Determination of the glass transition temperature of poly(styrene-co-divinylbenzene) by inverse gas chromatography

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(Received 14 April 1984; revised 16 July 1984)

Inverse gas chromatography (i.g.c.) was used to characterize the supermolecular structure of modified, moderately crosslinked poly(styrene-co-divinylbenzene) (5–20 wt%) and to determine the interactions with normal alcohols (C_1–C_6). For all copolymers a decrease of retention time with increasing molecular weight of alcohols from C_1 to C_3 followed by an increase for C_4 to C_6 alcohols was observed. It was found that with propanol or butanol the measured T_g values were close to those measured by d.s.c. The T_g values for poly(styrene-co-divinylbenzene) containing 5, 10 and 20 wt% divinylbenzene were: 102°C, 116°C and 133°C respectively. The highest alcohols (C_5 and C_6) acted as plasticizers and reduced the apparent T_g value. The relationship between the isosteric heat of adsorption and the number of carbon atoms in the alcohols was non-linear with a minimum corresponding to butanol.

(Keywords: poly(styrene-co-divinylbenzene); gas chromatography; glass transitions; heat of adsorption)

INTRODUCTION

The glass transition temperatures (T_g) of many polymers have been measured using inverse gas chromatography (i.g.c.)[1,2]. This method exploits the temperature dependence of interactions between polymer and adsorbate, termed the molecular probe. At the glass transition point, the character of such a dependence changes, clearly affecting the measured retention volumes. Thus, the T_g is taken to be the first significant deviation of a point from the straight line determined by the retention volume, V_g, measured at $T < T_g$ in the retention diagrams, i.e. in the plots log V_g vs. $1/T$.

The polymer tested is usually deposited on glass beads or on adsorbents of Chromosorb, Poropak or other similar types of materials[1-3]. Measurements are also carried out with columns packed with a mixture of inert filling and polymer powder[4]. It has been shown that T_g does not depend on the physical form of the polymer[2,4,5], e.g. on the thickness of deposited layer[1,2,6], except for extremely thin layers, below 280 nm[7]. The i.g.c. determined T_g may, however, depend on the conditions of measurements and on the kind of molecular probe applied. Controversy still exists as to whether thermodynamically good or bad solvents, with respect to the polymer, should be used as probes[1-19].

Highly crosslinked styrene–divinylbenzene (S–DVB) copolymers (with 35 wt% or more DVB) are widely used as chromatographic packing[20-22]. They are more commonly known under the trademarks Chromosorb, Poropak, etc. For these copolymers, the heats of adsorption of various probes, e.g. alcohols, were measured by i.g.c.[20] The adsorption isotherms of n-decane on the gel-type S–DVB copolymer containing 8% DVB were also measured by i.g.c.[23]

Here, we report on the results of our attempts to apply i.g.c. to the characterization of the supermolecular structure of modified, moderately crosslinked S–DVB copolymers and to determine their interaction with solvents. Firstly, we present the measurements in which C_1–C_6 normal alcohols are used as molecular probes.

EXPERIMENTAL

The copolymers were prepared by suspension copolymerization of styrene (Z.Ch. Oświęcim, Poland) and commercial divinylbenzene (Merck, FRG). The latter contained 38.4% *m*-DVB, 14.8% *p*-DVB, 33.0% *m*-ethylstyrene, and 11.5% *p*-ethylstyrene, by weight. The monomers were copolymerized in the presence of toluene (T)–n-heptane (H) mixtures used as inert diluents. The polymerization procedure has been described in detail elsewhere[24-28]. The copolymers in the form of regular beads of diameter 80–120 μm (cf. *Table 2*) were extracted with hot benzene and dried at 80°C–150°C for 120 h. As before, the composition of each sample is coded in its symbol as in the following example. The symbol 'HT 19 0.5/5' indicates that the ratio heptane:toluene was 1:9, by volume, the volume fraction of monomers (S+-DVB) in the system was 0.5, and the last digit (5) denotes the weight per cent of *p*- and *m*-DVB in the S–DVB mixture.

