Study by gas–liquid chromatography of the interactions between linear or branched polystyrenes and solvents in the temperature range 60°-200°C

M. Galin and M. C. Rupprecht
Centre de Recherches sur les Macromolécules, CNRS, 6, rue Boussingault, 67083 Strasbourg Cédex, France

(Received 28 October 1977)

Thermodynamic interactions between linear or branched polystyrene and various solvents have been studied by gas chromatography below and above the glass transition temperature. In the lower temperature range ($<80°C$) interactions between non-solvent probes (alkanes) and the polymer are restricted to adsorption phenomena; analysis of these effects leads to an estimation of the specific surface area of the inert support which is actually accessible to the polymer. In the higher temperature range ($140°–200°C$) the activity coefficients at infinite dilution and the Flory χ interaction parameters have been calculated taking into account both diffusion and adsorption of the probe into the polymer.

The use of gas chromatography for the thermodynamic study of interactions between polymeric materials and volatile solutes has been greatly developed during the last few years. Most of this research was recently reviewed by Guillet and Braun[1]. Three main research topics may be distinguished straightaway:

(1) thermodynamics of interactions between polymers and solvents at infinite dilution: the most reliable and rigorous results are related to non-polar systems avoiding specific interactions [poly(dimethyl siloxane) or poly(isobutylene hydrocarbons) for instance] in the liquid state ($t \gg t_g$)[2–4,5–8];

(2) melting and glass transitions of polymers: these thermal transitions lead to sharp discontinuities in the variations of the characteristic retention volume *versus* temperature[9–11];

(3) solute adsorption phenomena at the surface of glassy polymers $t < t_g$: determination of adsorption isotherms and of the specific area of the polymer[12–15].

We have focused our attention on the system polystyrene (PS)–polar and non-polar solutes taking into account the influence of the PS chain structure (linear or branched) with two main purposes: (a) the thermodynamic study of interactions, PS–solutes, in the liquid state ($140° < t < 200°C$); (b) the study of adsorption phenomena of non-solvents on the glassy polymer ($50° < t < 80°C$).

EXPERIMENTAL

Polymer samples

Linear PS was an anionic sample of low polydispersity: $\bar{M}_n = 7.6 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.08$, $t_g = 95.3°C$ as measured by differential scanning calorimetry (d.s.c.) with extrapolation to zero heating rate[16].

Four samples of star shape PS were used. Three and four branched PS stars were prepared by deactivation of living PS with triallyloxy and tetraallyloxy reagents, respectively[17,18]. Seven and twelve branched PS samples were obtained by block anionic copolymerization of styrene and divinylbenzene[19].

A trifunctional randomly branched sample was prepared by deactivation of difunctional living PS capped with 1,1-diphenylethylene units with triallyloxy-s-triazine. The most important molecular parameters of the branched PS under investigation are collected in *Table 1*.

Column preparation

Two different kinds of support were used: chromosorb W (60–80 mesh, AW, DMCS) characterized by a specific surface of 1.2 m²/g (measured by gas adsorption); glass beads (70–80 mesh, HMDS) characterized by a specific

Table 1 Gas chromatographic data and activity coefficient Ω^∞ at 150° C for the interactions of benzene and n-decane with linear and branched polystyrenes

					V_g^0 (cm³/g)		Ω^∞	
$\bar{p}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	g	t_g (°C)[16]	Benzene	n-Decane	Benzene	n-Decane
3	78	77	0.778	95.5	11.96	24.20	4.72	13.08
4	560		0.625	97.1	13.22	25.93	4.27	12.21
6.9	270	162	0.387	98.2	11.14	23.74	5.07	13.33
11.6	450	420	0.244	99	12.16	24.21	4.65	13.08
RTB[a]	550	300			11.10	22.95	5.09	13.79
linear PS	82	76		95.3	10.55	20.76	5.36	15.28

$\bar{p}$ = average number of branches in the star PS; $g = (\bar{S}^2)_b/(\bar{S}^2)_l$; [a] randomly trifunctional branched

0032–3861/78/1905–0506 $02.00

Table 2 Column parameters and surface area of the coating

Column code	Weight of inert support[a] (g)	Weight of polymer (g)	Surface area of the coating (m^2) A_L (C$_{10}$)	Surface area of the coating (m^2) A_L (C$_{16}$)[b]	Coating thickness (Å)	Specific surface area of chromosorb W (m^2/g) S_{sp} (C$_{10}$)	Specific surface area of chromosorb W (m^2/g) S_{sp} (C$_{16}$)
PS$_0$	20.06	0.031			1300		
PS$_1$	1.856	0.370	0.482		7200	0.259	
PS$_2$	1.6865	0.148	0.298		4600	0.177	
PS$_{2'}$	0.353	0.031		0.058	4600		0.165
PS$_3$	1.913	0.060	0.350	0.360	1600	0.183	0.185
PS$_4$	1.725	0.086					
PS$_{3\,br}$	1.175	0.117	0.212		5150	0.180	
PS$_{6.9br}$	0.957	0.111	0.200		5200	0.208	

[a] The inert support is chrom W 60–80 mesh in all cases but for column PS$_0$: regular glass beads $0.125 < \phi_{mm} < 0.16$, $S_{sp} = 0.016$ m^2/g

[b] A_L is calculated from retention volumes at 4 temperatures $60° < t < 87°$C through equation (7) with $\ln K_{S,0} = -16.2$, $-\Delta H_S = 15.5$ kcal/mol for n-hexadecane, according to Braun and Guillet's results[15]

surface of 0.016 m^2/g approximated by the geometric surface area).

