Inverse Gas Chromatography of Poly(n-Butyl Methacrylate): Effect of Flow Rate on Specific Retention Volume and Detection of Glass Transition Temperature

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Synopsis

Flow-rate effect on specific retention volume (V_g^0) was studied by eluting aliphatic, aromatic, and chlorinated aliphatic probes at infinite dilution on poly(n-butyl methacrylate) stationary phase at different temperatures from -10 to 150°C, encompassing both the glass transition (T_g) and the softening temperatures of the polymer. The effect became pronounced as the temperature was reduced below 100°C. V_g^0 decreased with an increase in the flow rate: first linearly at temperatures between 70 and 100°C, and then nonlinearly at all temperatures below 70°C. The retention diagrams of n-pentane, isooctane, and cyclohexane alone enabled the detection of glass transition. Dichloromethane gave a linear retention diagram through T_g without showing the flow-rate effect.

INTRODUCTION

The technique of inverse gas chromatography (IGC) and its application in studies on various physicochemical properties of polymer systems have been described in many publications, e.g., Refs. 1–6. IGC measurements have been greatly influenced by several parameters, viz., physical properties and composition of polymer stationary phase,[7-11] chemical nature and amount of probe,[9-14] nature of support material,[15] mass ratio of the polymer to the support in a column,[7-10,16-19] and flow rate of carrier gas.[12,16,20-24] The investigation on these effects have provided valuable information regarding the retention mechanism and phase transitions in polymers, especially the glass transition temperature (T_g). However, two aspects, namely, the suitability of a solvent as a probe for the detection of glass transition and the dependence of its specific retention volume (V_g^0) on the flow rate, are yet to be understood fully.

In an earlier study on poly(vinyl acetate) (PVAc),[20] it has been reported that, at a temperature close to T_g, V_g^0 could vary significantly with (or remain independent of) the flow rate depending upon the range (flow rate) selected. The estimated value of T_g of PVAc has also shown a decreasing trend with reducing flow rate. The flow rate should be treated, therefore, as an important parameter in deciding the accuracy and reliability of any information obtained from IGC measurements. There is no major report on this aspect after

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a previous publication[20] from this laboratory, to the best of our knowledge. The generalizations drawn earlier about the flow-rate effect on the retention behavior of a polymer stationary phase, however, must be reexamined and confirmed over a wide range of temperature as well as flow rate by using a different polymer.

In the present work, the effect of flow rate on the retention behavior of poly(n-butyl methacrylate) (PnBMA) has been investigated over the temperature range of -10 to $150°C$. This polymer has been selected for two reasons. First, its T_g is close to the ambient temperature, making it convenient to carry out IGC measurements in both the glassy and the melt regions of the polymer. Secondly, there appears to be a large difference between the reported values of V_g^0 of some common probes on PnBMA,[25,26] making it desirable to review this case. Fifteen probes differing in their chemical nature and solvent power for the polymer were employed in this study. They include all probes used in the previous work;[20] many probes are common with those in Refs. 25 and 26 for a comparative study.

EXPERIMENTAL

Materials

PnBMA was prepared by free-radical polymerization of the monomer in toluene at $70°C$ using benzoyl peroxide as the initiator. The polymer was precipitated by pouring the reaction mixture into methanol. It was washed repeatedly by excess of methanol, and dried in a vacuum oven at $50°C$ till constant weight was achieved. The viscosity-average molecular weight ($\bar{M}_v$) was determined from the intrinsic viscosity measured in benzene at $30°C$, using the Mark–Houwink equation,[27] and was found to be 372,000. The number-average molecular weight ($\bar{M}_n$) was determined with a Knaur membrane osmometer and was 91,000. The glass transition temperature was measured by the penetration method at the heating rate of $4°C/min$, employing a homemade thermomechanical analyzer, and was found to be $18 \pm 2°C$. This value has been taken as the reference T_g in the following discussion on IGC results. Chromatography or analytical grade solvents were used as the probes (Table I).

