tion part we use Alder's results:

$$W(\tilde{T},\tilde{v}) = \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{A_{nm}}{\tilde{V}^m}\right) \left(\frac{1}{\tilde{T}^{n-1}}\right) \tag{I-1}$$

The dimensionless constants A_{nm} are

$A_{11} = -7.0346$
$A_{12} = -7.2736$
$A_{13} = -1.2520$
$A_{14} = 6.0825$
$A_{15} = 6.8$
$A_{16} = 1.7$

$A_{21} = -0.330\,155\,80 \times 10^1$
$A_{22} = -0.981\,557\,82 \times 10^0$
$A_{23} = +0.220\,221\,15 \times 10^3$
$A_{24} = -0.191\,214\,78 \times 10^4$
$A_{25} = +0.864\,131\,58 \times 10^4$
$A_{26} = -0.229\,114\,64 \times 10^5$
$A_{27} = +0.353\,888\,09 \times 10^5$
$A_{28} = -0.293\,436\,43 \times 10^5$
$A_{29} = +0.100\,904\,78 \times 10^5$

$A_{31} = -0.118\,687\,77 \times 10^1$
$A_{32} = +0.724\,475\,07 \times 10^1$
$A_{33} = -0.174\,324\,07 \times 10^2$
$A_{34} = +0.196\,662\,11 \times 10^2$
$A_{35} = -0.851\,451\,88 \times 10^1$

$A_{41} = -0.517\,390\,49 \times 10^0$
$A_{42} = +0.252\,598\,12 \times 10^1$
$A_{43} = -0.412\,468\,08 \times 10^1$
$A_{44} = +0.234\,345\,64 \times 10^1$

When $n = 1, M = 6$; $n = 2, M = 9$; $n = 3, M = 5$; $n = 4, M = 4$.

Appendix II. Limiting Forms as $1/c \rightarrow 0$

Equation of state at atmospheric pressure

$$\frac{(4\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{\tilde{v}(1 - \tau/\tilde{v})^3} = \frac{1}{\tilde{T}}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} \tag{II-1}$$

Thermal expansion coefficient at atmospheric pressure

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P=1} \tag{II-2}$$

$$\alpha = \frac{\Omega(\tilde{T},\tilde{v}) - \dfrac{1}{\tilde{T}}\left(\dfrac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}}}{T\tilde{v}\left\{\left[\dfrac{2(\tau/\tilde{v})^2 - (8\tau/\tilde{v})}{(1 - \tau/\tilde{v})^4\tilde{v}^2}\right] - \dfrac{1}{\tilde{T}}\left(\dfrac{\partial^2 W}{\partial \tilde{v}^2}\right)_{\tilde{T}}\right\}} \tag{II-3}$$

where

$$\Omega(\tilde{T},\tilde{v}) = \frac{1}{\tilde{T}^2}\sum_{m=1}^{9}\frac{mA_{2m}}{\tilde{v}^{m+1}} + \frac{2}{\tilde{T}^3}\sum_{m=1}^{5}\frac{mA_{3m}}{\tilde{v}^{m+1}} + \frac{3}{\tilde{T}^4}\sum_{m=1}^{4}\frac{mA_{4m}}{\tilde{v}^{m+1}} \tag{II-4}$$

Thermal pressure coefficient at atmospheric pressure

$$\gamma \equiv (\partial P/\partial T)_V \tag{II-5}$$

$$\gamma = (P/T\tilde{P})[(\partial W/\partial v)_{\tilde{T}} - \tilde{T}\Omega(\tilde{T},\tilde{v})] \tag{II-6}$$

$$\tau = \pi\sqrt{2}/6 = 0.7405 \tag{II-7}$$

W is given in eq I-1 and $(\partial W/\partial \tilde{v})_{\tilde{T}}$ is given in eq 13.

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Studies of Polystyrene in the Region of the Glass Transition Temperature by Inverse Gas Chromatography

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ABSTRACT: The chromatographic behavior of polystyrene was investigated at temperatures encompassing its glass transition temperature (T_g) with packed columns ranging over three orders of magnitude of coating thickness. It is shown that the temperature of first deviation from the normal linear behavior due to surface adsorption is essentially unaffected by coating thickness and is to be identified with the glass transition temperature of the polymer as determined by other methods. A quantitative analysis of retention data measured under widely different conditions of surface to volume ratio of the stationary phase is given for both bulk retention and surface adsorption.

Anomalous behavior is frequently observed in gas–liquid chromatography in the temperature region associated with transitions in the stationary phase. For analytical purposes, such anomalies are undesirable, because they often alter the resolution of the column, and make interpretation of the retention time difficult due to changes in peak shape.

