dependent on the nature of the solvent. Further measurements are needed to establish the influence, if any, on the molecular weight of the sulfonation reaction. The solubility test showed that the modified copolymers are insoluble in chloroform but soluble in DMSO. The copolymers containing higher content of sulfonic groups are soluble in water also.

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Inverse Gas Chromatography in the Vicinity of T_g. Effects of the Probe Molecule

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ABSTRACT: The chromatographic behavior of polymer stationary phases in the vicinity of their glass transition temperature is discussed in terms of column parameters and magnitude of probe interactions with the stationary phase. Past failures of the method to detect a known transition of the polymer are critically examined and accounted for. It is shown that solubility of the probe in the polymer, while an important factor, is not sufficient to characterize the polymer-probe system near T_g. Interactions of the probe with both bulk and surface of the stationary phase must be considered in such studies. The relationship between the chromatographic behavior near T_g and the limiting value of the surface tension of the polymer-probe solution is established.

The generality of the detection of the glass transition temperature (T_g) of polymer stationary phases by inverse gas chomatography seems at present well established. Since the first communication of Smidsrød and Guillet[1] reporting a reversal from the normal chromatographic variation at T_g, a large variety of polymeric materials has been successfully investigated.[2–5] The glass transition temperatures so derived were in excellent agreement with results from other techniques.

During the same period, however, several studies revealed that, inexplicably, linear retention diagrams could be recorded through the T_g of the stationary phase.[6–8] Moreover, the requirement put forward by Smidsrød and Guillet,[1] that the probe must be a nonsolvent of the polymer investigated, has proven invalid in some instances.[7,8] As a result, the ability of the gas chromatographic (GC) technique to provide conclusive evidence as to the existence of a transition in a polymer stationary phase could be severely limited.

It is the purpose of this communication to investigate the reasons which have led to past failures and to assess the importance of the nature of the probe molecule in the detection of the glass transition temperature by inverse gas chromatography.

Experimental Section

Experimental procedure, instrumentation, and polymers were identical with those described in earlier publications.[4,9] The solid (mp 164 °C) perfluoro *n*-eicosane, kindly donated by R. H. Dettre (E. I. Du Pont de Nemours and Co.), was injected into the carrier gas stream with a solid sampler. Table I summarizes the column parameters of the present work.

Vapor pressures of probe molecules required to compute activity coefficients were taken from standard literature sources.[10]

Bulk and surface retention volumes needed to calculate limiting values of the solution surface tension, $(\partial\gamma/\partial w_1)^\infty$, were obtained from published retention diagrams. Their values at T_g were determined by extrapolation of the linear portions of the retention diagrams above and below T_g, for equilibrium bulk sorption and surface adsorption, respectively. In the latter case the surface retention volumes, denoted U_s, were expressed in cm^3 m^{-2}. The surface area of the stationary phase required to compute U_s was obtained from the accessible surface area of the inert support as determined in an earlier publication.[9]

Table I
Column Parameters for Poly(NIPAM), Poly(acrylonitrile), and Polystyrene Stationary Phases

Polymer	Packing and columns				Solutes
	Solvent	Inert support	Loading, wt %	Mass, g	
Poly(*N*-isopropylacrylamide)[a]	Chloroform	Chromosorb G AW, DMCS	3.8	0.715	*n*-Butyl alcohol Acetic acid *n*-Hexadecane Naphthalene
Poly(acrylonitrile)[b]	Dimethylformamide (DMF)	Chromosorb W 80–100 mesh	10.5	0.257	(Acetonitrile) *n*-Dodecane
		Unsupported powder, 60–100 mesh		0.200	DMF, benzonitrile, *n*-dodecane
Polystyrene	Benzene	Chromosorb G AW, DMCS 70–80 mesh	19.7	1.2724	Benzene
	Benzene	Chromosorb G AW, DMCS 70–80 mesh	12.5	2.0821	Perfluoro *n*-eicosane

[a] Polymer and column of ref 1. [b] Polymer and columns of ref 7.