Columns

PnBMA was deposited onto Chromosorb W, AW, DMCS, 80/100 mesh support from 1% (w/v) solution in benzene by slow evaporation of the solvent at $50°C$ under partial vacuum in a rotavaporator. The coated support was dried to constant weight in a vacuum oven at 5 Torr and $50°C$. It was sieved and packed quantitatively in an annealed copper tubing (150 cm × 0.625 cm). The column loading was estimated by calcination of the coated and uncoated supports at $550°C$ in triplicate under identical conditions. The polymer-to-support mass ratios for columns I and II prepared for this work were found to be 0.0741 and 0.1033, respectively.

We used the work of Braun and Guillet[16,19] as the reference in the selection of the column loading. They have demonstrated that the effective surface area of a porous support material decreases considerably with an increase in the

TABLE I
Probes and Characteristic Temperatures (°C) for Column II[a,b]

| Probe | Abbreviation | $T_2(L)$ | $T_2(U)$ | Difference from T_g (approx.) | |
				$T_2(L)$	$T_2(U)$
n-Pentane	nC_5	10	70	−10	50
n-Hexane	nC_6		70		50
n-Heptane	nC_7	50	80	30	60
n-Octane	nC_8	50	70	30	50
n-Nonane	nC_9	70	70	50	50
n-Decane	nC_{10}	70	80	50	60
iso-Octane	iC_8	80	110	60	90
Cyclohexane	cC_6	40	90	20	70
Dichloromethane	CH_2Cl_2	25	50	5	30
Chloroform	$CHCl_3$	50	70	30	50
Carbontetrachloride	CCl_4	50	70	30	50
1,1,2-Trichloroethane	C_2HCl_3	30	50	10	30
Benzene	C_6H_6	40	50	20	30
Toluene	Tol	50	70	30	50
p-Xylene	p-Xyl	50	70	30	50

[a] For nC_5, $T_{max} < 30°C$, and $T_{min} \sim 5$–$10°C$.
For cC_6, $T_{max} < 40°C$, and $T_{min} \sim 5$–$10°C$.
For iC_8, $T_{max}(U) = 80°C$, $T_{max}(L) = 50°C$, $T_{min}(U) = 30°C$, $T_{min}(L) = 10°C$, $T_1(U) = 10°C$, $T_1(L) = -7°C$.
[b] The uncertainty in these values is about 5°C.

size of a polymer adsorbate, and that it results in a coating thickness of a higher order of magnitude at a relatively lower column loading especially in the case of high molecular weight polymers. For example, a 10 wt % loading of polystyrene ($\overline{M}_v = 120,000$) on Chromosorb P has produced a 1×10^4 Å thick film.[16,19]

The column loadings in the range of 4–13 wt % polymer on Chromosorb W, AW, DMCS have been regularly employed in the studies on phase transitions as well as solution thermodynamics (cf. Refs. 7, 8, 26, and 27). Thick coatings cause many deteriorating effects on the chromatography of polymer stationary phases, the following being the most serious ones: At large column loadings, the peaks become excessively broad; a majority of probes can not attain bulk-sorption equilibrium in the column even at $T \gg T_g$; V_g^0 may tend to zero instead of the equilibrium value.[16,19] The results will show that a higher column loading is undesirable in the present work.

Chromatography

The dual column gas chromatograph (GC) and the method for IGC measurements were the same as described elsewhere.[20] In order to detect the elution peaks of trace quantities of the probes, the GC was fitted with a four-filament thermal conductivity detector and an Omniscribe strip-chart recorder with the response time of 0.3 s for the full-scale deflection of 1 mV on a 25-cm scale. The detector was maintained at 200°C and the injector at 150 or 200°C depending upon the boiling temperature of the probe used. The flow

rate of the carrier gas (dry hydrogen) was measured with a soap bubble flowmeter at the column-outlet that was kept open to the atmosphere. The inlet pressure of the column was measured with a mercury manometer and the atmospheric (outlet) pressure with a barometer. The traces of probes were mixed with air as the internal marker, and injected into the column with a Hamilton microsyringe (Model 701N) using the common technique.[28] A volumetrically adjustable liquid syringe (Hamilton model CR-700-20) was employed to dispense the known and fixed volume of the probe samples.