For the apparent density and swelling ratio measurements the samples were prepared in the following way (cf. ref. 25). The copolymers, swollen in toluene, were transferred into a small column and treated successively with acetone, methanol, butanol and hexanol, at room temperature. After each solvent had passed through the column, a sample of copolymer was withdrawn and the swelling ratio, W, in grams of solvent per gram of dry copolymer, determined by centrifugation. The sample was then dried at 25°C ± 0.5°C to constant weight and its

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0032-3861/85/081181-06$03.00

Table 1 Properties of poly(styrene-co-divinylbenzene)

		Density (g cm^{-3})			Toluene		Methanol		Butanol		Hexanol	
Samples	X	d	d_0	Porosity (%)	W	v_2	W	v_2	W	v_2	W	v_2
HT 19 0.5/5	24	1.03	1.03	0	1.80	0.32	0.14	0.85	0.17	0.82	0.14	0.85
HT 19 0.5/10	11	1.06	1.01	4.7	1.11	0.64	0.18	0.81	0.23	0.77	0.23	0.77
HT 19 0.5/20	7	1.07	1.01	5.3	0.79	0.89	0.35	0.68	0.42	0.64	0.42	0.68

X—number of styrene units between network junctions
d—true density
d_0—apparent density for samples pretreated with methanol
W—solvent regain g/g
v_2—volume fraction of polymer in swollen copolymer gels

apparent and true density measured according to procedures described before[25,27].

The alcohol probes were chromatographic standards supplied by Poly-Science (USA) and POCh (Poland). 0.5 μl of methanol, ethanol, n-propanol, n-butanol, n-pentanol, or n-hexanol were injected at each run. The copolymers were packed into chromatographic columns of 1 m length and $\frac{1}{8}''$ internal diameter, and conditioned for 24 h at 150°C in hydrogen.

A Varian (Aerograph series 2860) chromatograph with a thermal conductivity detector was used. The flow rate of the hydrogen carrier gas was 19 ± 0.03 cm^3/min. The retention times were measured to within 0.1 s. Methane was used as an inactive agent.

The isosteric heat of adsorption, q_{st}, was calculated from the slope of the least-squares line in the adsorption region of the retention diagrams (below T_g), according to the relation[29]:

$$q_{st} = R\frac{d(\log V_g)}{d(1/T)} + RT$$

where T is the average temperature in this region and R is the gas constant.

RESULTS AND DISCUSSION

The S–DVB copolymers were obtained by suspension copolymerization of the monomers in the presence of inert diluents. The degree of crosslinking was not too high: 5, 10 and 20 wt% of DVB (*Table 1*). The bead diameter was *ca.* 0.1 mm. The thickness of the polymer layer was thus 10^3 times higher than that for the samples deposited on fillings[1,11].

Stoichiometry predicts a small number of S units between network junctions (DVB units) in the copolymers, but due to the intrinsic inhomogeneity of S–DVB copolymers, the linear segments remain mobile at temperatures only slightly higher than that for polystyrene. The inhomogeneities of S–DVB copolymers originate at the beginning of the copolymerization process. At that stage, DVB units react relatively faster than do the S units and hence precursors of highly crosslinked microgels are formed[30–32]. The microgel precursors solvated by unreacted monomers (and diluents) are then entangled and linked together by essentially linear segments rich in S units. Those segments are probably responsible for the overall segmental mobility[27] that determines T_g values of S–DVB copolymers[33]. The inhomogeneity due to this mechanism of polymer formation leads to pecularities in the behaviour of S–DVB copolymers containing more than *ca.* 10 wt% DVB and obtained in the presence of inert diluents, namely, that porous copolymers undergoing a microsyneresis are formed. The microsyneresis manifests itself as differences in apparent densities (porosities) of the same copolymers pretreated with various solvents. The extent to which such differences are observed is dependent on the initial composition of the mixture used for the copolymer preparation[24–28].