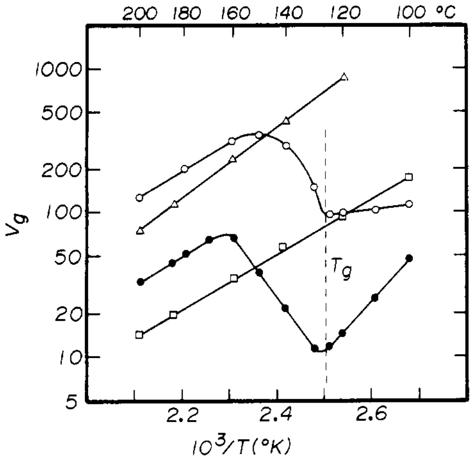

Figure 1. Retention diagrams for (●) *n*-hexadecane, (○) naphthalene, (□) *n*-butyl alcohol, and (△) acetic acid on poly(NIPAM). Data from ref 1.

Results and Discussion

The selection of a probe (solute) suitable for the detection of T_g by gas chromatography is guided by the early findings of Smidsrød and Guillet[1] on poly(*N*-isopropylacrylamide) (poly(NIPAM)). These authors indicated that reversal from the linear behavior was possible only with probes which were nonsolvents of the polymer (hexadecane, naphthalene). With solvents (acetic acid, butanol) a linear retention diagram, corresponding to bulk sorption, was recorded through T_g. These features are illustrated in Figure 1 reproducing the original data. It was also shown[1] that reversal from the linear behavior at T_g was attributable to a change in retention mechanism, from surface adsorption below T_g to bulk sorption above T_g. Nonsolvents of the polymer have since been used repeatedly to determine transition temperatures of polymer stationary phases.[2–5]

The suitability of nonsolvent solutes was, however, to be questioned when Guillet and Galin[7] reported their investigation on poly(acrylonitrile) (PAN) stationary phases. Their results, reproduced as retention diagrams in Figure 2, showed that only solvents or swelling agents (dimethylformamide, benzonitrile, acetonitrile) led to reversal and detection of T_g. A linear retention diagram, corresponding to surface adsorption, was recorded through T_g with dodecane. This was attributed[7] to the impossibility for a nonsolvent to penetrate the bulk polymer, even at temperatures above T_g.

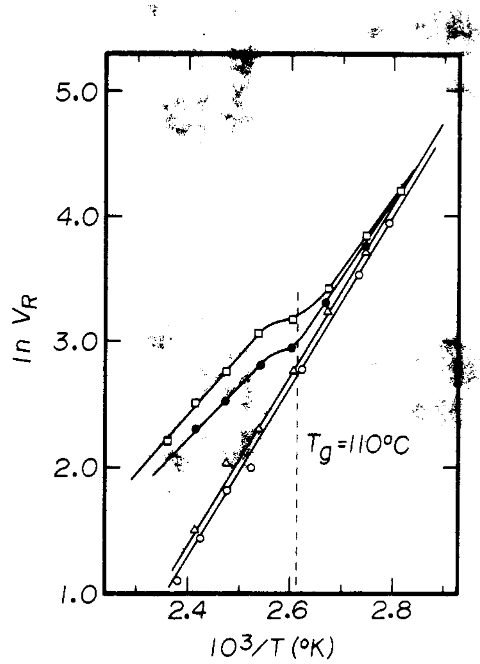

Figure 2. Retention diagrams for (△, ○) *n*-dodecane, (●) benzonitrile, and (□) DMF on poly(acrylonitrile). Data from ref 7.

Though such facts challenge the present understanding of the chromatographic behavior of polymers, recording of a linear retention diagram through T_g is conceivable. In the event of concurrent retention mechanisms, the retention volume, V_R, is given by the relation[9,11]

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

where K_b and K_a are the partition coefficients for bulk sorption and surface adsorption, w_L and A_L being the mass and surface area of the stationary phase. As a result surface adsorption can be the only retention mechanism, even above T_g, if the coating thickness is sufficiently small. This has been found[9] to be the case with *n*-hexadecane on polystyrene coated on Chromosorb G at a loading of 0.02% (estimated thickness, 20 Å). Similarly, for semicrystalline polymers the contribution from bulk sorption to overall retention is reduced by the presence of crystalline domains which remain impenetrable to the probe molecule. While most failures of the method result from such adverse experimental conditions, it is quite clear that in the case of PAN the column parameters (Table I) were well suited to record a strong departure from linearity. This finding draws at-