Each probe was injected at least three times, and the average retention time (t_R) corrected for the gas holdup in the apparatus was used to calculate V_g^0 from the well-known relation[29]

$$V_g^0 = F\left(\frac{P_o - P_w}{P_o}\right) \frac{273.16}{T_a} \frac{3}{2} \left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] \frac{t_R}{W_1}$$

where P_i and P_o are, respectively, the inlet and outlet pressures in the column, P_w is the water vapor pressure in the flowmeter at ambient temperature T_a (K), F is the flow rate, and W_1 is the weight of PnBMA in the column.

The measurements were carried out mostly by eluting infinitesimal small quantities of the probes on column II unless specified otherwise. The experimental error in V_g^0 was about 1.5%. On repeating the measurements at temperatures above 70°C, the results were found to be reproducible to $\pm 0.7\%$. On decreasing the temperature, the elution peaks became broad and their rear profile became asymmetric due to a slow and incomplete sorption of the probe vapors in the stationary phase. Thus, the reproducibility was reduced gradually to about 3–5% at $T \leq 10°C$. These kinetic effects on the peak shape were visible at temperatures as high as 90°C in the cases of n-octane, n-nonane, n-decane, and p-xylene, and 50°C in the cases of n-hexane, n-heptane, benzene, toluene, chloroform, carbontetrachloride, and 1,1,2-trichloroethane.

The amount of the probe also influenced the shape of the peak at and below 30°C. The V_g^0 values of the above-mentioned probes could not be determined reliably at and below 20°C because the proper elution was not possible with small amounts, while the large sample volumes caused the peak maxima to become flat. Their elution behavior, therefore, is described at higher temperatures alone.

On the other hand, dichloromethane showed very small asymmetry on the rear profile that too at temperatures below 10°C and without any appreciable tailing in the peak; its specific retention volume was independent of the amount injected. For n-pentane, cyclohexane, and isooctane, the asymmetry and tailing effects were observed at less than half-peak-height at temperatures below 30°C. However, their specific retention volumes were not affected appreciably outside the experimental error provided that the sample injected was less than 0.5 μL. If it was kept larger than 1.5 μL, the increase in the peak height was not proportional to the amount injected and the following were observed: The peak maxima was shifted to higher retention times; the tailing and asymmetry effects were enhanced; and the drift of the baseline, though temporary, was in the positive direction. This indicates that the glassy polymer was swollen by the probe vapors and that the number of probe moles

eluting in the sharp pulse portion of the peak had declined while those in the tail had increased. Therefore, a sufficiently large time gap was allowed to lapse between subsequent injections of the probes in order to prevent their elution on the diffused tail of a preceeding peak. The peak width at half-height was approximately four times that of t_R at $-10°C$. On raising the temperature, it was reduced gradually to become comparable to, or smaller than, t_R at about $20°C$ for each probe used.

The following sample volumes were found necessary and were injected to produce reasonably good peaks for the measurement of V_g^0:

Temperature	Probe (s)	Sample volume
Above 70°C	All	< 0.01 μL
30–70°C	All	≤ 0.1 μL
10–30°C	$nC_5, cC_6, iC_8,$ and CH_2Cl_2	0.2 μL
Below 10°C	nC_5 and iC_8	0.5 μL
	cC_6 and CH_2Cl_2	1.0 μL

The condition of infinite dilution of the probes in PnBMA is not fully satisfied, in the strict sense, at and below 30°C. However, the marginal increase in the amount of the probe has not introduced any serious error in the qualitative understanding of the dependence of V_g^0 on the flow rate, which is discussed in the next section.

RESULTS AND DISCUSSION

Flow Diagrams

The retention volume was found to be independent of the flow rate (F) at temperatures above 100°C only. In general, the values of V_g^0 have decreased linearly with an increase in the flow rate, in the temperature range of 70–100°C, and nonlinearly at all temperatures below 70°C. The plots of V_g^0 against F (flow diagrams) of some selected probes are shown in Figures 1–4 as an example of this behavior. The nonlinear plots may be divided into three regions, as in the case of PVAc,[20] that would represent (i) the plateau of flow rates normally exceeding 80 mL/min, (ii) the nonlinearity at intermediate flow rates, and (iii) the tendency for a linear variation at the flow rates below 40 mL/min. The flow-rate effect became more pronounced as the temperature was decreased to T_g; it was observed also at $T \ll T_g$. One may, thus, conclude that, at low temperatures and at high flow rates, the probes were retained mainly by the surface adsorption mechanism because the corresponding "residence time" in the column was not sufficient for the probes to penetrate the whole of the bulk-polymer phase.

