Evaluation of a Gas Chromatographic Method for the Determination of Glass Transitions in Polymers

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Received December 9, 1974

ABSTRACT: Studies of the gas chromatographic behavior of a variety of polymeric stationary phases with alkane or alkanol probes show that the occurrence of the typical *z*-shaped retention diagram is indeed a general feature which occurs just above the glass transition for all of the polymers studied. Under appropriate conditions of probe solubility and coating thickness such behavior may be considered as diagnostic for T_g, but the actual value of T_g corresponds most nearly with the onset of bulk sorption as estimated from the first deviation from linearity of the portion of the retention diagram corresponding to surface adsorption. The same general behavior is observed with both internally and externally plasticized samples, as well as with those whose glass transition is altered by changes in molecular weight or stereoregularity. It is concluded that the gas chromatographic method may be used with some confidence in the detection and estimation of the glass transition in polymers.

Early experiments by Smidsrod and Guillet[1] and by Lavoie and Guillet[2] showed that inverse gas chromatography could be used to study glass transition behavior in polymers. In a recent publication, Liebman, *et al.*,[3] reported the detection of the glass transition, T_g, and of a secondary transition, T_β, in poly(vinyl chloride) (PVC) by recording the chromatographic separation of cis–trans isomers as a function of temperature. For plasticized PVC, however, their experiments did not show the expected behavior. On this basis the authors concluded that the gas–liquid chromatography (glc) technique was not applicable to the study of plasticized polymers. This prompted us to reinvestigate the use of the so-called "molecular probe" method with particular reference to the study of glass transitions in plasticized PVC and polystyrene. Our results suggest that other experimental factors may have led to the failure of the Liebman technique, since we observe the expected behavior for both plasticized and unplasticized samples.

We also report the ability of the method to discriminate between polymer chains of differing stereoregularity, by determining the glass transition temperatures for three samples of poly(methyl methacrylate) (PMMA), which are predominantly isotactic, syndiotactic, and heterotactic, respectively.

Experimental Section

Polymers. Poly(vinyl chloride) was obtained from Imperial Oil Enterprises and is identical to that described as PVC(c) by Wallace, *et al.*[4] The polystyrene sample used for plasticizer experiments was an anionic polymer of M_v = 120,000 obtained from Polymer Corporation Ltd. The PMMA samples are labeled according to tacticity of the predominant triad; heterotactic PMMA was purchased from Fisher Scientific Co.; syndiotactic and isotactic PMMA were polymerized with butyllithium catalyst at −78° in THF and toluene, respectively, as described elsewhere.[5] The resultant tacticity was determined by nmr at 100 MHz for the syndiotactic (A) and isotactic (B) samples[5] (Chart I). Narrow MWD anionic polystyrenes were obtained from Pressure Chemical Co. Styrene–butadiene polymers were obtained from Cellomer Associates, Inc. Plasticizer was Eastman Kodak di-*n*-octyl *o*-phthalate.

Columns. The polymers were first dissolved in a suitable solvent and deposited onto an inert chromatographic support by slow evaporation of the solvent. For plasticized polymers, a known amount of plasticizer dissolved in the same solvent was added to the polymer solution. After vacuum drying, the support was packed into 0.25 in. o.d. copper columns, usually 30–100 cm in length. The weight of the stationary phase was determined by calcination. Both PVC and PS were coated onto Chromosorb G, AW DMCS 70–80 from THF while PMMA's were dissolved in benzene and deposited onto Chromosorb W (high performance). Polymer loadings ranged from 3 to 15%, the higher loadings usually giving more pronounced deviation from normal glc behavior and thus facilitating the identification of T_g. Other information pertaining to the columns is summarized in Table I.

Chart I

Sample	I	H	S
A	0.04	0.34	0.62
B	0.89	0.08	0.03

Data. Retention data were collected on a Hewlett Packard 5750 gas chromatograph equipped with dual flame ionization detectors, using nitrogen as a carrier gas and methane as a noninteracting marker. Flow measurements were carried out with a soap bubble meter. Specific retention volumes, V_g, are corrected for pressure drop along the column, measured with a mercury manometer. The amount of stationary phase is expressed in grams of polymer, excluding the plasticizer.