Table I
Column Parameters and Characteristic Temperatures for Polystyrene Stationary Phases

	Packing[a] and columns				Characteristic temp,[b] °C		
Column no.	Inert support	Loading, %	Av thickness, Å	Mass, g	Max.	Min.	First deviation
1	Chromosorb G, AW, DMCS, 70–80	19.7	17000	0.2317	165	112	96–98
2		12.5	10800	0.1140	143	107	98
3		4.87	4200	0.0443	134	104	97
4		0.979	850	0.00867	115	102	98
5		0.359	310	0.00288	Inflection point		98
6		0.0717	60	0.000702			98
7		0.022	19	0.000188			
8		0.0040[c]	3.5	0.000145			
10	Regular glass beads, 70–80	0.467	3550	0.0492	124	104	96

[a] Coating solvent was benzene. [b] T_g determined by DSC was 98°C. [c] Made by dilution of known solution.

Consequently most stationary phases are selected to avoid such behavior. Recently, however, it has been shown that a great deal of information can be obtained about the structure and interactions in polymer stationary phases by a closer and more quantitative study of retention mechanisms in the region of glass and melting transitions.[1] By investigating the retention behavior of a selection of standard solutes or "probe" molecules on a polymeric stationary phase, it is possible to identify both the glass[2,3] and melting transitions[4] and also to obtain an estimate of the degree of crystallinity. Moreover quantitative determination of the specific retention volumes provides a convenient method of determining thermodynamic quantities relating to the interaction of solute molecules with both the bulk[1,5] and the surface[6] of the polymer. Additional information can be derived relating to surface adsorption isotherms[6] and diffusion constants[7] of volatile probe molecules in polymeric materials.

Much of the published work on inverse chromatography of polymers has been devoted to the study of equilibrium thermodynamic properties of polymer–solute systems. However, the method is also quite useful for studying glass transitions, and in view of the theoretical and practical importance of these in polymer systems it appeared to be of interest to initiate a more quantitative investigation.

In the present study the chromatographic behavior of a well-characterized, narrow distribution, anionic polystyrene was investigated at temperatures encompassing the glass transition temperature under carefully controlled experimental conditions.

Experimental Section

Retention data were collected on a Hewlett-Packard 5750 gas chromatograph equipped with a dual flame ionization detector. The flow rate of nitrogen carrier gas was measured with a soap bubble flow meter and retention times were determined with a Hewlett-Packard 3370 A integrator modified to a 0.1 sec time base. Retention volumes were corrected for pressure gradient along the column, pressures at the inlet and outlet being read from a mercury manometer.

The retention volume V_R (cm^3) is herein defined as a 0°C retention volume as given by the relation:

$$V_R = t_R F \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}$$

where t_R is the net retention time, F the flow rate at 0°C (760 mm), P_i and P_0 being the inlet and outlet pressures. The specific retention volume V_g (cm^3 g^{-1}) and the surface retention volume U_s (cm^3 m^{-2}) are also extrapolated to 0°C and are defined by:

$$V_g = V_R/w_L$$

and

$$U_s = V_R/A_L$$

where w_L and A_L are the mass and surface area of the polymer stationary phase.

The polymer was dissolved in benzene and coated onto Chromosorb G, AW DMCS, 70–80 or 70–80 mesh regular glass beads by stirring and slow evaporation of the solvent. Percentage loading was obtained either by calcination, for loadings in excess of 1% (w/w), or directly from the known amounts of stationary phase and support brought together. Details of packing and column parameters are given in Table I.

The surface area of column 10 was computed from the geometric surface area of the glass beads. From their specific surface area, equal to $3/Rd$, where R and d are the radius and density of the bead, a value of 0.13 m^2 was obtained for column 10.

The polymer was a narrow distribution anionic polystyrene, viscosity-average molecular weight, $\bar{M}_v$, 120000, donated by Polysar Limited.

Differential scanning calorimetric (DSC) traces were obtained on a Du Pont 990 thermal analyzer. The glass transition temperature, T_g, was taken as the intersection of the base line with the sloping portion, at a scan rate of 10°C/min. An average value over three determinations was recorded.