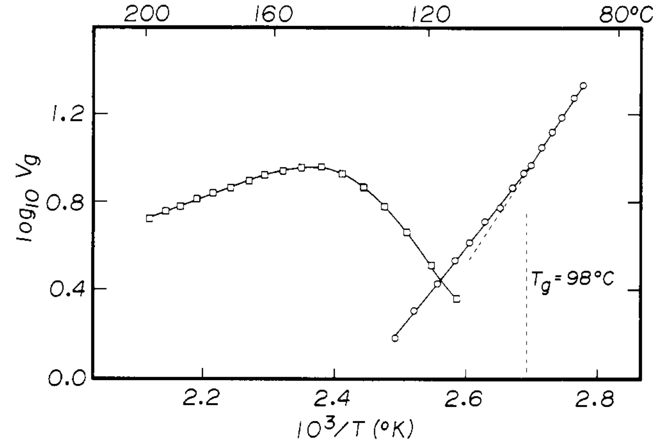

Figure 3. Retention diagrams for (□) benzene on polystyrene (19.7%) and for (○) perfluoro n-eicosane on polystyrene (12.5%).

tention to the magnitude of polymer-probe interaction in the vicinity of the transition temperature.

Since it may be argued that both poly(NIPAM) and PAN are strongly hydrogen bonded polymers, further insight was sought from a better known stationary phase, polystyrene. Earlier work by Lavoie[12] had shown that a strong reversal from the linear behavior was to be recorded with both linear alkanes and alkanols. The effect of the nature of the solute on retention characteristics was further studied by including a good solvent of the polymer, benzene, and a perfluorinated n-eicosane. The results of these experiments are given in Figure 3 as retention diagrams. For benzene on polystyrene, and in contrast to butanol on poly(NIPAM), reversal was observed. It was found, however, that in the immediate vicinity of T_g abnormally broad peaks were observed, possibly due to occurrence of bulk sorption even below T_g, and were therefore omitted from Figure 3. For the perfluoro n-eicosane departure from linearity at T_g is most gradual despite a thick polystyrene coating. Such behavior can, in fact, be correlated with the known GC characteristics of perfluorinated solutes.[13] Due to their scant solubility in hydrocarbon stationary phases, extremely long columns are required to perform any separation. The large difference in retention behavior recorded with benzene and perfluoro eicosane on polystyrene thus demonstrates the importance of the solubility of the probe in the detection of the glass transition temperature by gas chromatography.

The retention behavior on PAN was then re-examined in the light of these results and compared with other polymer stationary phases. The solubility of a probe in a polymer, expressed as an activity coefficient, is given in gas–liquid chromatography (GLC), when neglecting gas phase nonideality, by the relation,[14]

$$(a_1/w_1)^\infty = (273.16Rw_L)/(p_1{}^0M_1V_R) \qquad (2)$$

and hence

$$V_R = (273.16Rw_L)/[p_1{}^0M_1(a_1/w_1)^\infty] \qquad (3)$$

where $(a_1/w_1)^\infty$ is the infinite dilution weight fraction activity coefficient, $p_1{}^0$ and M_1 the saturated vapor pressure and molecular weight of the probe, and R the gas constant. Table II lists activity coefficients taken from literature sources[1,4,7,15,16] for selected solutes in polystyrene (PS), poly(vinyl chloride) (PVC), poly(NIPAM), and PAN at comparable temperatures (T_g + 50). Solutes that are solvents (S) of the polymer yield small activity coefficients while the nonsolvents (NS) are characterized by larger values. Their relevance to describe reversal from the linear behavior is directly expressed in eq 3. In otherwise identical conditions of solute vapor pressure it is seen that the more soluble the probe in the polymer (hence the smaller the activity coefficient), the larger the bulk retention volume and consequently the more pronounced the reversal. If one then extrapolates the trend in activity coefficients for solvents and nonsolvents, a very large value would be expected for n-dodecane (NS) on PAN, considering the already large activity coefficient obtained with solvents of the polymer. As a result of a correspondingly small bulk retention volume one could conceive of a nearly linear retention diagram through T_g, irrespective of the coating thickness, as observed experimentally in the case of the sparingly soluble perfluoro alkane on PS (Figure 3).