The increase in the values of V_g^0 above the plateau indicates the onset of bulk sorption as the flow rate is reduced below a critical value. The greater the slope of the curve, the greater is the contribution of bulk sorption to the measured retention volume. The largest increase is shown by cyclohexane (Fig. 1) followed by n-pentane (Fig. 2) and isooctane (Fig. 3). At very low flow rates, it became essential to inject larger amounts of the probes than desirable in
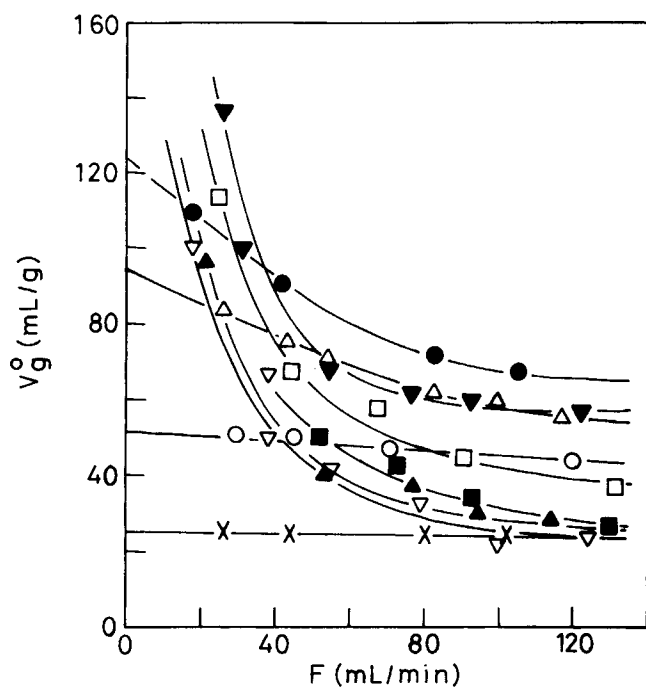
Fig. 1. Flow-rate effect on V_g^0 of cyclohexane at different temperatures (°C): (□) -7; (■) 0; (▲) 5; (▽) 10; (▼) 20; (●) 25; (△) 50; (○) 70; (✕) 100.
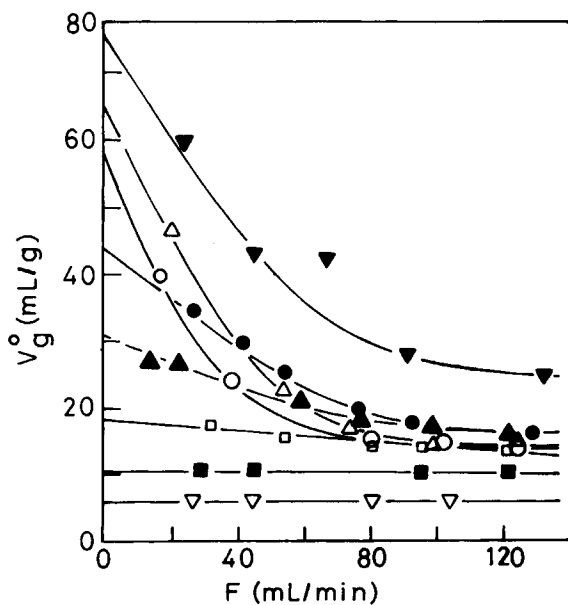
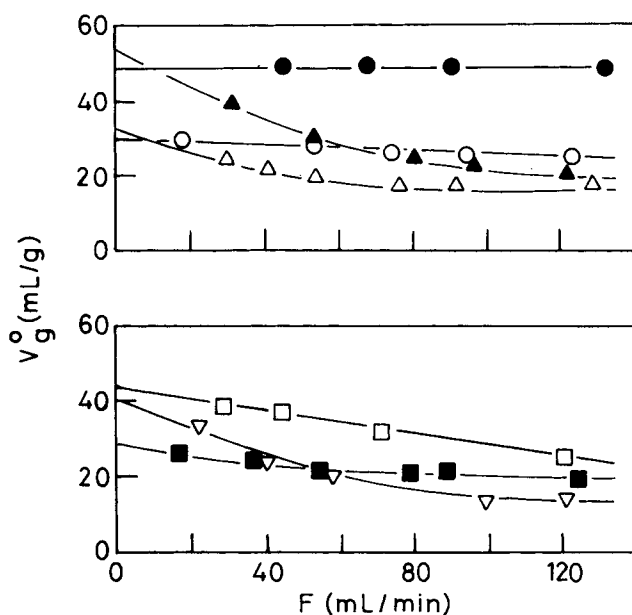Fig. 2. Flow-rate effect on V_g^0 of n-pentane at different temperatures (°C): (▼) -7; (△) 5; (○) 10; (●) 20; (▲) 30; (□) 50; (■) 70; (▽) 100.