Results and Discussion

The partition of solute molecules between moving and stationary phases is expressed in terms of a retention volume V_R in gas chromatography and is a characteristic of the particular solute–solvent system investigated. In gas–liquid chromatography (GLC), a plot of the logarithm of the retention volume versus the reciprocal of absolute temperature should be a straight line whose slope is related to the heat of solution. Polymer stationary phases undergoing their glass transition (T_g) deviate from such linearity, leading to a typical z-shaped retention diagram as depicted in Figure 1. Such departures from linearity and reversal from the normal behavior have been attributed to a change in retention mechanism occurring at the phase transition.[2] In early studies it was unclear which point of the retention diagram, the minimum or first deviation from linearity (T_1), should represent the glass transition temperature.[3] More recent studies[8] identify T_1 and T_g for a variety of polymers. While below T_g (region I) retention proceeds by surface adsorption, increasing molecular mobility in the polymer phase at and above T_g (region II) is accompanied by in-

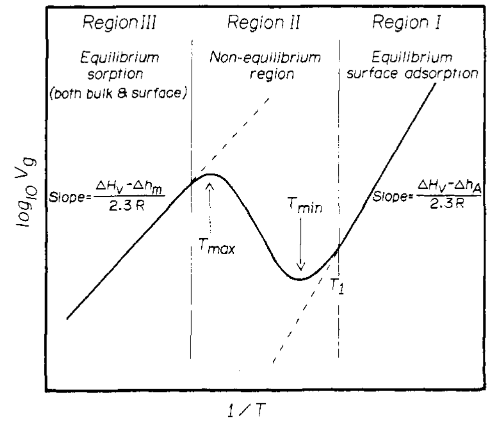

Figure 1. Typical retention diagram through T_g of polymer stationary phases.

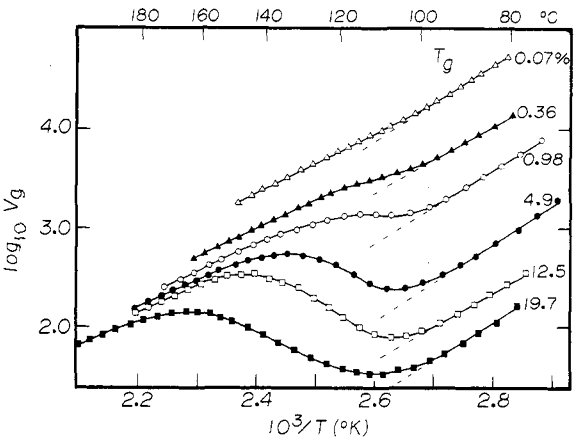

Figure 2. Effect of loading (%) on retention diagram for *n*-hexadecane on polystyrene (columns 1 to 6).

creasing retention volumes due to bulk sorption. At even higher temperatures (region III) equilibrium conditions are restored and bulk retention volumes decrease with increasing temperature.

In GLC where bulk sorption is the only retention mechanism, specific retention volumes (V_g) should be independent of the mass of stationary phase and carrier gas flow rate. Similarly, in gas–solid chromatography (GSC) the meaningful datum is a surface retention volume (U_s), retention volume per unit surface area of adsorbent. It has been shown that when both effects are present retention data on low molecular weight stationary phases can be satisfactorily represented by the relation[9]

$$V_R = K_b w_L + K_a A_L \tag{1}$$

where V_R is the retention volume, K_b and K_a are the partition coefficients for bulk sorption and surface adsorption, and w_L and A_L are the mass and surface area of the stationary phase. Although both retention mechanisms are operative with polymer stationary phases near T_g, eq 1 cannot account for the z-shaped retention diagrams experimentally observed.

Effect of Coating Thickness

Figure 2 represents the retention diagrams measured on several polystyrene columns with *n*-hexadecane as the probe (solute). The percentage loading of polystyrene varied from 19.7 to 0.07% (w/w). It is seen that considerable changes in the shape of the retention diagrams are brought about by changing the surface to volume ratio of the stationary phase. As the loading was decreased, reversal from the normal linear behavior became less pronounced. At low enough surface coverage ($\leq$0.36% loading) the minimum was no longer detectable.

These changes in the shape of the retention diagram with percentage loading are reported in Table I through three characteristic temperatures, those of the maximum, minimum, and first deviation from linearity (T_1). In contrast to the large variations in the temperatures of both maximum and minimum, T_1 remained remarkably constant, at about 96–98°C. In addition, T_1 was nearly identical with the glass transition temperature of the polymer as measured by DSC. Since the minimum is not observed on every retention diagram, these observations confirm that the temperature of first deviation, T_1, is the datum most nearly corresponding to T_g, the glass transition temperature. Identification of T_1 with T_g is further supported by theoretical considerations. Departure from the linear surface adsorption region is observed at the first detectable contribution from bulk sorption to the total retention volume, indicative of the penetration of solute molecules into the bulk polymer. On the other hand, the minimum only corresponds to equal rates of change of bulk sorption and surface adsorption with temperature.