PS was coated on the inert support by evaporation from its benzene solutions. The column parameters are given in *Table 2* for linear and branched PS.

The gas chromatographic device, the probe purification and the general procedure for measurements were the same as in a previous communication[20].

Data reduction

The retention time at temperature T is converted to a specific retention volume V_g^0 (the retention volume per g of stationary phase, measured at 273.2K, at infinite dilution of the probe) through the classical relation:

$$V_g^0 = \frac{V_N}{\omega}\frac{273}{T} = \frac{(t_r - t_m)}{\omega}\frac{273.2}{T_a}Q\frac{P_0 - P_{H_2O}}{P_0}J \qquad (1)$$

with

$$J = 3/2\,[(P_i/P_0)^2 - 1]\,/\,[(P_i/P_0)^3 - 1] \qquad (1a)$$

where t_r is the retention time from injection to peak maximum for the solute; t_m is the time required for air to pass through the column; Q is the volume flow rate of the carrier gas (helium) measured at the column outlet and at ambient temperature T_a; P_i is the inlet pressure; P_0 is the atmospheric pressure; P_{H_2O} is the vapour pressure of water at T_a and ω is the weight of polymer in the column.

For temperatures around or below the glass transition temperature, retention times are strongly dependent on the amount of probe, and thus they were systematically extrapolated to zero probe volume. In the same way, they may depend on the gas vector flow rate at any temperature whenever thermodynamic equilibrium is not reached instantaneously: in these cases too, they were also extrapolated to zero flow rate. On the other hand, within the narrow range of temperature above T_g under investigation, we have assumed linear variations of $\ln V_g^0$ vs. $1/T$.

Adsorption on the polymeric stationary phase surface

According to Martin and Conder *et al.*[21,22] the net gas–liquid retention volume V_N is the sum of two independent contributions, dissolution of the probe in the bulk and adsorption on the surface of the stationary phase:

$$V_N = K_B V_L + K_S A_L \qquad (2)$$

where V_L and A_L are the volume and the active surface of the stationary phase and where K_B and K_S are the bulk and surface partition coefficient of the solute.

For the system consisting of a glassy polymer and a nonsolvent, it may be assumed that the retention mechanism is restricted to surface adsorption:

$$V_N = K_S A_L \qquad (2a)$$

Moreover, Guillet and Braun have shown for the system PS–hexadecane[15] that $\log V_N$ is a linear function of $1/T$ without any significant discontinuity around the glass transition temperature:

$$\ln V_N = \ln K_S A_L \qquad (3)$$

with

$$\ln K_S = \ln K_{S,0} - (\Delta H_S/RT)$$

where ΔH_S is the enthalpy of adsorption of the probe. This allows the determination of the bulk absorption at any temperature above T_g, taking into account the contribution of adsorption which may be easily extrapolated from its linear variation *versus* $1/T$ at $T < T_g$. This procedure is clearly restricted to non-solvent probes.

A more general method has been proposed by Martin, Martire and Conder *et al.*[21–23]. It rests on the measurements of the retention volume for a series of columns of the same total weight but of different loadings. According to equation (2) the variation of V_N/V_L is a linear function of $1/V_L$ and it allows the determination of K_B (ordinate at the origin) and K_S (slope) if A_L is known for the latter coefficient. Nevertheless, the determination of reliable values of K_B and K_S needs two important requirements for a given loading: the experimental V_N values must be extrapolated to infinite dilution of the probe and to zero flow rate of the gas vector before extrapolation to infinite loading. This procedure, which ensures that the experimental data is representative of the thermodynamic equilibrium, has been already applied by Prausnitz *et al.* to PS and different solvents[6], and by several other workers to various systems[24–26].

V_g^{0b}, which measures the contribution of the bulk absorption to the total retention volume, is readily available by extrapolating V_g^0 *versus* $1/\omega$, or better *versus* the inverse of column coverage W/ω (weight of chromosorb W/weight of polymer), to zero value (infinite thickness of the polymer film).