No microsyneresis was observed for the copolymer HT 19 0.5/5 (*Table 1*). The copolymers containing 10 and 20 wt% DVB are gels when dried out from toluene, but become porous when pretreated with a bad solvent. The apparent densities and porosities of the samples pretreated with methanol are given in *Table 1*. Further evidence for the microsyneresis of the copolymer gel is provided by the solvent regain measurements. An increase in swelling ratio, *W*, in alcohols with an increase in the degree of crosslinking (*Table 1*) can hardly be explained otherwise than by assuming that new pores are being formed in bad solvents (alcohols). A local collapse of gel portions, not followed by shrinkage of the whole bead, seems to be responsible for such behaviour. For toluene, the swelling ratio decreases with increasing degree of crosslinking of copolymers as it should also for polymer networks.

The data on the swelling ratios and the volume fractions of polymer in swollen copolymer gels (v_2) calculated therefrom confirm that methanol is the worst solvent for S–DVB copolymers; the swelling ratios for higher alcohols are somewhat higher, in accordance with the decreasing differences in the solubility parameters of the alcohol–polystyrene pairs (*Table 3*). One should notice, however, that at least two effects, namely, the swelling ability and formation of new pores, are superimposed on each other and both influence the swelling ration measurements.

In the preliminary i.g.c. measurements, the effect of flow rate on the retention volumes has been measured at

Table 2 Column characteristics

Samples	Bead diameter (mm)	Weight of copolymer (g)	Surface of copolymer in i.g.c. column (m^2)
HT 19 0.5/5	0.08 ± 0.05	4.2	0.030
HT 19 0.5/10	0.12 ± 0.06	4.2	0.020
HT 19 0.5/20	0.12 ± 0.05	4.8	0.022

Table 3 Solubility parameters (δ_1) and the isosteric heats of adsorption (q_{st}) for the alcohols

	Alcohols	δ_1 (MPa$^{1/2}$)	δ_1–δ_2 [a] (MPa$^{1/2}$)	q_{st} (KJ mol^{-1}) HT 19 0.5/ 5	10	20
C_1	CH_3OH	29.7	11.1	13.3	14.3	11.7
C_2	C_2H_5OH	26.0	7.4	12.0	10.3	8.1
C_3	C_3H_7OH	24.3	5.7	9.1	7.9	6.5
C_4	n-C_4H_9OH	23.3	4.7	7.0	6.7	6.5
C_5	n-$C_5H_{11}OH$	22.3	3.7	9.4	7.2	6.4
C_6	n-$C_6H_{13}OH$	21.9	3.3	14.2	13.0	8.1

[a] $\delta_2 = 18.6$ MPa$^{1/2}$ (ref. 35)

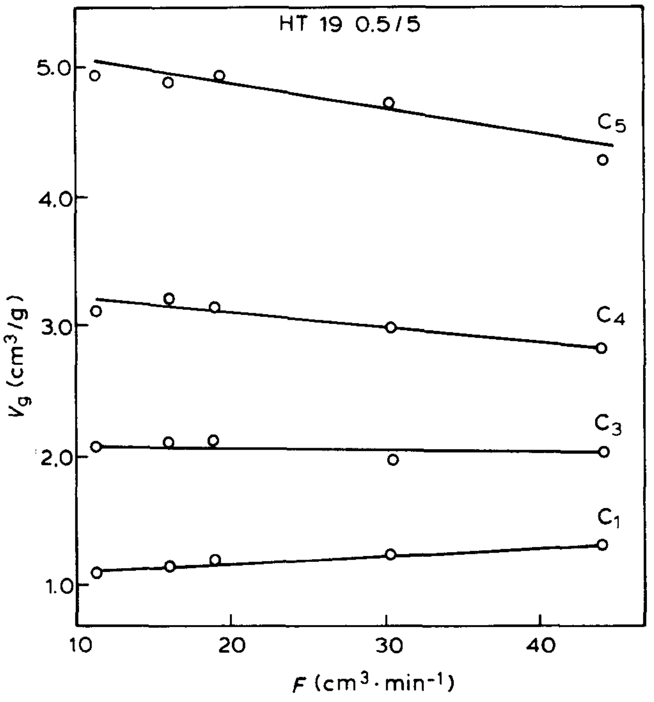

Figure 1 Relationship between retention volume for normal alcohols at 182°C and rate of gas flow for HT 19 0.5/5 copolymer

182°C (mixed adsorption–absorption region). The results are shown in *Figure 1*. It can be seen that the flow rate in the range studied does not alter the results significantly.