The maximum is reached when the increase in bulk sorption due to the increase in probe diffusion constant D is balanced by the decrease in retention due to increased volatility of the probe. Nonequilibrium arises when the rate of diffusion of the solute into and out of the stationary phase is no longer large enough to assure equilibrium during passage of the solute band in the column. This leads to a decrease of the retention volume from its equilibrium value. The variation of the temperature of the maximum with coating thickness is thus easily understood. The thinner coatings show lower maxima because the distance the probe molecule must diffuse is less.

Together with changes in the shape of the retention diagram, a definite dependence of specific retention volumes V_g on loading is discernible in Figure 2. If the total retention volume in region III were effectively independent of thickness, all points should fall on a common line. It is seen that as loading is decreased, the specific retention volume increases because the surface term in eq 1 is no longer negligible. The reason for this can be seen more readily by rewriting eq 1 in the form:

$$V_g \equiv V_R/w_L = K_b + K_a(A_L/w_L) \tag{2}$$

Since the surface area of the coating A_L changes very little with changes in w_L, the weight of the stationary phase (vide infra), and K_b and K_a are constants for the particular polymer-probe system, it is apparent that as w_L is reduced, the second term in eq 2 will become correspondingly larger, and at lower coating weights may indeed become comparable in magnitude to the first term.

It is common practice in the study of inverse chromatography to use eq 2 to correct for surface contributions to the bulk retention term by measuring V_g at a series of coating weights and extrapolating to infinite w_L, where the second term becomes zero. However, as pointed out by Braun and Guillet,[10] this procedure is not generally valid for polymeric stationary phases because of the restricted diffusion in very thick coatings. This effect is demonstrated graphically in Figure 3 which shows, on a log–log scale, the variation of V_g with polystyrene loading at 128°C (T_g + 30°C). It is immediately apparent that an extrapolation to infinite thickness would yield a meaningless retention volume ($V_g \rightarrow 0$). This exceptional feature, characteristic of polymer station-

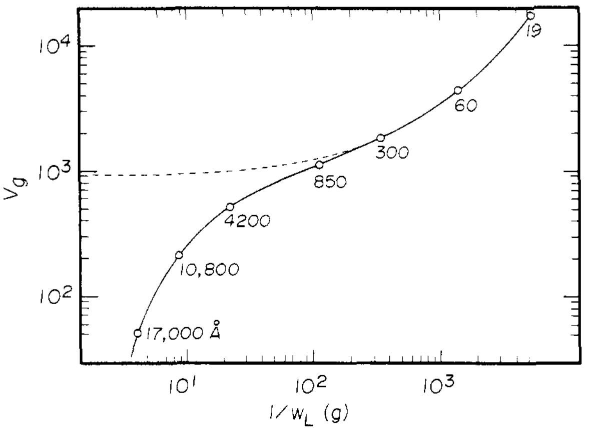

Figure 3. Variation of V_g with coating thickness for n-hexadecane on polystyrene at 128°C. Dashed line is ideal behavior.

ary phases above T_g, is due to the fact that as the coating thickness is increased, the probe molecule can no longer diffuse through the entire coating thickness during the time of passage of the peak, and hence the retention volume per unit mass (V_g) is reduced. Only at much higher temperatures with considerably higher rates of diffusion would the normal chromatographic variation, illustrated by the dashed line, be observed. It is therefore important that in using eq 2 to correct for surface effects considerable care be taken that all points are obtained in a region where diffusion is not rate controlling. This means that the values of V_g used must be independent of carrier gas flow rate in the column.

Experimental Determination of T_l

The identification of the temperature of first deviation from linearity, T_l, with the glass transition temperature of the polymer stationary phase called for an appropriate method for its experimental determination. To that effect a computer program was devised to enhance the effects of such departure from linearity, thereby allowing T_l to be determined more exactly. Since at temperatures below T_l a linear retention diagram should be recorded, the slopes of the lines through any number of experimental points should be constant. If i is the running index having value 1 at the lowest temperature, the slopes through points 1 to i should remain constant until the first point to deviate from the straight line ($i = d$) is included in the computation of the slope. Similarly the derivative to the experimental curve, at each point, should change sharply from point $i = d$ onward. To minimize the effects of the scatter in experimental points on the derivative, a small number of points can be included to yield a smoothed derivative over points $i - m$ to i. The temperature of the first deviation from linearity, T_l, would thus be obtained when both slopes, overall (1 to i) and smoothed derivative ($i - m$ to i), depart from a constant value.