For low-temperature experiments the columns were immersed in a methanol-filled dewar whose temperature was lowered by successive additions of liquid nitrogen. Short 1/16 in. o.d. leads connected the columns to injection port and detector. Methane was found suitable as a noninteracting marker even at subambient temperatures. The flow rates used ranged from 10 to 70 cm^3 min^{-1} which are those used in conventional analytical glc. Although the flow rate affects the shape of the retention diagram in the "nonequilibrium" region, the straight line portions are usually independent of flow rate and mass of the injected probe molecule. These effects are dealt with in more detail in a subsequent publication.[7]

Differential scanning calorimetric (dsc) traces were obtained on a Perkin-Elmer DSC 1B and a Du Pont 990 thermal analyzer. Direct use of coated chromatographic support proved not feasible and for plasticized samples films were cast under similar conditions, thin enough to ensure good homogeneity. T_g was taken as the intersection of the base line with the sloping portion, at a scan rate of 10°C/min. The quoted values represent an average over three determinations, with an accuracy of ±2°. The glass transition temperatures determined by dsc are reported on the retention diagrams for comparison purposes.

Results and Discussion

In glc, solvent–solute interactions can be related to the specific retention volume.[1] The generalized retention diagram of the logarithm of the specific retention volume versus reciprocal of the absolute temperature is a linear plot in the absence of any transition. A *z*-shaped curve such as shown in Figure 1 is indicative of a glass transition.[1,2] At $T < T_g$ the solvent–solute interaction is essentially surface adsorption, while at $T > T_g$ it is suitably described by an expression such as[6]

$$V_g = K_{ab}V_L + K_sA_L \qquad (1)$$

where K_{ab} and K_s are partition coefficients pertaining to bulk sorption and surface adsorption, respectively, V_L and A_L being the volume and surface area of the stationary

Table I
Stationary Phases and Column Parameters

Stationary phase		Packing and column				
Polymer	Identification	Solvent	Support	Loading, %	Mass, g	Column
Polystyrene	$M = 51{,}000$	Benzene	Chromosorb G, AW, DMCS, 50–60	2.41	0.088	A
	$M = 4{,}000$	Benzene	Chromosorb G, AW, DMCS, 50–60	3.21	0.038	B
	$M = 2{,}100$	Benzene	Chromosorb G, AW, DMCS, 50–60	3.21	0.037	C
Poly(methyl methacrylate)	Syndiotactic	Benzene	Chromosorb W, high performance, 80–100	7.84	0.4810	D
	Isotactic	Benzene	Chromosorb W, high performance, 80–100	6.21	0.2745	E
	Heterotactic	Benzene	Chromosorb W, high performance, 80–100	8.78	0.4863	F
Styrene-butadiene	85% styrene	Benzene	Chromosorb G, NAW, 70–80	8.54	0.3424	G
	45% styrene	Benzene	Chromosorb G, AW, DMCS, 60–80	6.62	0.1892	H
	23% styrene	Benzene	Chromosorb G, AW, DMCS, 60–80	7.95	0.2248	I
Poly(vinyl chloride	0% DOP	THF	Chromosorb G, AW, DMCS, 70–80	11.1	0.4571	J
	4.8% DOP	THF	Chromosorb G, AW, DMCS, 70–80	11.7	0.3668	K
	9.9% DOP	THF	Chromosorb G, NAW, 70–80	10.7	0.4499	L
	20.9% DOP	THF	Chromosorb G, NAW, 70–80	9.6	0.4025	M
Polystyrene $M = 120{,}000$	0% DOP	Benzene	Chromosorb G, AW, DMCS, 70–80	12.5	0.1140	N
	5.0% DOP	THF	Chromosorb G, NAW, 70–80	9.2	0.3811	O
	10.9 % DOP	THF	Chromosorb G, NAW, 70–80	8.6	0.3494	P

phase. Since the surface to volume ratio can be varied either by changing the amount of polymer on a certain support or by choosing a support with different surface area, the retention diagram will be dependent on experimental conditions. In general, the difference observed at T_g is directly related to the coating thickness.