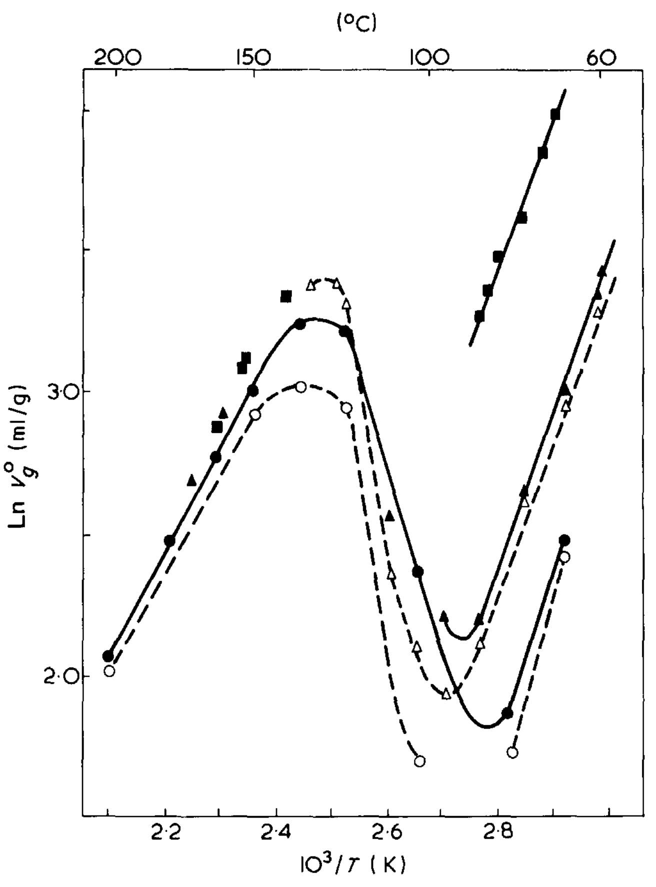

Figure 1 Effect of loading and of flow rate on V_g^0 experimental values for n-decane–PS system: ○, PS_1, Q = 10 ml/min; ●, PS_1, $Q \rightarrow 0$; △, PS_2, Q = 10 ml/min; ▲, PS_2, $Q \rightarrow 0$; ■, PS_3, $Q \rightarrow 0$

RESULTS AND DISCUSSION

Study of linear polystyrene

We have studied the interactions between linear PS and two solutes, n-decane and benzene as typical non-solvent and solvent, over a wide range of temperature between 50° and 200°C using chromosorb W (4 columns of different loadings) or glass beads as inert support (*Table 2*). The observed variations of ln V_g^0 *versus* $1/T$, plotted in *Figures 1* and *2*, show the well known Z shape characteristic of systems presenting a thermal transition.

Solute–polymer interactions below the glass transition temperature

Study of the n-decane–polystyrene system (C_{10}–PS). Below 80°C, V_g^0 is barely sensitive to the gas flow rate or to the probe volume, and it is a decreasing function of the column loading (*Figure 1*). Within the narrow range of temperature investigated 50°–80°, ln V_g^0 is a linear increasing function of $1/T$. Assuming that the C_{10}–PS interactions are restricted to surface adsorption, these experimental results may be used to calculate the chromosorb W area accessible to the polymer and then the thickness of the PS film by the method of Guillet and Braun. They may be further used to evaluate the contribution of surface adsorption to the total experimental retention volume at any temperature above T_g.

Evaluation of the thickness of the PS film. Equation (3) may be written in a reduced form:

$$\ln V_g^0 = \ln K_{S,0}^0 - (\Delta H_S/RT) + \ln A_L - \ln \omega \qquad (4)$$

with

$$K_{S,0}^0 = K_{S,0} \times (273/T)$$

Using glass beads of known specific area (0.016 m^2/g) we have calculated the following thermodynamic constants for the system C_{10}–PS:

$$\ln K_{S,0}^0 = -11.5; \ \Delta H_S = -9.3 \text{ kcal/mol}$$

which lead to the active surface A_L of the polymeric film in the three columns PS_1, PS_2 and PS_3. We have checked these values for the columns PS'_2 and PS_3 using hexadecane as the probe, and taking into account the thermodynamic constants measured for the same system C_{16}–PS by Guillet and Braun[15]. Our experimental data are given in *Table 2*. The values of the specific area of chromosorb W accessible to the polymer calculated for the two different probes, C_{10} and C_{16} are in excellent agreement (better than 5%). This area does not depend in a significant way on column loading and is practically constant, in good agreement with Guillet's results. The surface area of chromosorb W accessible to PS ($\bar{M}_n$ = 76 000) has a value of only 0.2 m^2/g which is by far lower than the homologous values deduced from gas adsorption (1.2 m^2/g) and yet significantly lower than that deduced from adsorption of low molecular weight solutes (β,β'-thiodipropionitrile 0.4 m^2/g [27]). The decrease of the specific area accessible to the probe with its molecular weight is a typical trend related to the relative dimensions of the probe molecule and of the smallest pores of the inert support.

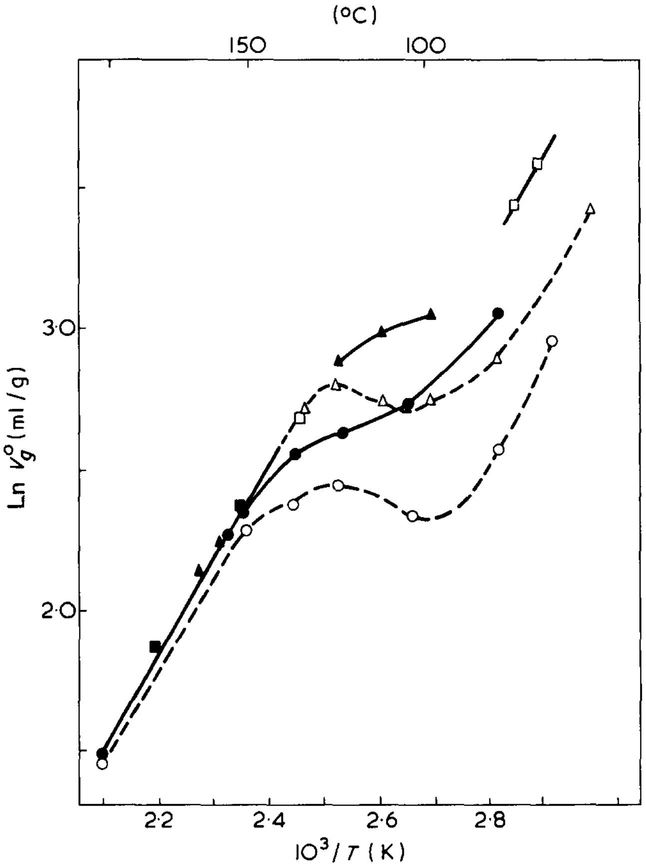

Figure 2 Effect of loading and of flow rate on V_g^0 experimental values for benzene–PS system: ○, PS_1, Q = 10 ml/min; ●, PS_1, $Q \rightarrow 0$; △, PS_2, Q = 10 ml/min; ▲, PS_2, $Q \rightarrow 0$; □, PS_3, Q = 10 ml/min