This procedure was tested on a retention diagram which exhibited only a slight departure from linearity rather than reversal from the linear behavior, for n-hexadecane on polystyrene, column 6 (0.07%). In order to discriminate between scatter in experimental data and actual departure from linearity it is clear that a large number of retention data points are required. To that effect retention volumes were measured with this system at approximately 0.75°C apart over the range of temperature of interest, as shown in Figure 4. The corresponding slopes were computed from the best straight line through the experimental points, 1 to i or $i - m$ to i, determined by a linear least-squares method. The results of these computations are included in Figure 4 as overall slope (1 to i) and smoothed derivative ($i - m$ to i). A value of 5 for m was found to represent a suitable compromise between scatter and sensitivity. It is seen that both overall slope and smoothed derivative depart markedly from a nearly constant value, at essentially the same temperature, $T_l = 98.0$. The magnitude of the change in slope and most particularly the derivative at T_l is considerably greater than the corresponding changes in the experimental retention diagram, thereby allowing for a precise determination of T_l.

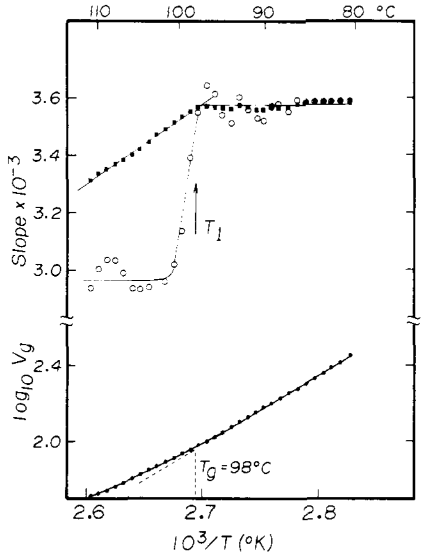

Figure 4. (■) Overall slope and (○) derivative of (●) retention diagram for n-hexadecane on polystyrene (column 6).

Surface Adsorption

Polymer stationary phases offer an attractive route to investigate liquid surface effects. While in most previous work neither K_a nor A_L of eq 1 were known, the existence of a single retention mechanism on polymers below T_g allows eq 1 to be written as

$$V_R = K_a A_L \tag{3}$$

It is thus possible to determine surface partition coefficients for a polymer–solute system from retention volumes measured with a stationary phase of known surface area, such as a polymer coated on glass beads whose geometric surface area can be easily computed. By comparison of retention volumes measured for the same polymer–solute system the surface area of any stationary phase of that polymer can in turn be determined. By rewriting K_a so as to introduce the heat of adsorption, $-\Delta H_a$,

$$\ln K_a = \ln K_{a,0} - (\Delta H_a/RT) \tag{4}$$

one has for eq 3

$$\ln V_R = \ln K_{a,0} + \ln A_L - (\Delta H_a/RT) \tag{5}$$

Figure 5 shows the retention diagrams measured on two polystyrene columns with approximately the same coating thickness on glass beads (column 10) and Chromosorb G (column 3). The effect of the much larger surface area of the latter column is shown by the greater values of V_g below the glass transition. In the region of bulk sorption the V_g values are identical, as predicted by theory. Analyzing the retention data measured below T_g on column 10 with a linear least-squares method according to eq 5 yielded $\ln K_{a,0} = -16.20 \pm 0.15$ and $-\Delta H_a = 15.5 \pm 0.1$ kcal/mol. As a result, surface areas of any polystyrene stationary

Table II
Surface Areas of Chromosorb G,[a] Columns No. 1 to 8

Column identification	1	2	3	4	5	6	7	8
Coating thickness, Å	17000	10800	4200	850	310	60	19	3.5
I, surface areas, m^2 [b]	0.108	0.092	0.100	0.101	0.092	0.110	0.103	0.414
II, surface areas, m^2 [c]		0.088	0.098	0.109	0.105	0.097	0.114	0.202
	0.083	0.084	0.105	0.112	0.104	0.100	0.112	0.200
	0.078	0.085	0.099	0.108	0.105	0.104	0.113	0.199
	0.082	0.084	0.097	0.106	0.105	0.100	0.112	0.201
	0.079	0.086	0.101	0.108	0.107	0.102	0.110	0.199
Av	0.080 ± 0.002	0.085 ± 0.001	0.100 ± 0.002	0.108 ± 0.001	0.105 ± 0.001	0.101 ± 0.002	0.112 ± 0.001	0.200 ± 0.001
Diff (II − I)/II, %	−35	−8.2	0 (ref)	+6.5	+12.4	−8.9	+8.0	−107

[a] Chromosorb G uncoated has a surface area ~0.6–1.3 m^2/g. [b] Calculated using column 3 as reference. [c] From retention volumes at several temperatures T, $T < T_g$, through eq 7.