The retention diagrams for the HT 19 0.5/5 copolymer are presented in *Figure 2*. The retention volumes in the adsorption region (right-hand-side branches of curves) decrease from methanol to propanol, to increase again for higher alcohols.

The retention diagrams in *Figure 2* are significantly different from those measured for nonspecific adsorbents such as graphitized carbon black or Poropak *Q* where the retention volumes increase smoothly with increasing molecular weight of alcohols[20], although Poropak *Q*, being a copolymer of commercial DVB with high specific surface area (*ca.* 700 m^2/g), is chemically similar to the copolymers being studied[21]. Probably the differences in supermolecular structures of the copolymers are responsible for their differing behaviour.

The log V_g vs. $1/T$ curves in *Figure 2* have different shapes for different alcohols. Methanol, which is considered to be a D-type adsorbate, weakly interacts with the copolymers. In almost all ranges of temperatures its retention diagrams are linear, similar to those for the hexadecane–polystyrene system, with the latter being in the form of a thin layer deposited on an inert support[1,17]. For ethanol, the retention curves are similar to those measured for thick layers of polymer[17], but already for propanol, the non-equilibrium adsorption–absorption range becomes very broad. In the range of temperatures studied, the absorption equilibrium for C_5 and C_6 alcohols was not reached. Because of small diffusion coefficients through the copolymer gel the probes are unable to penetrate through the whole volume of beads and an increase in retention volume is observed. The non-equilibrium region was found to be broader the higher was the degree of crosslinking of the copolymer. The effect of crosslinking degree on the retention diagrams for ethanol and butanol is presented in *Figures 3* and *4*.

The results of the regression analysis applied to the adsorption region (below T_g) are presented in *Table 4*. As can be deduced from *Figure 2*, the slopes of the lines and therefore the values of the isosteric heats of adsorption, q_{st}, decrease for alcohols in the order $C_1 > C_2 > C_3 > C_4$ and then increase for the higher alcohols, following a roughly similar relationship for polymer–solvent interaction expressed by differences in the solubility parameters (cf. *Figure 5*).