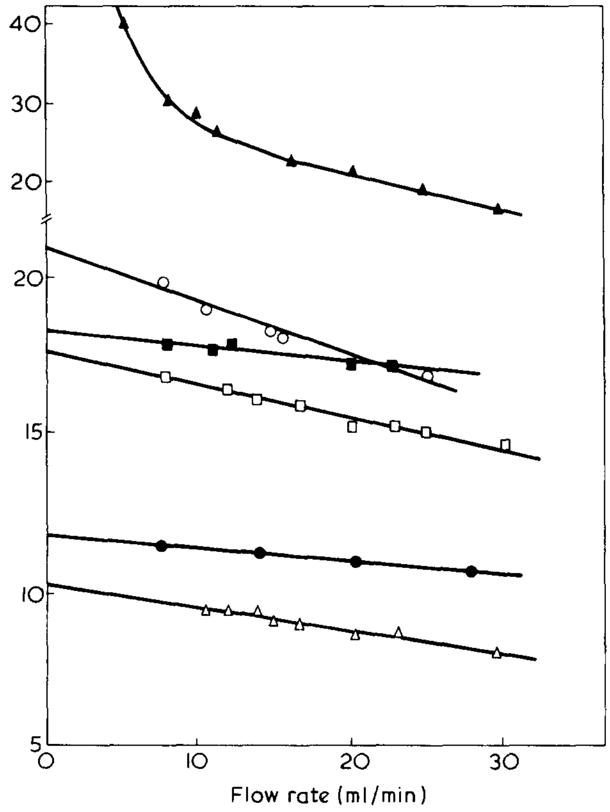

Figure 3 Effect of flow rate on V_g^0 experimental values for different probes at different temperatures: ▲, PS_2 –benzene 61.5°C; △, PS_1 – benzene 150°C; □, PS_1 – toluene 150°C; ■, PS_2 – toluene 150°C; ○, PS_1 – n-decane 150°C; ●, PS_1 – n-decane 180°C

Study of the benzene–polystyrene system (C_6H_6–PS). In sharp contrast with the previous case, the retention volumes of C_6H_6 on PS are strongly dependent on both the probe volume and the gas vector flow rate in a non-linear manner. For instance, the V_g^0 variations are much more important within the range of low flow rates, and it is not possible to evaluate an asymptotic value within the range of high flow rates, as shown in *Figure 3*. Since benzene is a good solvent for PS, bulk sorption of the probe is no longer negligible, even though surface adsorption remains the major phenomenon at $T < T_g$. Quantitative interpretation of the experimental results is not easily performed in this case.

Solute–polymer interactions above the glass transition temperature

Calculation of the thermodynamic parameters, Ω^∞, χ and χ_H. The activity coefficient of the probe at infinite dilution in the polymer phase, based on the weight fraction, may be calculated from the corresponding V_g^0 bulk values according to the method Patterson *et al.*[28]:

$$\ln\Omega^\infty = \ln\left(\frac{a_1}{\omega_1}\right)^\infty = \ln\frac{273.2\,R}{P_1^0 V_g^0 M_1} - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (5)$$

where subscript 1 refers to the volatile component and subscript 2 to the polymer; a_1 is the activity and ω_1 is the weight fraction; M_1 is the molecular weight; P_1^0 is the saturation vapour pressure at temperature T; V_1 is the liquid state molar volume; B_{11} is the gas state second virial coefficient of component 1 at T.

The polymer–solvent interaction parameter at infinite dilution χ^* as defined in the Flory–Huggins theory based on segment fraction[29] is correlated with the preceeding activity coefficient through the relationship:

$$\ln\Omega^\infty = \ln\frac{v_1^*}{v_2^*} + 1 - \frac{M_1 v_1^*}{\bar{M}_2 v_2^*} + \chi^* \qquad (6)$$

where v^* are reduction parameters.

The physical parameters of both the solvent and the polymer may be found directly from the literature or calculated from the literature data: vapour pressures and specific volumes of solvents at various temperatures were calculated using critical constants taken from Dreisbach compilation[30]; solute virial coefficients, B_{11} were computed from the corresponding state equation of McGlashan and Potter[31] for hydrocarbons, and from the virial equations of Kreglewski[32] for chloroform and dioxane; polystyrene densities were obtained from Flory *et al.*[33]; the values of reduction parameters v^* are taken from Patterson *et al.*[34] or from Prausnitz *et al.*[35].

In all cases, the experimental V_g^0 values obtained with probe amounts as low as possible were extrapolated to zero probe volume. Moreover, since the polymer phase remains highly viscous even at high temperature, the thermodynamic equilibrium is not reached instantaneously for thick films as shown by the strong dependence of V_g^0 values on gas flow rate. The lower the temperature and the lower the probe affinity for PS, the stronger the influence of the gas flow rate (*Figure 3*). The V_g^0 values thus require to be extrapolated to zero gas flow rate. On the other hand it is necessary to correct the experimental retention volumes for the contribution of surface adsorption in order to measure bulk absorption only. We have used systematically Martin's method for all the solutes independently of their affinity for PS and also Guillet's method for the non-solvents of PS.