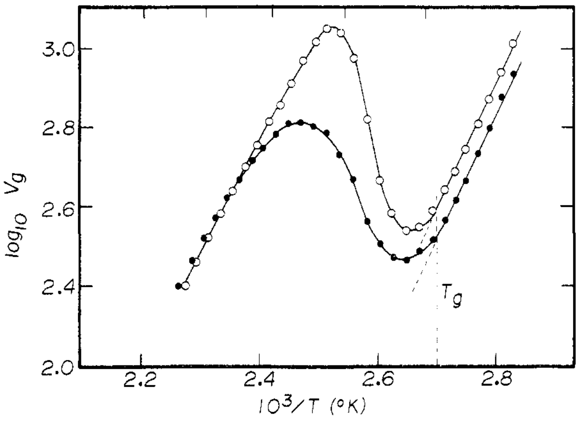

Figure 5. Retention diagrams for *n*-hexadecane on polystyrene coated on (○) glass beads and (●) Chromosorb G (columns 10 and 3).

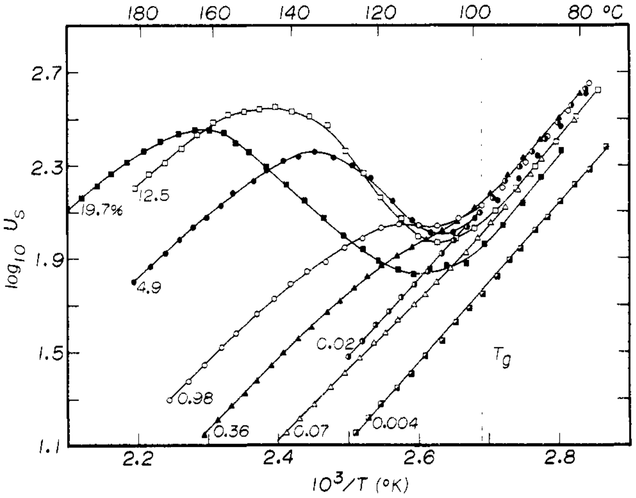

Figure 6. Surface retention volumes for *n*-hexadecane on polystyrene (columns 1 to 8).

phase can be determined from its retention volume by the relation:

$$\ln A_L = \ln V_R - \ln K_{a,0} + (\Delta H_a/RT) \qquad (6)$$

or if specific retention volumes are used,

$$\ln A_L = \ln V_g + \ln w_L - \ln K_{a,0} + (\Delta H_a/RT) \qquad (7)$$

From the retention data obtained below T_g on columns 1 to 8 the corresponding surface areas were determined through eq 7. The values computed at several temperatures are reported in Table II together with the average value obtained.

Alternatively, one could compute the specific surface area from the surface area of the stationary phase and the known amounts of polymer and inert support in any packing since:

$$A_L = w_L S_{PS}([100/x] - 1) \qquad (8)$$

where x is the percentage loading. Quite clearly the specific surface area of the support so determined, S_{PS}, corresponds to coverage by polystyrene molecules and is hereafter referred to as the accessible surface area. A value of 0.11 m^2/g was determined for the accessible surface area of Chromosorb G, AW DMCS for polystyrene in column 3 (4.87%). From this value the surface areas of columns 1 to 8 were computed through eq 8 and the results are compared in Table II. It is seen that with the exception of column 8 both methods of computation yield essentially the same values, indicating that over almost three orders of magnitude of coating thickness the accessible surface area of the support is substantially unchanged. This is best illustrated in Figure 6 representing the surface retention volumes measured on columns 1 to 8. With the exception of column 8, surface retention volumes measured below T_g fall on a common line as one would expect if eq 3 holds, namely if a single retention mechanism is operative below T_g. In this case the values of the surface retention volumes U_s are in $cm^3\ m^{-2}$, corrected to 0°C.

The value found for the accessible surface area of the inert support, S_{PS}, called for a reconsideration of the film thicknesses previously reported for packed columns on Chromosorb. Commonly quoted specific surface areas for Chromosorb G range from 0.6 to 1.3 $m^2\ g^{-1}$.[11] It is, however, recognized that such figures, obtained from nitrogen adsorption measurements (S_{N_2}), are inadequate to compute surface areas of liquid stationary phases coated on inert supports.[12] In particular, Perret and Purnell[13] reported a decrease in specific surface area of Chromosorb P for acetone vapors as compared with inert gases, down from 4 to 2 $m^2\ g^{-1}$. That an even greater decrease were to characterize a bulky polystyrene molecule compared with acetone would hardly be surprising. Such a decrease in accessible surface area is believed to originate from the "bridging" of a number of the finer pores of the diatomaceous earth. As a result of the limited accessible area the film thicknesses achieved are considerably larger than was previously assumed. Average film thicknesses for all packings investigated were computed from the bulk density of the polymer and S_{PS}. These values are reported in Table I. It is seen that for loadings in excess of 1%, film thicknesses larger than 10^3 Å are obtained. At the highest loading used in the present work, 19.7%, a thickness of 17000 Å was computed, similar to those commonly obtained in capillary columns.