Fig. 3. Flow-rate effect on V_g^0 of isooctane at different temperatures (°C): (●) −7; (○) 5; (■) 10; (△) 20; (▽) 30; (▲) 50; (□) 70.

most of the cases; consequently, the reproducibility was adversely affected due to the peak broadening. Hence, the data obtained at flow rates smaller than 20 mL/min have been excluded from this paper.

The flow diagrams have been found to be nonlinear at all temperatures below 70°C in the cases of *n*-octane, *n*-nonane, *n*-decane, toluene, and
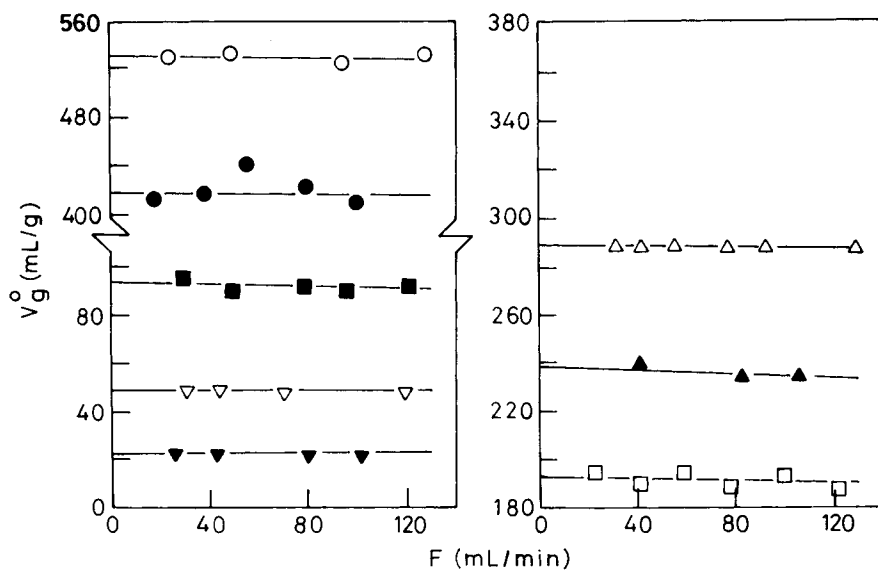