The linear variations of V_g^0 *versus* W/ω benzene, toluene, n-decane and the four columns of linear PS are plotted in *Figure 4*. The contribution of surface adsorption to the total retention volume measured by the slope depends on both the column loading and the nature of the probe. For a given probe, such as the non-solvent n-decane, the con-

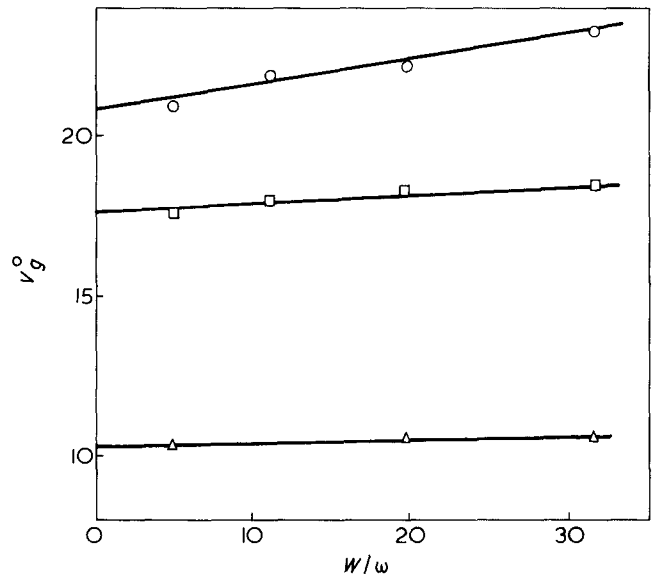

Figure 4 Variation of V_g^0 vs. inverse of column coverage (W/ω) for △, benzene; □, toluene and ○, decane on $PS_{1,2,3,4}$ at 150°C

tribution of surface adsorption is, as expected, a decreasing function of the column loading; it decreases from 11% to zero when column loading increases from 3% (PS_3) to 20% (PS_1). For a given column loading, the contribution of surface adsorption is clearly higher for a non-solvent than for a solvent of PS: it decreases from 11% for n-decane to 5% for benzene (PS_3 column).

The correction of the experimental data for n-decane surface adsorption according to Guillet's method leads to bulk V_g^0 values in fairly good agreement with the previous ones for the three columns (*Table 3*).

For column loadings higher than 15%, the contribution of the surface adsorption to the total retention volume is negligible whatever the probe is, but the influence of gas flow rate becomes very important.

For a moderate column loading of about 8% the opposite influences of surface adsorption and gas flow rate are nearly equivalent so that the experimental V_g^0 value, measured at a moderate flow rate (10–15 ml/min), and extrapolated to zero probe volume is quite close to the bulk V_g^0 value. This approximation may be of interest in cases when a great accuracy is not required, since it avoids the tedious extrapolations to zero gas flow rate and to infinite column loading.

We have calculated the activity coefficient at infinite dilution Ω^∞ of different probes in linear PS between 140° and 200°C, from the corresponding V_g^0 bulk values. Our results are collected in *Table 4*.

We have compared our results at 150°C with literature data in *Table 5*. For all the common probes except cyclohexane our results are in fairly good agreement with Newman and Prausnitz's values[24] (differences lower than 5%). On the other hand, the data obtained by Lipatov and Nesterov[26] for PS coated either on Teflon or glass beads are significantly higher whatever the common probe is. Nevertheless, the contributions of surface adsorption evaluated for benzene and for a film thickness of 2000 Å (5 and 2% at 150° and 200°C, respectively) are quite compatible with our own determinations. Finally, Covitz's values[36] are systematically lower; this may be tentatively attributed to the lack of correction for surface adsorption, even if this correction may be of little importance for the high column loadings used.

Table 3 Influence of column loading on V_g^0 (cm^3/g) values at 150°C for n-decane–PS system

	ω/W (%)	Exp. value	Surface contribution (a)	(b)	Bulk contribution
PS_1	19.93	21.0	0.3	0.3	20.7
PS_2	8.78	21.9	1.0	1.1	20.9
PS_3	3.14	23.4	2.5	2.6	20.9

(a) Calculated by Guillet's method; (b) calculated by Martin's method

As a general trend the calculated values of Ω^∞ are much more scattered for the non-solvents of PS for which surface adsorption is higher.

On the other hand, Ω^∞ is a rather strongly decreasing function of temperature for the non-solvents of PS, while Ω^∞ goes through a minimum with increasing temperature for the good solvents. The χ_H interaction parameter (enthalpic contribution to the χ parameter $\chi = \chi_H + \chi_S$) is easily deduced from the variation of Ω^∞ vs. T according to

$$\chi_H = -\frac{T}{\Omega^\infty}\frac{\partial\Omega^\infty}{\partial T} \qquad (7)$$

At 150°C the χ_H values of about 2.9 and 3.3 for heptane and decane decrease down to 0.1, 0.4 and 0.3 for benzene, toluene and ethylbenzene, respectively. For cyclohexane (θ solvent for PS at 34.5°C) χ_H has the intermediate value of about 1.7.