In view of the film thickness achieved in column 8 (3.5 Å) and the constancy of S_{PS} with surface coverage, the discrepancy (107%) in surface area noted in Table II for column 8 is not unexpected. It is believed that at such low surface coverage the amount of polymer introduced is no longer sufficient to ensure monolayer coverage of the accessible surface area. As a result, the surface area of the stationary phase is effectively less than computed from eq 8, as is apparent from Figure 6. In the case of polystyrene on Chromosorb G, complete surface coverage is maintained down to at least 0.02% loading, corresponding to column 7.

Bulk Retention Volumes

Because of the fact that at temperatures below T_g retention is due to surface adsorption only, the relative contribution of bulk sorption at temperatures above T_g can be determined from extrapolation of such surface retention data to higher temperatures. This extrapolation procedure is justified by the absence of any discontinuity in the temperature variation of the surface retention volume at T_g as shown by the retention diagram for column 7 (0.02%), which remained linear through T_g (Figure 6). True bulk retention volumes (V_{bulk}) can be computed through eq 1 by the relation

$$V_{bulk} = K_s w_L = V_R - V_{ads} = V_R - K_a A_L \qquad (9)$$

where the surface retention volumes (V_{ads}) are computed through eq 5 rewritten as,

$$\ln V_{ads} = \ln K_a A_L = A(A_L,K_{a,0}) - (\Delta H_a/RT) \qquad (10)$$

where the constants $A(A_L,K_{a,0})$ and ΔH_a are determined as the intercept and slope of the best straight line through the corresponding retention data measured below T_g. It is worth pointing out that for such a procedure to be applicable, the surface area of the stationary phase, A_L, need not be known. Figure 7 shows the bulk specific retention volumes (V_{bulk}/w_L) computed from the retention data represented in Figure 2 for columns 1 to 6 analyzed according to eq 9 and 10. It is seen that in the region corresponding to equilibrium sorption (i.e., above the maximum) the points fall on a common line. The values at low coating weights (0.07% and lower) do not fit as well because surface adsorption accounted for more than 80% of the total retention volumes, even at the highest temperature, and a relatively small error in the surface term can lead to a large error in the bulk term.

The results presented in Figures 6 and 7 clearly support and justify the working hypothesis underlying the present work: i.e., the existence of a single surface retention mechanism below T_g and the beginning of bulk retention at or above T_g. They indicate also that eq 1 describing retention data, when both surface adsorption and bulk sorption are operative in a column, is basically valid with polymer stationary phases above T_g, under conditions where equilibrium is reached during passage of the solute band through the column. Finally it is apparent from Figure 7 that equilibrium bulk sorption exhibits its characteristic linear temperature variation from about T_g + 20°C upwards.

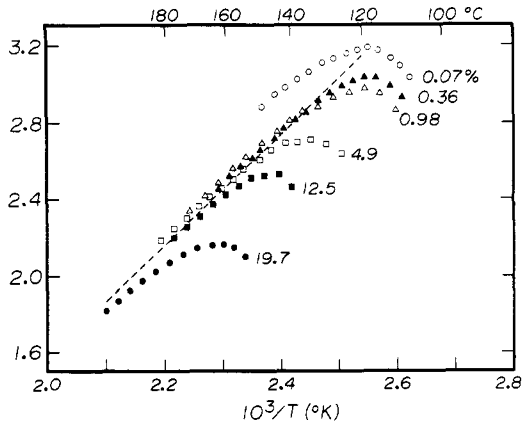

Figure 7. Bulk retention volumes for n-hexadecane on polystyrene (columns 1 to 6).

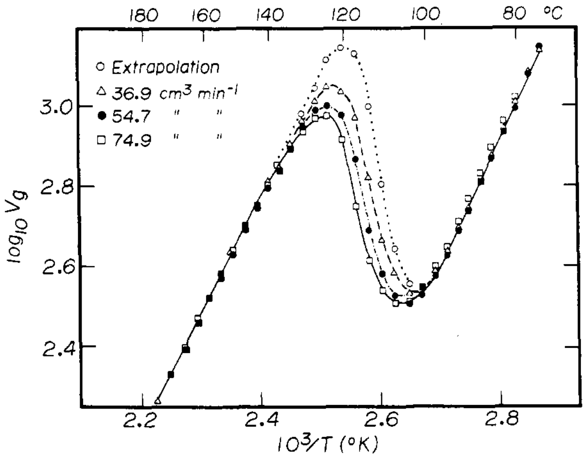

Figure 8. Effect of flow rate on retention diagram for n-hexadecane on polystyrene (column 10).