The first deviation from linearity represents the onset of bulk sorption which is believed to be related to the glass transition of the stationary phase. A more general description of the theory will be the subject of a further communication.[7]

Polystyrene. Early studies by Lavoie and Guillet[2] showed that the glass transition for atactic polystyrene and PMMA could be related to the minimum of the z-shaped retention diagram obtained with typical hydrocarbon probes such as dodecane or hexadecane. From theoretical considerations the glass transition should more properly be related to the temperature at which the straight line por-

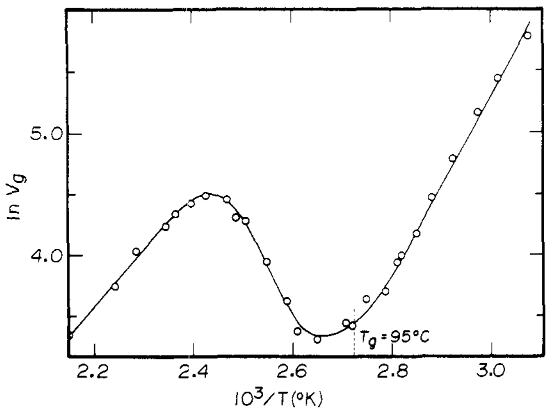

Figure 1. Retention diagram for *n*-dodecane on polystyrene, M = 51,000: column A, flow, F = 29.8 cm^3 min^{-1}.

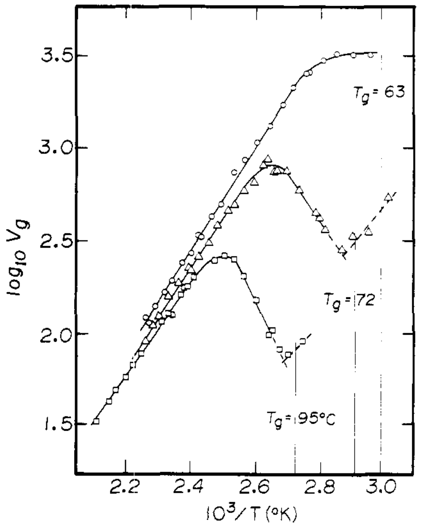

Figure 2. Retention diagrams for *n*-tetradecane on polystyrene (columns C, B, and A): (○) M = 2100, (△) M = 4000, (□) M = 51,000.

tion corresponding to surface adsorption begins to deviate due to the occurrence of bulk sorption. Figure 1 shows experimental data for anionic polystyrene ($\bar{M}_n$ = 51,000) using *n*-dodecane as probe and essentially the same behavior is observed, the glass transition occurring around the first deviation from linearity at about 95°. Columns were then prepared using anionic PS samples of low molecular weight, with the results shown in Figure 2. Because of their low molecular weights, these samples have considerably lower glass transitions, which is also reflected in their chromatographic behavior.

Hydrocarbon probes usually give reasonably symmetrical peaks, even in the nonequilibrium region just above T_g, but other probe molecules such as the linear alkanols do not. It is often not possible to extrapolate to zero concentration of the probe because of peak spreading, but as long as the sample size is kept constant for each injection, typical *z*-shaped diagrams suitable for identification of T_g are obtained even with asymmetric peaks. Such data for two of the narrow distribution styrenes are shown in Figures 3 and 4. These experiments clearly show the value of the glc technique for identifying glass transitions in amorphous polymers.

Plasticized PVC. Figure 5 shows the retention diagrams for PVC with four different plasticizer amounts, 0, 4.8, 9.9, and 20.9% (w/w) di-*n*-octyl phthalate (DOP). The typical

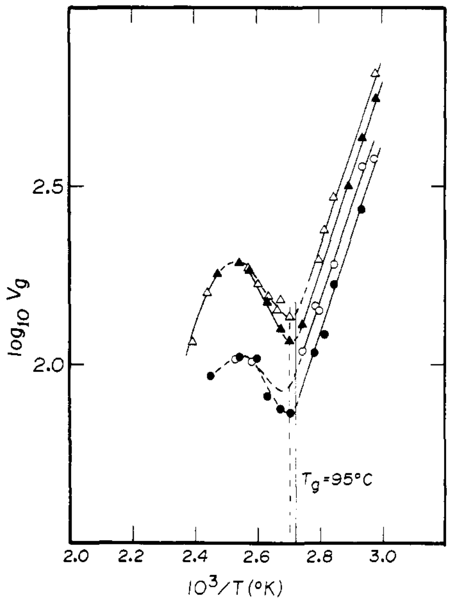

Figure 3. Retention diagrams for *n*-octyl alcohol and *n*-nonyl alcohol on polystyrene, M = 51,000. Sample size in arbitrary units (column A): *n*-octyl alcohol (○) 20, (●) 40; *n*-nonyl alcohol (△) 20, (▲) 40.