Table II
Weight Fraction Activity Coefficients for Polystyrene, Poly(vinyl chloride), Poly(NIPAM), and Poly(acrylonitrile)

Polymer	Temp[a]	Solute and nature[b]	Wt fraction activity coefficient $(a_1/w_1)^\infty$
Polystyrene[c]	150	Chlorobenzene (S)	3.72
		Styrene (S)	4.11
		Toluene (S)	5.22
		2-Butanone (poor S)	9.44
		Acetonitrile (NS)	19.8
		n-Hexadecane[d] (NS)	16
	128	Perfluoro n-eicosane[d] (NS)	~15 000
Poly(vinyl chloride)[d]	130	n-Decane (NS)	42
Poly(NIPAM)[e]	180	Acetic acid (S)	0.58
		n-Butyl alcohol (S)	2.4
		n-Hexadecane (NS)	40
Poly(acrylonitrile)[f]	145	Acetonitrile (SW)	13
	160	Dimethylformamide (S)	16
	170	Benzonitrile (SW)	~60

[a] Approximately T_g + 50 °C. [b] S, solvent of the polymer; SW, swelling agent; NS, nonsolvent. [c] Reference 16. [d] Reference 15. [e] Recomputed from mole fraction $\gamma_1{}^\infty$. [f] Computed from ref 7.

The magnitude of the activity coefficient cannot, however, account completely for the ability of a polymer–solute system to exhibit a certain reversal from linearity at T_g. As is apparent from Figure 2, reversal is never very pronounced on PAN stationary phase with either solvents or swelling agents. In comparison, other polymer–solute systems, characterized by comparable or even larger activity coefficients (Table II), be it hexadecane on PS[9] and poly(NIPAM)[1] or decane on PVC,[4] exhibit strong reversals from linearity. In these cases neither loading (w_L/A_L) nor crystallinity can be invoked to explain the observed differences.

Because of the dual retention mechanism in the vicinity of T_g, one ought to consider the magnitude of solute interaction with both the bulk and the surface of the polymer stationary phase. These quantities are suitably described, as in eq 1, by the partition coefficients K_b and K_a or alternatively by the corresponding bulk and surface retention volumes, V_g (cm^3 g^{-1}) and U_s (cm^3 m^{-2}), to which they are directly related.[13] To maximize reversal from linearity at T_g the bulk interaction term, K_bw_L, should be as large and the surface interaction term, K_aA_L, as small as possible. Since the partition coefficients K_b and K_a truly express the polymer–solute interaction, independently of any column parameter, the ratio K_b/K_a should represent the sought for "potential" for reversal from the linear behavior. As each partition coefficient is characterized by a slightly different

Table III
Bulk to Surface Retention Ratios and Limiting Surface Tensions for Selected Polymer–Solute Systems

Polymer	Solute	T_g, °C	$(V_g/U_s)_{T_g}$, m²/g	$(\partial\gamma/\partial w_1)^\infty{}_{T_g}$, dyn/cm	$(a_1/w_1)^\infty{}_{T_g+50}$
Polystyrene	n-Hexadecane[a]	98	27.4	−0.50	16
Poly(NIPAM)	n-Hexadecane[b]	130	25.4	−0.58	40
Poly(vinyl chloride)	n-Decane[c]	80	11.0	−1.9	42
Poly(methyl methacrylate), H	n-Dodecane[c]	85	7.9	−2.2	49
Poly(acrylonitrile)	Acetonitrile[d]	110	1.3	−62	13

[a] Retention volume of ref 9. [b] Retention volume of ref 1. [c] Retention volume of ref 4. [d] Retention volume of ref 7.

temperature dependence, this ratio should be determined at the point of interest, the glass transition temperature.

The ratio of bulk to surface partition coefficients, or more correctly the reciprocal of this ratio, has precise physical significance. It expresses the excess concentration of solute molecules on the surface over that in the bulk polymer. Martin,[11] in early studies of liquid surface effects in GLC, has pointed out the relation between partition coefficients and surface tension of the stationary phase–solute solution. It can be shown that, since[17]

$$\Gamma_1^{(1)} = -(x_1/RT)(\partial\gamma/\partial x_1)^\infty \tag{4}$$

where $\Gamma_1^{(1)}$ is the excess concentration of solute on the surface over that in the solution, x_1 the mole fraction of solute, and γ the surface tension, one has for the partition coefficients,[18]

$$(\partial\gamma/\partial x_1)^\infty = -RTn_2(K_a/K_b) \tag{5}$$

where n_2 is the number of moles of stationary phase per unit mass. Introducing a weight composition variable as commonly done for polymer solutions, one has

$$(\partial\gamma/\partial w_1)^\infty = -(RT/M_1)(K_a/K_b) \tag{6}$$

and for the retention volumes

$$(\partial\gamma/\partial w_1)^\infty = -(RT/M_1)(U_s/V_g) \tag{7}$$

These equations relate the GC partition coefficients (retention volumes) to the limiting value of the surface tension of stationary phase–solute solution.