Recently, Nesterov and Lipatov[14] have reported GC studies of polystyrene and poly(methyl methacrylate) coatings on glass and Teflon substrates. They observed effects rather similar to those we report when the thickness of the coating is reduced, but attributed these to ordering effects in thin coatings caused by the proximity of a strongly absorbing surface such as glass. Although such "order" may indeed be induced in polymer substrates, the data of Nesterov and Lipatov cannot be considered conclusive since they neglected to take account of the surface adsorption term, which we have shown in the present studies to account for a major part of the total retention in thin coatings. When suitable corrections are made for the surface retention term, by the procedures outlined herein, this technique might well provide unambiguous evidence for the ordering of polymer substrates close to reactive surfaces.

Flow Rate Effects

While it has been shown that in appropriate temperature domains invariance of both surface adsorption and bulk sorption can be observed on polymer stationary phases, the retention volumes measured in the nonequilibrium region (region II in Figure 1) cannot be accommodated by eq 1. A further distinctive feature of this region is represented by the drastic dependence of retention volumes on the flow rate of carrier gas. Figure 8 shows the retention volumes measured with the same n-hexadecane–polystyrene system on column 10 at three different flow rates. Retention volumes were essentially independent of flow rate both at high temperatures for equilibrium bulk sorption and below T_g for surface adsorption. However, they become flow rate dependent in the nonequilibrium region, as seen in Figure 9

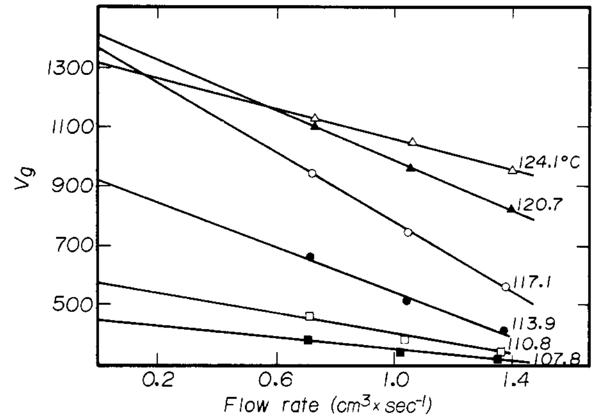

Figure 9. Extrapolation to zero flow rate of retention volumes for *n*-hexadecane on polystyrene (column 10).

which shows data extrapolated to zero flow rate. These extrapolated values are also included in Figure 8. It is seen that extrapolation of measured retention volumes to zero flow rate extends the linear region associated with equilibrium bulk sorption over a wider temperature range. However, the possibilities of extrapolations to zero flow rate are somewhat limited. Owing to the size of the effect, precise extrapolations are restricted to a temperature range where a relatively moderate variation with flow rate is recorded.

The origin of the flow rate dependence of retention volumes for bulk sorption can be readily understood. Since nonequilibrium is attributed to the slow diffusion of solute molecules in the stationary phase, a change of carrier gas flow rate affects the rate of movement of a band of solute through the column and the "residence time" over the stationary phase. As the flow rate is decreased, the polymer–solute system is allowed to come closer to or even reach equilibrium, leading to larger specific retention volumes. For larger coating thicknesses, faster flow rates increase the extent of the nonequilibrium region. While it may appear from Figure 8 that flow rate has only a minor effect on the retention diagram, it should be remembered that it is the linear velocity in the column rather than the volume flow rate which is the determining factor. Depending on experimental conditions (diameter of the column, nature of the support, packed or capillary columns, etc.) quite extensive changes in linear velocity and hence in retention diagrams can be brought about at identical volume flow rates.

In conclusion, the results of this study have shown that when equilibrium conditions are reached in a GC column, retention volumes measured on polymer stationary phases over three orders of magnitude of coating thickness can be quantitatively analyzed in terms of the contributions from only two terms, one relating to bulk sorption and the other to surface adsorption. From the retention data measured below T_g both surface areas of the stationary phases and accessible surface areas of the inert support can be determined, because the bulk sorption of hydrocarbon probes in polystyrene is negligible. The generality of the phenomenon of chromatographic reversal at T_g with a wide variety of polymers and probe molecules suggests that this conclusion may also apply extensively to polymers other than polystyrene. This would permit an easy method of estimating the magnitude of surface adsorption terms for the bulk liquid above T_g by extrapolation of data obtained below T_g and assuming no change in surface area or heat of adsorption at T_g.

It is also demonstrated that a reliable estimate of T_g may be obtained by evaluating T_1, the temperature at which the first derivation is observed from the linear surface retention diagram.

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