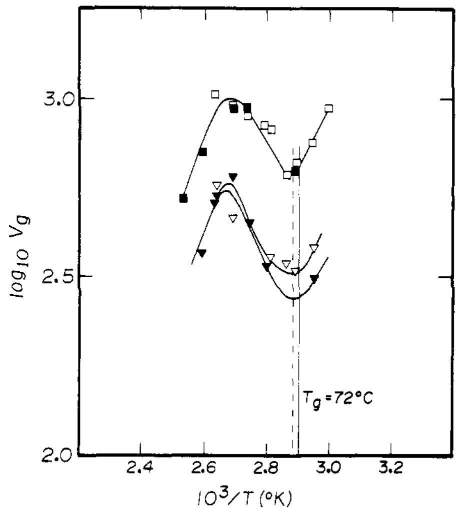

Figure 4. Retention diagrams for *n*-nonyl alcohol and *n*-decyl alcohol on polystyrene, M = 4000. Sample size in arbitrary units (column B): *n*-nonyl alcohol (▽) 20, (▼) 40; *n*-decyl alcohol (□) 20, (■) 40.

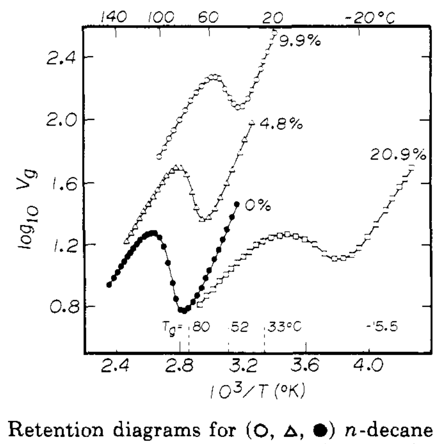

Figure 5. Retention diagrams for (○, △, ●) *n*-decane and (□) *n*-pentane on poly(vinyl chloride) plasticized with DOP: column J, flow, F = 22.2 cm^3 min^{-1}; column K, F = 29.7; column L, F = 59.7; column M, F = 18.0.

Table II
Glass Transition Temperatures by Gas Chromatography and Dsc (deg C)

	Minimum	First deviation, T_1	DSC
		PMMA	
I	88	60	57
S	131	105	118
H	101.5	81.5	79
		PVC–DOP	
% DOP			
0	80	71.5	80
4.8	64	57.5	52 (5.2% DOP)
9.9	40.5	34.5	33
20.9	−10	−20	−15.5
		Styrene–Butadiene	
%S			
23	−49	−55	−56
45	−29	−39	−38.5
85	54	47	50

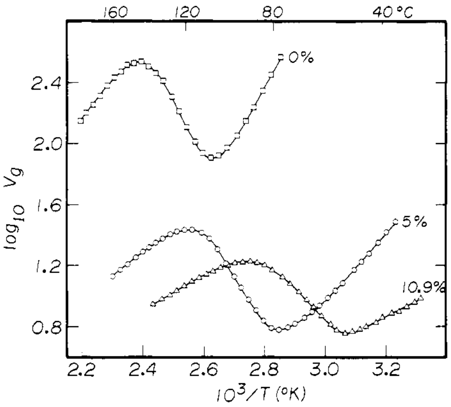

Figure 6. Retention diagrams for (□) *n*-hexadecane, (○) *n*-nonane, and (△) *n*-heptane on polystyrene (M = 120,000) plasticized with DOP: column N, flow, F = 41.0 cm^3 min^{-1}; column O, F = 14.6; column P, F = 12.0.

z-shaped curve is exhibited by the three plasticized polymers as well as the unplasticized one. Increasing amounts of plasticizer are seen to shift the curves toward lower temperatures. Comparison between the values of T_g obtained from the first deviation from linearity of the retention diagram and those given by dsc (Table II) shows a good correlation and illustrates the applicability of inverse chromatography to plasticized polymers.