Different values of the same order of magnitude were obtained by the static method for PS and various solvents at 25°C: $\chi = 1.4$ and $\chi_H > 2$ for cyclohexane[33], $\chi = 0.6$ for chloroform[37] or at 50°C: $\chi^* = 0.40$ for toluene and $\chi^* = 0.85$ for dioxane[44]. The direct comparison of these data with our results is not rigorous becauce of the too large differences in the experimental temperatures and in the physical states of the polymer: liquid for our temperature range *versus* glassy for literature data. It has to be pointed out that the gas chromatographic technique was recently applied below the glass transition point (at 50°C) in order to calculate the χ interaction parameter of PS with various solvents, without taking into account the contribution of surface adsorption to the total retention volume[44]. In spite of this rough approximation the gas chromatographic data seem to be in good agreement with those derived from the static vapour pressure method.

Calculation of the diffusion coefficients of toluene and n-decane in polystyrene. The study of V_g^0 variation *versus* the flow rate of the vector gas in the case of the PS_1 column allows the determination of the diffusion coefficients of the probe in the polymeric phase. According to Van Deemter, the length of a theoretical plate may be expressed as follows:

$$H = A + B/u + Cu \qquad (8)$$

where A, B and C are constants related respectively to

Table 4 Values of specific retention volume V_g^0 bulk (cm^3/g) and of thermodynamic parameters for PS and some solvents at infinite dilution

	140°C			160°C			180°C			200°C		
Solute	V_g^0	Ω^∞	χ^*	V_g^0	Ω^∞	χ^*	V_g^0	Ω^∞	χ^*	V_g^0	Ω^∞	χ^*
n-Heptane	5.08	16.81	1.49	3.92	14.61	1.348	3.09	13.04	1.234	2.49	11.89	1.142
n-Decane	25.57	16.58	1.509	17.02	14.07	1.345	11.75	12.43	1.221	8.36	11.29	1.125
Benzene	12.73	5.38	0.591	8.82	5.36	0.587	6.31	5.37	0.589	4.64	5.43	0.600
Toluene	22.28	5.44	0.570	14.78	5.34	0.551	10.16	5.32	0.548	7.21	5.36	0.555
Ethylbenzene	36.13	5.55	0.580	22.72	5.47	0.565	14.88	5.48	0.567	10.10	5.54	0.578
Cyclohexane	7.00	9.63	1.054	5.29	8.84	0.969	4.10	8.31	0.907	3.25	7.82	0.846
Dioxane	17.03			11.76			8.39			6.16		
Dimethylformamide	37.97	11.03	1.29	23.96	10.34	1.22	15.77	9.94	1.18	10.75	9.68	1.16

Standard deviation on V_g^0 ± 2%, Ω^∞ ± 4%

Table 5 Comparison between the thermodynamic parameters at 150°C for PS and some solvents obtained by various authors

	Prausnitz[6]	Covitz[35]	Olabisi[24]			Lipatov[26]			This work		
Solute	Ω^∞	Ω^∞ (146.8°C)	Ω^∞	χ	χ^*	Ω^∞	Ω^∞	χ	Ω^∞	χ^*	χ_H
n-Heptane							18.5	1.327	15.64	1.42	2.89
n-Octane			7.9						14.83	1.37	
n-Decane									15.28	1.43	3.30
Cyclohexane	12.2		11.0	1.07	1.21				9.20	1.01	
Benzene	5.44	4.27				5.76	6.45	0.552	5.36	0.59	0.11
Toluene	5.22	4.43	5.3	0.46	0.58	6.28	6.90	0.615	5.38	0.56	0.28
Ethylbenzene	4.96	4.51							5.50	0.57	0.27
Chloroform									3.32	0.59	
p-Dioxane	5.17	4.33							5.52	0.72	
Dimethylformamide	10.6								10.64	1.25	
$\bar{M}_n$ of PS $\times 10^{-3}$	97.6	96.2	110			190			76		
Support	Fluoropak	Chrom P	Fluoropak			Teflon	Glass beads		Chrom W		
Weight of PS/weight of support (%)	>20	10.5	13.5						3.1 – 20		
Film thickness (Å)						5700 – 34 300			1600 – 7200		
Treatment of data	V_g^0 extrapolated to $D = 0, V_L \rightarrow \infty$		V_g^0 extrapolated to $D = 0, V_L \rightarrow \infty$			V_g^0 extrapolated to $V_L \rightarrow \infty$			V_g^0 extrapolated to $D = 0, V_L \rightarrow \infty$		

Table 6 Diffusion coefficients for the system PS—toluene or n-decane

Probe	t(°C)	H (cm) (for u = 10 cm/sec)	Van Deemter C (sec^{-1})	k	$D \times 10^7$ (cm^2/sec)
Toluene	149	4.9	0.26	1.5	3.2
	166	2.4	0.16	1.25	5.3
	180	1.45	0.09	1.0	2.8
n-Decane	163	4.3	0.25	1.5	3.3

eddy and molecular diffusion and to the resistance to mass transfer; u is the linear flow rate. H is a linear function of u for the high values of the flow rate, and the diffusion coefficient may be deduced from the slope C according to:

$$C = 2/3\ [k/(1+k)^2]\,(d_f^2/D) \tag{9}$$

where d_f is the thickness of the stationary phase (deduced from adsorption measurements of n-decane below T_g), D is the diffusion coefficient of the probe molecule in the polymer and k is the partition ratio[38].

The experimental results related to toluene and n-decane are collected in *Table 6*. The values of the plate heights thus obtained are by far higher than those of the classical stationary phases used in analytical chromatography; they still remain higher than those of a polymeric phase like poly(dimethyl siloxane) (H = 0.8 mm for n-heptane at 90°C). On the other hand, they are sharply increasing function of the gas flow rate: the values of the diffusion coefficients are low and of the same order of magnitude as those measured by Duda[39] for ethylbenzene (2.2×10^{-7} cm^2/sec at 170°C). A similar fair agreement may be noticed for the activation energy of the diffusion process 4 kcal/mol for toluene (our measurements) as compared with 5.8 kcal/mol for ethylbenzene[39].