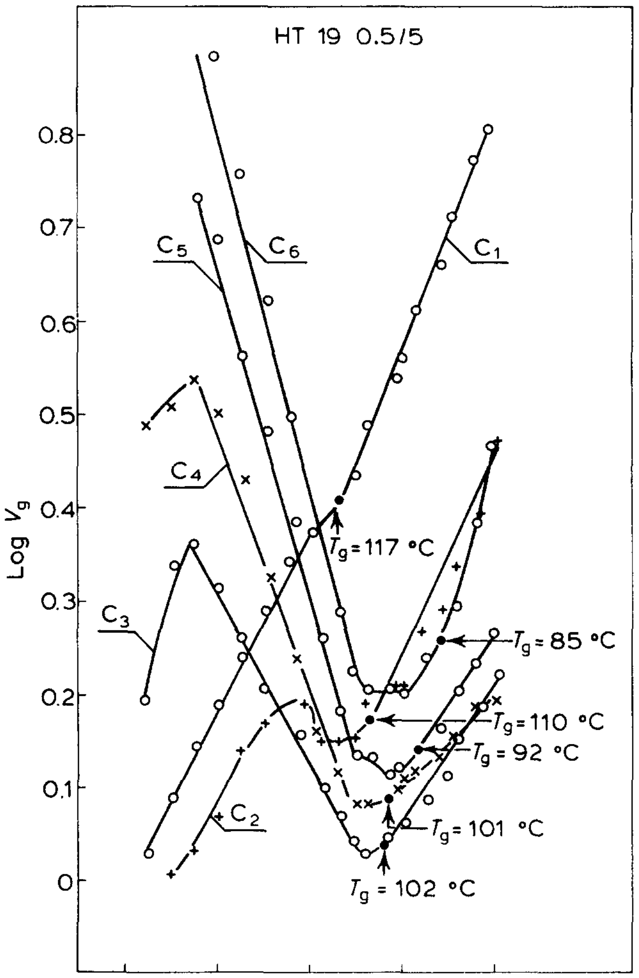

Figure 2 Retention diagram for normal alcohols as molecular probes with HT 19 0.5/5 copolymer