Upon plasticization, PVC becomes more penetrable to low molecular weight species and the diffusion coefficients for plasticized PVC have been found to increase with the amount of plasticizer.[8] Such findings are corroborated by these experiments, even if only qualitatively. The maximum of the retention diagram is attained when equilibrium is no longer reached during the passage of the chromatographic peak, that is the diffusion coefficient has become too small. The columns containing 0, 4.8, and 9.9% were packed with the same support and coating thickness and investigated with the same solute. The maximum of each curve is seen to occur at progressively lower temperatures as would be predicted from such considerations.

Plasticized Polystyrene. The applicability of the molecular probe method was further extended to include plasticized PS. The plots of the retention diagrams for 0, 5.0, and 10.9% (w/w) DOP in PS are given in Figure 6. As for PVC, the method is responsive to the changes imparted by the plasticizer and the glass temperature is seen to decrease with increasing amounts of plasticizer. Actual values for the temperature of the first deviation from linearity are reported in Table I. The results are seen to be similar, even when quite different probes are used. Polystyrene containing 20% DOP gave unreproducible results, possibly due to competitive adsorption of the plasticizer by the support during the coating procedure.

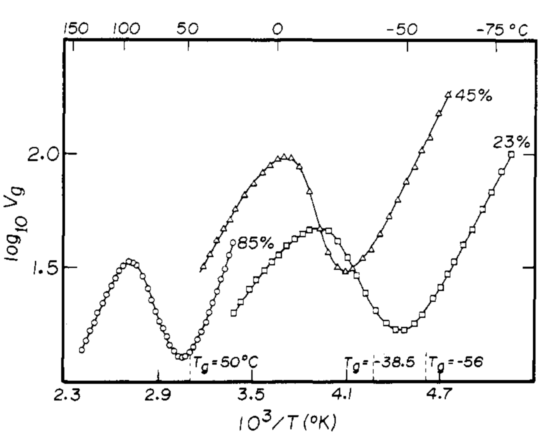

Figure 7. Retention diagrams for (○) *n*-octane, (△) *n*-pentane, and (□) *n*-butane on styrene–butadiene copolymers. Composition of copolymers is given as per cent styrene: column G, flow, F = 13.9 cm^3 min^{-1}; column H, F = 36.9; column I, F = 24.0.

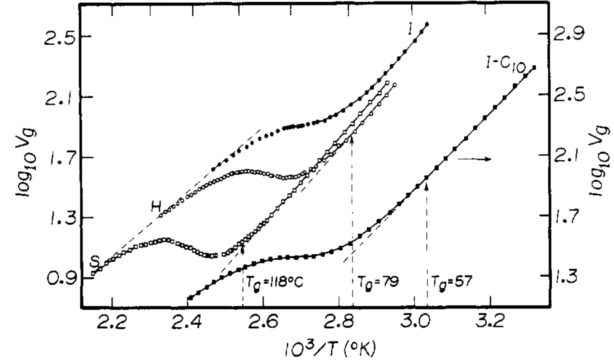

Figure 8. Retention diagrams for *n*-dodecane on (I) isotactic, (S) syndiotactic, and (H) heterotactic poly(methyl methacrylate) and for *n*-decane on isotactic PMMA (■): column D, flow, F = 46.4 cm^3 min^{-1}; column E, F = 70.3 (●) and 36.1 (■); column F, F = 46.6.

Styrene–Butadiene Copolymers. The glass transition of polystyrene can also be altered by copolymerization with another monomer, such as butadiene. Data on three copolymers containing 23, 45, and 85% styrene, respectively, are shown in Figure 7. The glass transitions range from −56 to +50°, which requires the use of smaller alkanes such as *n*-butane and *n*-pentane as probes, but again, excellent agreement is found between T_g determined by dsc and the first deviation value from glc (Table II).