Study of branched polystyrenes

We have focused our attention on two different systems: a non-solvent, n-decane below and above the glass transition temperature and a good solvent, benzene, above the glass transition temperature. In spite of different molecular weights ($\bar{M}_w$ = 78, 270, 450×10^3 for the star samples with 3, 6.9 and 11.6 branches, respectively, *versus* $\bar{M}_w = 82 \times 10^3$ for the linear PS) the radius of gyration of all the polymers roughly approximated by their values in θ solvent (calculated according to the relations $\bar{S}_b^2/\bar{S}_l^2 = g = (3p-2)/p^2$ [40], $(\bar{S}_l^2)^{1/2} = 0.347\,\bar{M}_w^{0.5}$ [41]) do not differ by more than 15% [$(\bar{S}_b^2)^{1/2}$ = 86, 112 and 114 Å for star samples *versus* 99 Å for the linear one]. Assuming in a first approximation that the adsorption enthalpy of n-decane on PS is not affected by polymer structure, the values of the specific area of chromosorb W calculated from the experimental V_g^0 data related to the system star shaped PS—n-decane between 60° and 85°C are in fairly good agreement with those calculated in the same conditions for linear PS (*Table 1*).

Within the temperature range above the glass transition temperature (150°–200°C), the V_g^0 bulk values of both n-decane and benzene are slightly higher for the branched samples than for the linear one, but this difference decreases with increasing temperature. At 150°C, for instance, (*Table 1*) the V_g^0 difference may reach 20%, significantly higher than the experimental accuracy, which may be estimated to about 5% for measurements at a single column loading. Such an increase of V_g^0 when going from linear to a branched structure has already been pointed out by Patterson *et al.* in the case of polyethylene—hydrocarbon systems[42].

Our experimental data are plotted as ln V_g^0 *versus* $1/T$ in *Figure 5*. For the experiments restricted to two characteristic different probes and to a rather narrow temperature range, the polymer structure (shape and functionality of the branching point) seems to be of minor importance, all the experimental data related to the different branched polymers reasonably fitting a single line. This allows the determination of average values of the Ω^∞ and χ_H parameters. For the branched samples, the χ_H values at 150°C for benzene and n-decane are respectively, −0.98 and 0.94 *versus* 0.11 and 3.3 for the linear polymer (compared with the value of 3.1 at 150°C for the PS—hexadecane system[43]).

CONCLUSION

Polymer—solvent interactions at infinite dilution of solvent were investigated for linear and branched polystyrenes and hydrocarbons or polar solvents using inverse gas chromatography over a wide range of temperature.

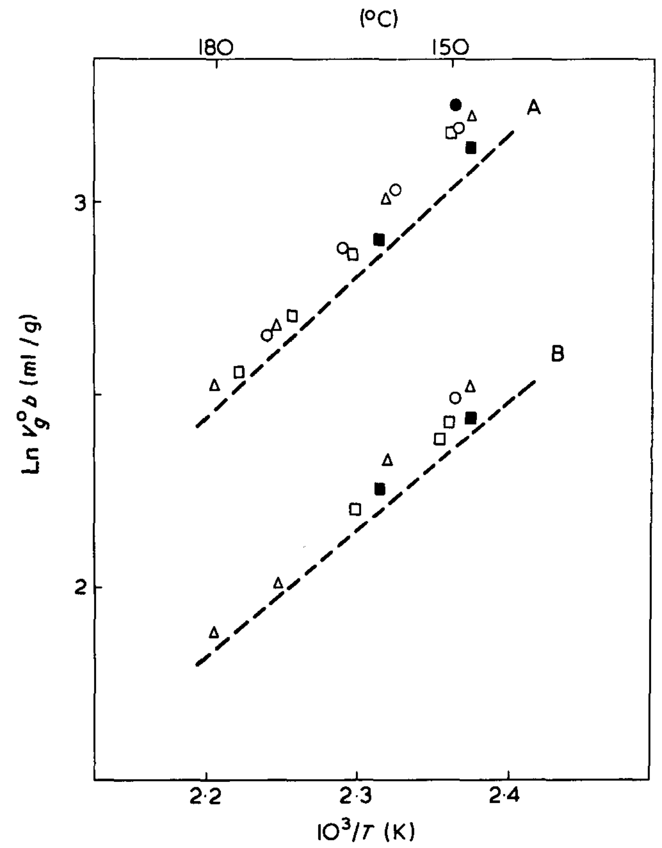

Figure 5 Retention diagram of n-decane and of benzene on branched PS: A, n-decane; B, benzene.

$\bar{p}$	3	4	6.9	11.6	RTB	linear PS
Symbol	△	●	□	○	■	– – – –

At temperatures higher than the glass transition point (140°–200°C), the thermodynamic parameters Ω^∞ and χ, calculated taking into account the adsorption of the probe at the surface of the polymeric film, were found in good agreement with literature data for linear PS. For aliphatic and aromatic hydrocarbons, χ_H is a decreasing function of temperature. The behaviour of star-shaped PS bearing 3 to 12 branches is not very different from that of the linear homologues of the same radius of gyration in spite of a drastically higher segment density; at 150°C, Ω^∞ and χ_H decrease by about 10 and 30%, respectively, when going from the linear to the star samples. Furthermore, the quantitative study of the variations of V_g^0 *versus* the flow rate of the gas vector lead to the determination of the diffusion constants of n-decane and toluene in PS at 150°C.