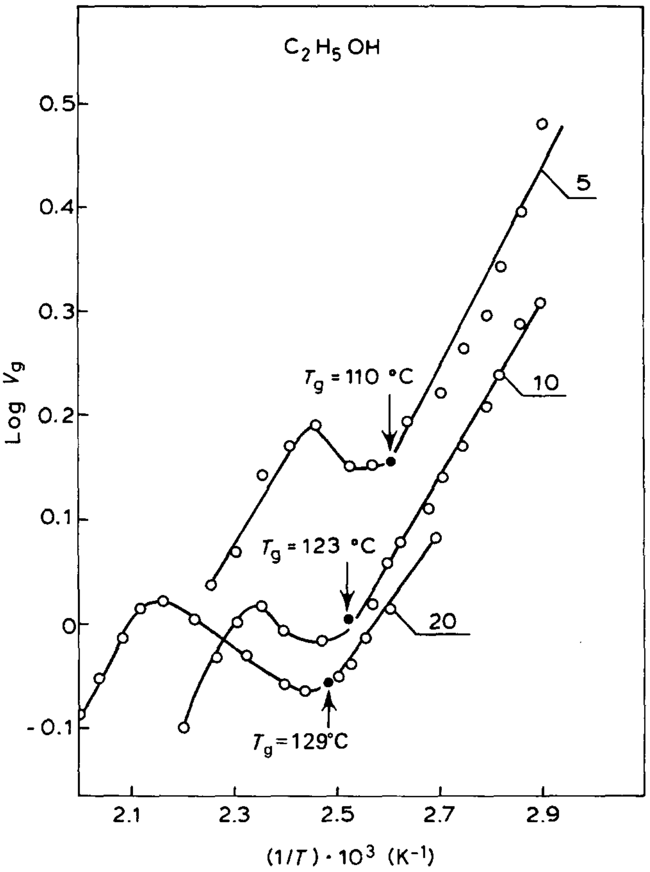

Figure 3 Retention diagram for S–DVB copolymers and ethanol as molecular probe

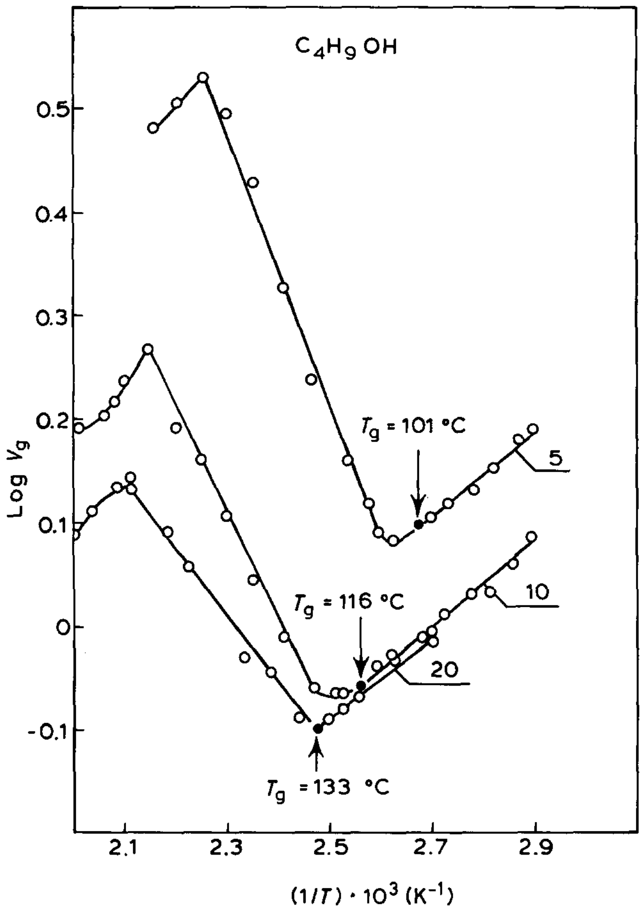

Figure 4 Retention diagram for S–DVB copolymers and butanol as molecular probe

Table 4 Regression analysis of the adsorption region of retention diagrams

	HT 19 0.5/20					
	C_1	C_2	C_3	C_4	C_5	C_6
Regression line	1001.5 × −2.32	647.1 × −1.68	380.2 × −1.05	369.1 × −0.99	496.1 × −1.00	629.7 × −1.62
Correlation coefficient	0.9988	0.9975	0.9999	0.9987	0.9994	0.9974
Standard deviation	0.0040	0.0046	0.0009	0.0020	0.0013	0.0043
Number of points	8	6	7	7	6	5
Confidence interval						
0.95 ±	0.010	0.011	0.002	0.005	0.004	0.011
0.99 ±	0.014	0.016	0.003	0.007	0.005	0.017
	HT 19 0.5/10					
Regression line	1360.8 × −3.15	836.7 × −2.12	518.8 × −1.52	402.6 × −0.91	540.0 × −1.41	148.4 × −3.90
Correlation coefficient	0.9996	0.9990	0.9942	0.9975	0.9967	0.9949
Standard deviation	0.0047	0.0044	0.0069	0.0027	0.0033	0.0091
Number of points	11	10	11	8	7	5
Confidence interval						
0.95 ±	0.010	0.010	0.015	0.006	0.008	0.024
0.99 ±	0.015	0.014	0.022	0.009	0.012	0.037
	HT 19 0.5/5					
Regression line	1219.6 × −2.73	1011.1 × −2.50	806.7 × −2.12	471.0 × −1.17	881.4 × 2.28	1081 × −5.56
Correlation coefficient	0.9994	0.9960	0.9985	0.9942	0.9981	0.9980
Standard deviation	0.0043	0.0080	0.0035	0.0036	0.0029	0.0052
Number of points	9	7	7	6	4	3
Confidence interval						
0.95 ±	0.010	0.019	0.008	0.009	0.008	0.016
0.99 ±	0.014	0.028	0.012	0.013	0.014	0.030

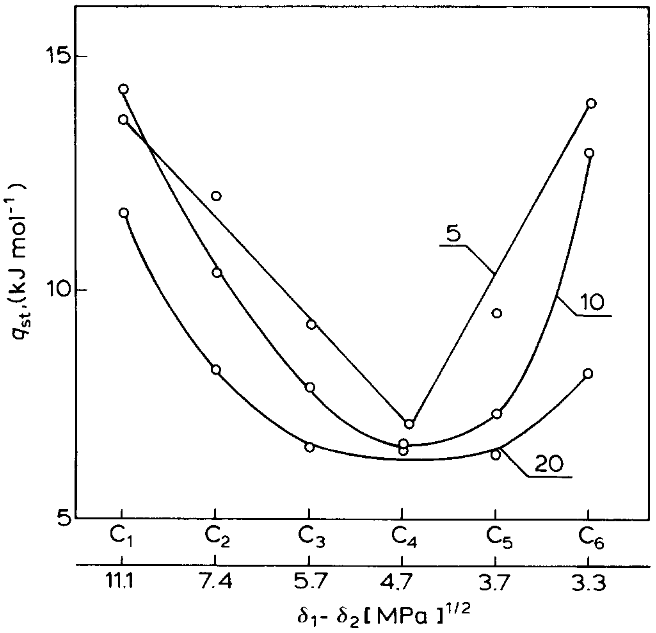

Figure 5 Isosteric heat of adsorption, q_{st}, as a function of the chain length of alcohols used as molecular probes for S–DVB copolymers crosslinked with 5, 10, 20 wt% of DVB