Fig. 4. Flow-rate effect on V_g^0 of dichloromethane at different temperatures: (○) 5; (●) 10; (△) 20; (▲) 25; (□) 30; (■) 50; (▽) 70; (▼) 100.
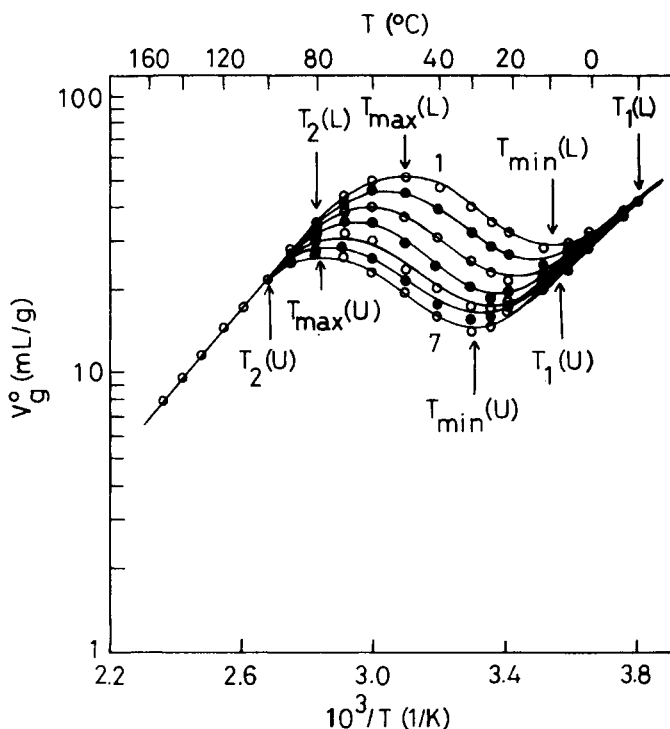
Fig. 5. Retention diagrams of isooctane at different flow rates (mL/min): (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 100; (7) 120.

p-xylene; below 50°C in the cases of n-pentane, cyclohexane, carbontetrachloride, and benzene; and below 30°C in the cases of n-hexane, n-heptane, chloroform, and 1,1,2-trichloroethane. Isooctane has shown the nonlinear behavior at temperatures between 10 and 50°C, and the plateau at $T < 10°C$ (Fig. 3). The flow-rate effect is negligibly small in the case of dichloromethane (Fig. 4).

Retention Diagrams

The physical significance of the flow-rate dependence of V_g^0 can be realized fully from the plots of $\log V_g^0$ against the reciprocal of absolute temperature (retention diagrams). The representative plots are shown in Figures 5–7. The retention diagrams are usually characterized by four temperatures,[3,4,20] as illustrated in Figure 5, and briefly described below for clarity in the following discussion. The single, straight line plot at temperatures below T_g shows that the probe is retained only by the adsorption on the surface of the polymer stationary phase. The first deviation (T_1) from the linear plot indicates the onset of bulk sorption of the probe in the stationary phase as the temperature is raised from under T_g. In IGC studies, T_1 is commonly identified with the glass transition of the polymer. The second deviation from the linearity (T_2) appears much above T_g. This is the lowest temperature at which the condition of bulk-sorption equilibrium in the column could be established. At $T > T_2$, the probe is absorbed by the bulk polymer instantaneously; the relative
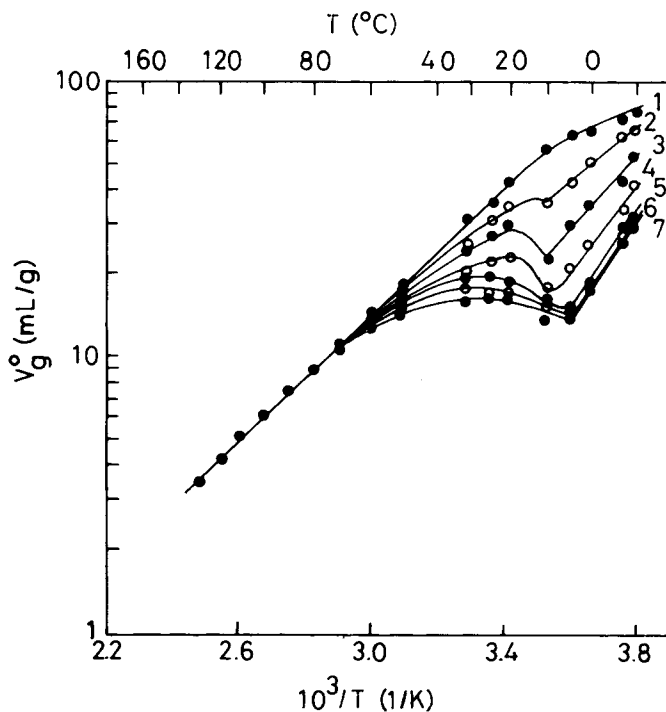
Fig. 6. Retention diagrams of n-pentane at different flow rates (mL/min): (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 100; (7) 120.

contribution of the surface adsorption to the net retention volume becomes negligibly small; the retention diagram becomes linear. The region between T_1 and T_2 is called the nonequilibrium-sorption region where T_{min} and T_{max} signify the maxima and minima.