Equation 5, originally developed by Martin, was little used in GLC owing to the difficulty of directly measuring surface partition coefficients. Some such studies[18] combining gas chromatographic and static surface tension measurements revealed the inadequacies of stationary phase surface areas derived from inert support specific surface areas. However, with polymer stationary phases at temperatures below T_g a single retention mechanism prevails[1,9] and eq 1 reduces to

$$V_R = K_aA_L \tag{8}$$

thereby allowing for the determination of surface partition coefficients. Furthermore, it was shown[9] that the surface area of polymer stationary phases per gram of inert support, while greatly reduced from nitrogen adsorption surface areas, was remarkably constant over three orders of magnitude of coating thickness, enabling a direct computation of surface areas of coated supports. As a result, both bulk and surface partition coefficients (retention volumes) can be determined from the linear parts of a single retention diagram encompassing T_g.

Table III lists bulk to surface retention volume ratios and limiting values of solution surface tension for selected polymer–solute systems. The corresponding activity coefficients were included for the purpose of comparison. It is seen that the larger values of the bulk to surface ratio are associated with those retention diagrams exhibiting the stronger reversals, for similar coating thickness (w_L/A_L). More importantly, no direct correlation is to be found between the V_g/U_s ratios and the corresponding activity coefficients. This is evidenced by the pairs hexadecane–PS and acetonitrile–PAN on the one hand, and hexadecane–poly(NIPAM) and dodecane–PMMA on the other, which are characterized by similar activity coefficients but widely differing V_g/U_s ratios. This ratio thus appears as a most suitable parameter to describe the potential for reversal of any polymer–solute system. As already pointed out, the actual detection of the transition temperature is dependent on a judicious choice of column parameters.

In the case of PAN it is seen that the ratio of bulk to surface retention volumes is considerably smaller than for any other polymer–solute system listed. This, in conjunction with smaller activity coefficients, strongly suggests that surface adsorption is the predominant retention mechanism. Upon a further lowering of the solubility of the probe in the polymer, as brought about by using dodecane rather than acetonitrile, bulk sorption would be expected to afford an essentially negligible contribution to overall retention, leading to a linear retention diagram through T_g.

These results also indicate that the suitability of a particular probe to detect the glass transition of a polymer stationary phase cannot be analyzed in the simpler terms of its solvent–nonsolvent nature. The actual magnitude of polymer–probe interaction, i.e., both bulk and surface retention volumes, must be determined. It can, however, be stated that, in general, both solvent and nonsolvent solutes should be appropriate for such experiments.

In contrast to these findings poly(NIPAM) has been shown[1] to exhibit an uncharacteristic retention behavior with solutes which are solvents of the polymer. A linear retention diagram, corresponding exclusively to bulk sorption, was recorded through T_g with both butanol and acetic acid (Figure 1). Considering that reversal is indeed observed with nonsolvents and that only substances capable of hydrogen bond formation are solvents of the polymer, it is conceivable that solvents affect the structure of the bulk polymer, namely by depressing its glass transition temperature. To gain further insight into these systems the chromatographic behavior of poly(NIPAM) was reinvestigated under experimental conditions designed so as to approximate infinite dilution of the probe as closely as possible, thereby preventing any plasticization. The results of these experiments with n-butyl alcohol are shown in Figure 4 as a retention diagram. While no reversal as such could be observed, a change in slope was detected at about 130 °C, the reported T_g of poly(NIPAM). Since the same retention mechanism, bulk sorption, was found in both linear portions, this cannot be ascribed to a transition from surface to bulk retention.