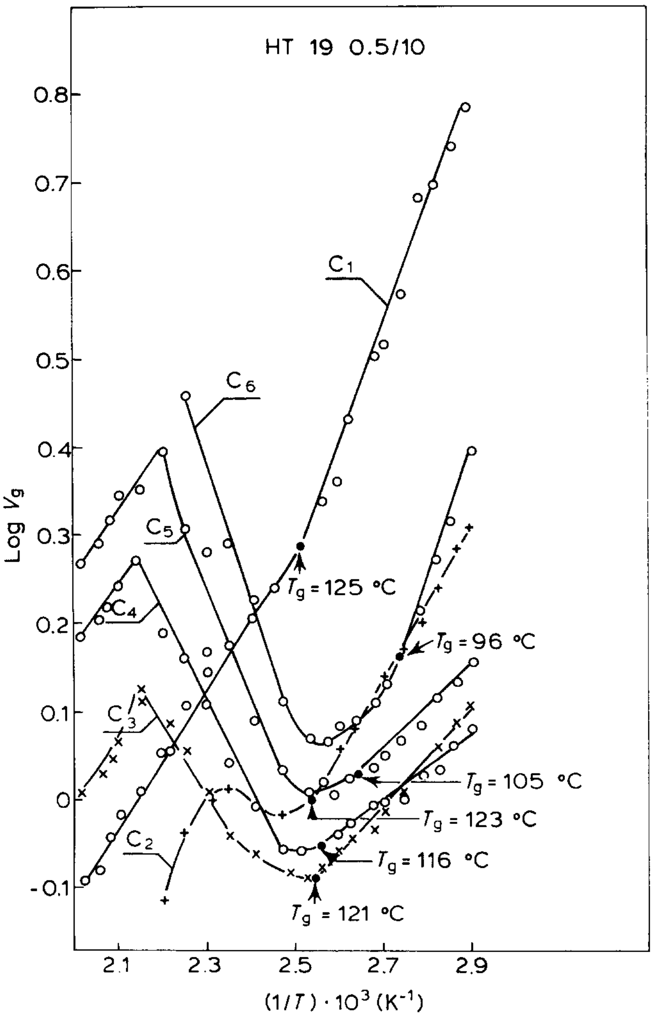

Figure 6 Retention diagrams for normal alcohols as molecular probes with HT 19 0.5/10 copolymer

The decrease of the isosteric heat of adsorption with increasing length of the alcohol chains is a striking result since for Poropak Q[20], as well as for graphitized carbon black[29], a linear relationship between q_{st} and the number of carbon atoms in alcohols has been found. It is probable that the heterogeneity of the relatively loosely crosslinked gel allows the alcohols of smaller molecular size to penetrate and interact with a larger proportion of copolymer than is the case for alcohols with larger sized molecules. For C_4 the situation returns to normal, i.e. the heat of adsorption increases with increasing size of the alcohol molecules.

A deviation of a point from the straight line beyond the confidence interval of 0.95 determines an apparent T_g of copolymers (*Figure 2*). As has been found for other polymers, the T_g is not determined by the minimum of the retention volume in the retention diagram, but by a significant segmental mobility occurring at somewhat lower temperatures[1,2]. The values of T_g determined by d.s.c.[33] are given in *Table 5*. For HT 19 0.5/5 copolymer, for example, it is 103°C. The same value was obtained by using propanol as the molecular probe and it was also found that the retention volumes were the lowest for