Various trends in the present retention diagrams have many qualitative similarities with those for PVAc.[20] For example, the characteristic temperatures show an increasing trend with the flow rate. However, there is a major disagreement at $T < T_g$. In the case of PVAc, the retention curves at different flow rates were converged into a straight-line plot at $T \simeq T_g$, its slope being determined solely by the heat of adsorption of the probe in the column, because the plateau in the corresponding flow-diagram was extended to zero flow rate as the temperature was reduced to below T_g. Although all previous probes have been included in the present study, the PnBMA–isooctane pair alone conforms to that behavior at about 20°C below T_g (Figs. 3 and 5). The retention diagram of PnBMA–dichloromethane is linear and independent of the flow rate (Fig. 7). The plots of all other probes have been shifted upwards as $F \rightarrow 0$, and do not converge (Figs. 6 and 7). The magnitude of the deviation in each case is substantially larger than that for PVAc.

The retention diagram of cyclohexane in Figure 7 is incomplete because of the uncertainty in the extrapolation of V_g^0 at low flow rates due to the asymptotic nature of V_g^0 vs. F curves in Figure 1. The strong kinetic effect on the peak shape has made it difficult to obtain reliable data at lower flow rates, particularly at $T < 50°C$. Thus, an unambiguous value could not be assigned
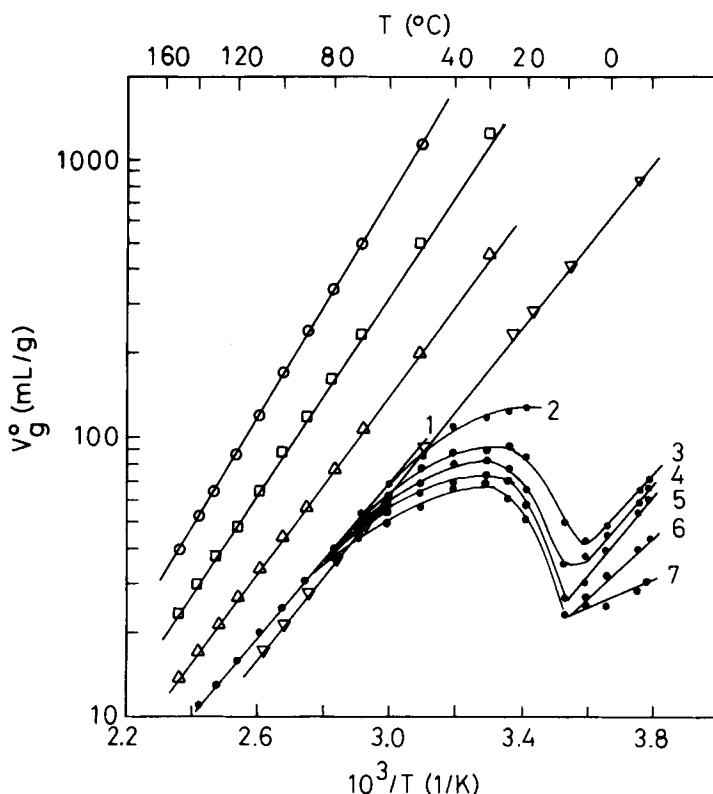
Fig. 7. Retention diagrams of benzene (△), toluene, (□), and p-xylene (○) at zero flow rate using extrapolated data and cyclohexane (●) at different flow rates (mL/min): (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 100; and (7) 120. Dichloromethane (▽) gives a flow-rate independent plot

for the glass transition temperature of PnBMA by using IGC, except in the case of isooctane that gives a value at about 0°C (Fig. 5). T_1 and T_{min} have been estimated in the range of zero to 10°C. It appears to be more appropriate to treat T_1 not as a T_g but as a measure of the effects of the chemical environment and the dynamic conditions in a GC column on the glass transition of the polymer. The values of T_2 suggest that, as $F \to 0$, the bulk sorption of a probe in PnBMA is established at a relatively lower temperature sometimes close to T_g (Table I).