To assess the significance of such a retention diagram, both activity coefficients and Flory χ parameters were computed from these data. The Flory χ parameter, when

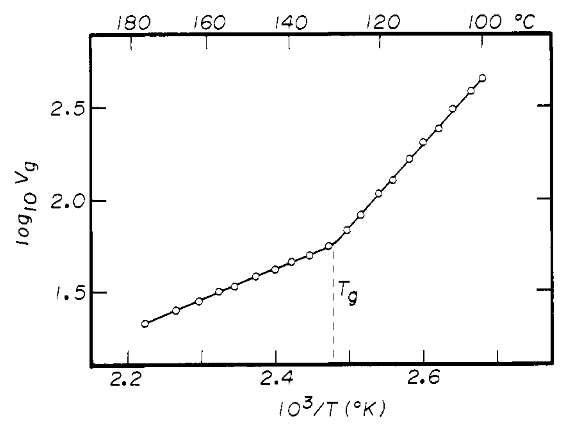

Figure 4. Retention diagram for *n*-butyl alcohol on poly(NIPAM).

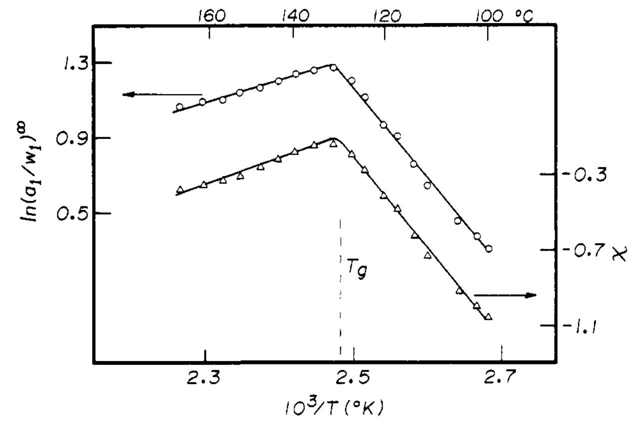

Figure 5. Temperature dependence of (○) activity coefficient and (△) χ parameter for *n*-butyl alcohol in poly(NIPAM).

neglecting gas phase nonideality, is related to the GC retention volume by the equation[14]

$$\chi = \ln [(273.16 R v_2 w_L)/(p_1{}^0 V_R V_1)] - 1 \qquad (9)$$

where v_2 is the specific volume of the polymer and V_1 the molar volume of the solute. The results of these computations, shown in Figure 5, indicate the existence of strong polymer–solute interactions, as evidenced by the small activity coefficients and negative χ parameters. The partial molar heats of mixing, $\Delta h_1{}^\infty$, derived from the relation[14]

$$\Delta h_1{}^\infty = R[(\partial \ln (a_1/w_1)^\infty/\partial(1/T)] \qquad (10)$$

were considerably different above and below T_g, 1.8 ± 0.2 and −9.7 ± 0.4 kcal/mol, respectively. A positive $\Delta h_1{}^\infty$, indicating resistance to mixing, may appear surprising in view of the magnitude of the χ parameters. In general solvents of the polymer exhibit small interaction parameters and near-zero partial molar heats of mixing while nonsolvents are characterized by large χ parameters and sizable, positive $\Delta h_1{}^\infty$. However, it should be borne in mind that $\Delta h_1{}^\infty$ only represents the difference in molar heat of the solute in the pure polymer and the pure liquid. Since a hydrogen bonding energy of about 5.5 kcal/mol has been reported for pure *n*-butyl alcohol[19] the interaction between nonassociated butanol and poly(NIPAM) is in effect quite large, −3.7 and −15.2 kcal/mol, respectively. The existence of a change in partial molar heat of mixing at T_g, and hence the possibility of detection of the transition temperature therefrom, nonetheless remains a unique observation among the numerous polymer–solute systems so far investigated. While the mechanism of bulk sorption at temperatures below T_g is somewhat unclear, it can only be theorized that, unlike other polymer–solute systems, a change in the type of polymer–solute interaction rather than retention mechanism takes place at T_g.

Conclusions

The effects of the solute molecule on the retention behavior of polymer stationary phases in the vicinity of T_g have been investigated. It is shown that, apart from suitable conditions of coating thickness, the solubility of the probe in the polymer (activity coefficient) is inadequate to characterize the GC behavior of the polymer–solute system in the vicinity of T_g. The magnitude of solute interaction with both bulk and surface of the polymer must be determined. The ratio of bulk to surface partition coefficients (retention volumes) is the critical parameter in the detection of the transition temperature. This ratio is directly related to the limiting value of the solution surface tension which can be evaluated from chromatographic data. It is found that, in general, both solvents and nonsolvents of the polymer are suitable in these studies.

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