait and Abushihada[4] claimed that there was a good agreement between χ values obtained from vapour pressure and g.l.c. methods. However, the g.l.c. method is preferable to the vapour pressure method, because the latter requires long periods of time to ensure equilibrium conditions, and the range of temperatures over which the method can be used satisfactorily is limited by the necessity of temperature control. Thus, the χ-values reported[4] are for temperatures below 50°C. The g.l.c. method can be used over a wide temperature range, but, as pointed out earlier, care should be exercised in taking retention data.

The χ-parameters of this work are higher than those of Covitz and King[17]. In their calculation of χ-parameters they neglected the last term of equation (3) of our work; and they also neglected the last term of equation (2) of our work in the calculation of Ω_1^∞. The B_{11} values calculated there assume negative values. Thus the last term in equation (3) increases the value of χ in our work with respect to that calculated by Covitz and King.

Glass transition behaviour of polystyrene has been determined by g.l.c.[5,6,7] using benzene and toluene as solvents in the temperature range 55°–220°C. As seen in *Figures 1* and *2*, similar glass transitions were observed at 78° ± 5°C for both of the solvents used. The phase transition curve determined with benzene as solvent was more accurate than that of toluene. Comparison of the glass transition temperature obtained in this work with the value given by Savaşçi[11], obtained by d.s.c. measurements (80° ± 5°C) for the same polymer, shows a good agreement. This justifies the use of g.l.c. in determining glass transition temperatures of polymers. Braun and Guillet[6] reported the glass transition of an anionic polystyrene with viscosity average molecular weight of 120 000, as 96°–98°C. Their result was also in good agreement with the result obtained by d.s.c. The difference in the glass transition temperatures of polystyrene obtained by us, and by Braun and Guillet, respectively, is due mainly to the difference in the properties of polystyrenes used. However, Lipatov and Nesterov[18] claimed that the surface nature, e.g. the type of support used, affected the glass transition temperatures. For instance, they reported that the transition point was higher (89°C) for polystyrene on a glass surface, than with a Teflon surface (82°C).

In conclusion, we believe that these results demonstrate the usefulness of the g.l.c. method for determining the thermodynamic properties of polymers. However, the success of this method relies on retention data remaining independent of flow rate, sample size and coverage ratio.

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