IGC measurements were repeated at 50, 70, and 100°C by using column I. As compared to column II, the flow-rate effect on V_g^0 was less pronounced, and the values of T_2 and T_{max} were also small. However, the extrapolated values of V_g^0 at zero flow rate are in good agreement with those of column II at and above 70°C (Table II). Therefore, it may be concluded that the extrapolation to zero flow rate yields the bulk-sorption retention data at and above 70°C.

In comparison to the present results, the V_g^0 values in Ref. 25 are lower by about 9.8–17%, while those in Ref. 26 are higher by about 26% at 100°C and 41 to 46% at 150°C (Table III). If the column loading is to affect V_g^0 to this extent in this range of temperature, the reverse trend should have been true.[16,19] In the case of PVAc also, the data in Ref. 26 differ to almost the

TABLE II
Comparison of V_g^0 Values (mL/g) on Columns I and II

Probe	100°C		70°C	
	I	II	I	II
nC_5	6.15	6.07	10.62	11.09
nC_6	12.54	12.23	22.55	24.52
nC_7	24.38	25.07	51.76	56.27
nC_8	48.98	48.86	126.64	126.74
nC_9	96.35	96.23		
nC_{10}	187.89	188.76	624.63	623.52
iC_8	22.21	22.27	32.84	33.54
cC_6	24.22	24.86	42.86	48.10
CH_2Cl_2	21.65	21.54	49.31	47.22
$CHCl_3$	44.26	44.59	112.89	112.04
CCl_4	34.71	34.68	76.02	76.84
C_2HCl_3	55.39	56.61	144.13	143.28
C_6H_6	43.60	43.90	102.67	102.91
Tol	87.28	87.80	232.05	236.16
p-Xyl	169.09	170.97	507.21	514.96

TABLE III
Comparison of V_g^0 Values (mL/g) from Different Sources[a]

Probe	100°C		140°C			150°C	
	This work[@,*]	Ref. 26[#]	This work[@]	Ref. 25[$]	Ref. 26[#,ɛ]	This work[@]	Ref. 26[#]
nC_6	12.4	15.9					
nC_8			17.09	14.77			
nC_{10}			51.86	44.30			
iC_8			9.80	8.59			
cC_6			10.57	9.53			
$CHCl_3$	44.4	55.8	16.21	14.64	23.5	13.24	11.2
CCl_4			13.91	12.40			
C_6H_6	43.8	55.3	16.91	14.95	23.9	13.74	19.4
Tol	87.5	110.7				23.7	34.9
p-Xyl	170.0	211.1				40.1	57.5

[a] Column loadings are: [@] 9.8 wt % PnBMA on Chromosorb W, AW, DMCS; [#] Approx. 15 wt % PnBMA on Chromosorb P; [$] 8.2 wt % PnBMA on Chromosorb G, AW, DMCS; and [ɛ] the values were interpolated at this temperature; [*] the average value on columns I and II (Table II).

same extent from other studies.[20,21,30,†] However, the present data for PnBMA fall between those in the literature[25,26] and, hence, are more reliable.

CONCLUSION

V_g^0 is very sensitive to the flow rate because the probes require a certain minimum "residence" or "contact" time in the column in order to penetrate into the bulk-polymer phase beyond the surface of PnBMA even at temperatures as high as $T_g + 80$°C. At low flow rates, the vapors of both good and

[†] In Ref. 30, only Flory–Huggins interaction parameters are available for comparison.

poor solvents could diffuse into the glassy polymer; some probes are capable of diffusing to the extent of approaching close to the bulk-sorption equilibrium conditions as $F \to 0$. As a result, V_g^0 may vary linearly or nonlinearly with (or may remain independent of) the flow rate depending upon its range and the column temperature. The magnitude of the deviation in the retention-diagram also decreases as $F \to 0$, making the detection of the glass transition by IGC more difficult and less reliable. However, the extrapolation of V_g^0 to zero flow rate, though necessary even at 100°C, may provide the bulk-sorption equilibrium retention data for the derivation of solution parameters for the present PnBMA–probe systems at and above 70°C.

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