Poly(methyl methacrylate). Figure 8 shows the retention diagrams for syndiotactic, heterotactic, and isotactic PMMA with *n*-dodecane, as well as isotactic with *n*-decane to determine more accurately its first deviation from linearity. Chromatographic determination of the glass transition agrees quite well with the dsc data (Table II), except for syndiotactic PMMA. In this case the value determined by glc seems more reasonable than that determined by dsc

Table III
Heats of Solution and Adsorption

Stationary phase			Heats,[a] kcal/mol	
Polymer	Identification	Solute	Solution	Adsorption
	% styrene			
Styrene–butadiene	85	n-Octane	7.0 ± 0.1	9.1 ± 0.1
	45	n-Pentane	5.5 ± 0.2	7.4 ± 0.2
	23	n-Butane		6.0 ± 0.1
	% DOP			
Poly(vinyl chloride)	0	n-Decane	6.9 ± 0.1	11.0 ± 0.1
	4.8	n-Decane	7.7 ± 0.1	10.8 ± 0.2
	9.9	n-Decane	8.2 ± 0.1	12.0 ± 0.1
	20.9	n-Pentane	5.1 ± 0.1	7.5 ± 0.1
	% DOP			
Polystyrene	0	n-Hexadecane	11.7 ± 0.1	15.5 ± 0.2
	5.0	n-Nonane	7.1 ± 0.1	10.6 ± 0.1
Poly(methyl methacrylate)	Heterotactic	n-Dodecane	7.6 ± 0.1	12.7 ± 0.1
	Syndiotactic	n-Dodecane	7.6 ± 0.1	13.1 ± 0.1
	Isotactic	n-Dodecane	7.7 ± 0.2	13.0 ± 0.1
	Isotactic	n-Decane	7.0 ± 0.1	12.0 ± 0.1

[a] Error as standard deviation.

in view of the relatively low content (60%) of syndiotactic units in the polymer. However, the reason for the large discrepancy (13°) between the two procedures remains unresolved. The differences between these three stereoregular forms of the polymer are immediately noticeable from the diagrams. The "flatness" of the retention diagram, as compared to either PS or PVC, is due to the use of higher surface area support and of lower coating weight (6% for isotactic). The similarity of retention volume behavior in the portions of the diagram, where either surface adsorption or bulk sorption clearly predominates, is an indication that n-dodecane shows no specific interactions related to the tactic structure of the bulk of the polymer.

General Considerations. The successful application of the molecular probe method to the determination of the glass transition temperature of polymer stationary phases requires a careful design of experimental conditions. The detection of a transition temperature based on a change of retention mechanism is directly dependent on the surface to volume ratio (A_L/V_L) of the stationary phase, as expressed in eq 1. If too low a coating thickness or an inert support of very high surface area is used, this change of retention mechanism may no longer be detectable. Even at large coating thicknesses a probe of suitable solubility must be found to ensure its detection.[7] Consequently the absence of a discontinuity in a retention diagram cannot always be construed as evidence against the existence of a phase transition. By using (nonpolar) alkane probes, whenever possible, retention volumes are most commonly found independent of sample size over a large range of sample size, thus avoiding less precise extrapolation procedures.

The accuracy achievable in the determination of the temperature of first deviation, T_1, depends ultimately on the magnitude of the deviation (experimental conditions) and the density of experimental points. In the present work the error on T_1 is estimated at about ±2°.

Thermodynamic Parameters. As has been noted previously,[1] the slopes of the straight line portions of these curves can be related to the heats of solution and adsorption, respectively, for the hydrocarbon probes on the polymer. The values of the slopes obtained in these experiments are summarized in Table III.

Conclusions

The results of these studies confirm that the molecular probe technique gives values of T_g which correlate well with those from differential thermal analysis for a wide variety of polymers and copolymers. The method applies regardless of whether variations in T_g are caused by molecular weight, structure, and tacticity or due to internal or external plasticization.

Acknowledgment. We wish to thank the National Research Council of Canada and the Dunlop Research Centre of Sheridan Park, Ontario, for financial support of this work, and the Canada Council for fellowship support (to J.-M.B.). We are grateful to H. L. Williams for the use of the Du Pont thermal analyzer.

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