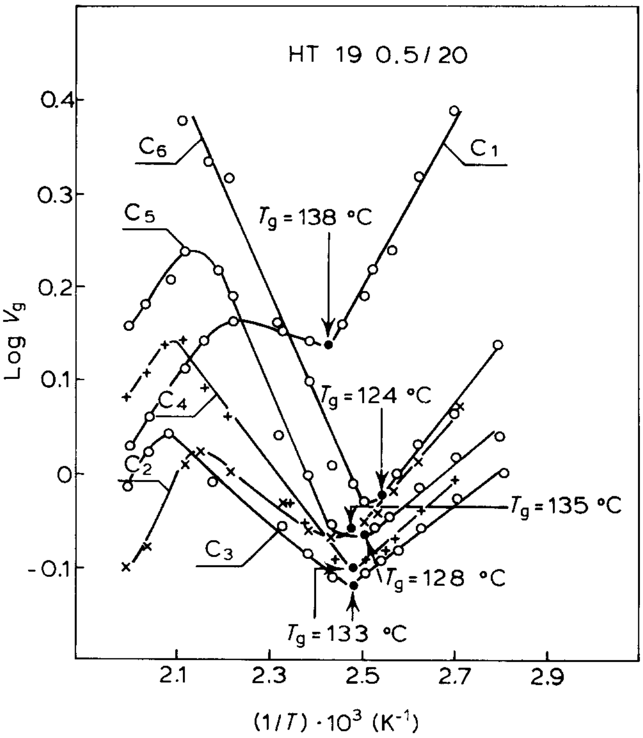

Figure 7 Retention diagrams for normal alcohols as molecular probes with HT 19 0.5/20 copolymer

Table 5 Apparent values of T_g

Alcohols	T_g (°C) HT 19 0.5/ 5	10	00
C_1	117	125	138
C_2	110	123	135
C_3	102	121	133
C_4	101	116	133
C_5	92	105	128
C_6	85	96	124
d.s.c.[33]	103	116	128.5

propanol. The higher alcohols act as plasticizers and reduce the T_g value. As Deshpande pointed out, not all adsorbates used in the i.g.c. method measure the true T_g value of a polymer[9]. Good solvents tend to reduce T_g and some of the bad solvents shift T_g towards higher temperatures.

The retention diagram for HT 19 0.5/10 copolymer is similar to that of a less crosslinked copolymer (*Figure 6*). For all alcohols, however, the retention volumes are lower, as also are the slopes of lines in the adsorption region.

The heats of adsorption for the copolymer crosslinked with 10% DVB are lower than those for the 5% DVB copolymers (*Table 3*, *Figure 5*). The lowest value has been found for butanol, although propanol again has the lowest retention volumes. The T_g value similar to that measured by d.c.s. determines butanol as being the probe giving the lowest value (*Table 5*).

The retention diagrams for HT 19 0.5/20 copolymer are presented in *Figure 7*. Here the retention volumes are even lower than for the less crosslinked copolymers and so are the slopes in the adsorption region that determine the heats of adsorption. It is probable that the higher surface area than that found in the less crosslinked copolymers, possibly further increased by a local microsyneresis, primarily affects the retention volumes.

Again, the minimum retention volumes were measured for propanol, but the T_g corresponding to that measured by d.s.c. was determined using n-pentanol as a molecular probe.

The apparent T_g values were read out from retention diagrams as the significant deviation from the straight lines through 7 points provided the correlation coefficients were as high as 0.9999 (propanol) and 0.9987 (butanol) (*Table 4*). For HT 19 0.5/20 copolymer, as opposed to the other two, the apparent T_g values measured by using propanol and butanol lie at the minima of retention times.

CONCLUSION

The i.g.c. method with n-alcohols as molecular probes can be used to estimate the temperature of first segmental mobility in S–DVB copolymers. With propanol or butanol the measured T_g values are close to those determined by d.s.c.

The relationship between the isosteric heat of adsorption and the number of carbon atoms in the alcohols is non-linear with a minimum corresponding to butanol. For all copolymers a decrease in retention time with increasing molecular weight of alcohol from C_1 to C_3 followed by its increase for C_4 to C_6 alcohols is observed.

Since such behaviour differs from that for the non-specific absorbents such as Poropak *Q* or graphitized carbon black, one could expect that the supermolecular structure of S–DVB copolymers has an effect on their interactions with alcohols.

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