At temperatures lower than the glass transition point, the polymer–solvent interactions are restricted to adsorption phenomena for non-solvent, allowing us to calculate that only about 20% of the specific surface area of the inert support is readily accessible to the polymer.

ACKNOWLEDGEMENTS

This work was supported in part by the Délégation Générale à la Recherche Scientifique et Technique. (contrat no. 74–7–1380).

REFERENCES

1 Braun, J. M. and Guillet, J. E. *Adv. Polym. Sci.* Springer–Verlag, Berlin 1976, **21**, p.107

2 Summers, W. R., Tewari, Y. B. and Schreiber, H. P. *Macromolecules* 1972, **5**, 12

3 Lichtenthaler, R. N., Liu, D. D. and Prausnitz, J. M. *Ber. Bunsenges.* 1974, **78**, 470

4 Hammers, W. E., Bos, B. C., Vaas, L. H., Loomans, Y. J. W. A. and De Ligny, C. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 401

5 Hammers, W. E. and De Ligny, C. L. *Rec. Trav. Chem.* 1971, **90**, 912

6 Newman, R. D. and Prausnitz, J. M. *J. Phys. Chem.* 1972, **76**, 1492

7 Leung, Y. K. and Eichinger, B. E. *Macromolecules* 1974, **7**, 685

8 Marcille, P., Audebert, R. and Quivoron, C. *J. Chim. Phys.* 1975, **1**, 78

9 Alishoev, V. R., Berezkin, V. G. and Melnikova, Yu. *J. Phys. Chem. (Moscow)* 1965, **39**, 200

10 Lavoie, A. and Guillet, J. E. *Macromolecules* 1969, **2**, 443

11 Guillet, J. E. and Stein, A. N. *Macromolecules* 1970, **3**, 102

12 Gray, D. G. and Guillet, J. E. *Macromolecules* 1972, **5**, 316

13 Sund, E., Haanaes, E., Smidrød, O. and Ugelstad, J. *J. Appl. Polym. Sci.* 1972, **16**, 1869

14 Courval, G. J. and Gray, D. G. *Macromolecules* 1975, **8**, 326, 916

15 Braun, J. M. and Guillet, J. E. *Macromolecules* 1975, **8**, 882

16 Rietsch, F., Daveloose, D. and Froelich, D. *Polymer* 1976, **17**, 859

17 Herz, J., Hert, M. and Strazielle, C. *Makromol. Chem.* 1972, **160**, 213

18 Strazielle, C. and Herz, J. *Eur. Polym. J.* 1977, **13**, 223

19 Zilliox, J. G. *Makromol. Chem.* 1972, **156**, 121

20 Galin, M. *Macromolecules* 1977, **10**, 1239

21 Martin, R. L. *Anal. Chem.* 1961, **33**, 347

22 Conder, J. R., Locke, D. C. and Purnell, J. H. *J. Phys. Chem.* 1972, **76**, 1492

23 Martire, D. E. in 'Progress in gas chromatography', (Ed. J. H. Purnell) Wiley–Interscience, New York, 1968, p.93

24 Olabisi, O. *Macromolecules* 1975, **8**, 316

25 Cheng, Y. L. and Bonner, D. C. *Macromolecules* 1974, **7**, 687

26 Lipatov, Yu. S. and Nesterov, A. E. *Macromolecules* 1975, **8**, 889

27 Martire, D. E., Pecsok, R. L. and Purnell, J. H. *Trans. Faraday Soc.* 1965, **61**, 2496

28 Patterson, D., Tewari, Y. B., Scheiber, H. P. and Guillet, J. E. *Macromolecules* 1971, **4**, 356

29 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035

30 Dreisbach, R. R. *Adv. Chem. Ser.* Am. Chem. Soc, Washington DC 1955 No 15, 1959 No 22, 1961 No 29

31 McGlashan, M. L. and Potter, D. J. B. *Proc. Roy. Soc. (A)* 1962, **267**, 478

32 Kreglewski, A. *J. Phys. Chem.* 1969, **73**, 608

33 Höcker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251

34 Deshpande, D. D., Patterson, D., Schreiber, H. P. and Su, C. S. *Macromolecules* 1974, **7**, 530

35 Bonner, D. C. and Prausnitz, J. M. *AIChE J.* 1973, **19**, 943

36 Covitz, F. H. and King, J. W. *J. Polym. Sci. (A-1)* 1972, **10**, 689

37 Bawn, C. E. H. and Wajid, M. A. *Trans. Faraday Soc.* 1956, **52**, 1658

38 Millen, W. and Hawkes, S. J. *J. Polym. Sci. (Polym. Lett.)* 1977, **15**, 463

39 Duda, J. L., Kimmerly, G. K., Sigelko, W. L. and Vrentas, J. S. *Ind. Eng. Chem. Fundam.* 1973, **12**, 133

40 Orofino, T. A. *Polymer* 1961, **2**, 305

41 Decker, D. *Makromol. Chem.* 1969, **125**, 136

42 Schreiber, H. P., Tewari, Y. B. and Patterson, D. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 15

43 Braun, J. M. *PhD Dissertation* University of Toronto (1975)

44 Tait, P. J. T. and Abushihada, A. M. *Polymer* 1977, **18**, 810