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INVESTIGATION OF THE SURFACE STRUCTURE OF POLYMERS BY CHROMATOGRAPHIC METHODS

VI. DETERMINATION OF GLASS TRANSITION TEMPERATURE OF MACROPOROUS COPOLYMERS BY GAS CHROMATOGRAPHY

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SUMMARY

By employing the method of inverse gas chromatography and using the retention diagrams of methanol and heptane in the temperature range between -55 and $+180°C$, the glass transition temperatures, T_g, were determined for glycidyl methacrylate–ethylene dimethacrylate ($T_g = 40°C$) and styrene–divinylbenzene ($T_g = 100°C$) macroporous copolymers. The standard method (differential thermal analysis) failed in these instances. For macroporous copolymers, a disturbance is observed in the dependence on reciprocal of temperature, not only for the retention volume, but also for the peak asymmetry, width and area, which is proportional to the response. Using the dependence log $V_{MeOH}/V_{C_7H_{16}}$, not only T_g, but also a change in the polarity of the individual types of copolymers can be determined. At low temperatures ($-55°C$), the polarities of macroporous copolymers approach each other owing to the "freezing" of polymer chains. Constant properties are assumed by the polymer surface only above T_g where the polarity decreases in the order macroporous glycidyl methacrylate–ethylene dimethacrylate copolymer, the above methacrylate copolymer with chemically bonded PEG and styrene–divinylbenzene copolymer (Synachrom E5). A similar picture of the polarity of these polymers is also provided by the enthalpy of solution (ΔH_s) and enthalpy of adsorption (ΔH_a) of methanol and heptane determined for the copolymers investigated.

INTRODUCTION

The use of gas chromatography in the determination of the glass transition temperature (T_g) of homopolymers deposited on a solid carrier was suggested in 1969 by Guillet and co-workers[1,2]; later, they verified this possibility for polyethylene, polystyrene, poly(vinyl chloride), poly(methyl methacrylate) and polyacrylonitrile[3–7]. He also established some principles for the "molecular probe" method[1]. The solutes must be a non-solvent–precipitant for the given polymer, and their molecules must

be larger than the free volume in the glassy state of the polymer. At temperatures below T_g, the retention of the solutes by the polymer is low; at temperatures above T_g, the solute enters the polymeric matrix, thus raising its own retention with temperature. Changes from the adsorption retention below T_g to the solvent retention above T_g may be used in the determination of T_g, crystallinity, enthalpy of sorption and solution and the crystallization rate of the polymers. By using this method, the first- and second-order transition temperatures were determined for polypropylene.

For cross-linked and macroporous copolymers, T_g has not yet been studied by this method. Being engaged in the preparation and investigation of strongly cross-linked macroporous methacrylate copolymers, we were interested in the possibility of determinating their T_g values and in the effects of porous structure on this quantity. First measurements revealed that with macroporous copolymers neither differential scanning calorimetry (DSC) nor differential thermal analysis (DTA) can be employed in the determination of T_g; neither of the measurements gave the expected apparatus response[8].

In this study, we examined the possibility of determining the T_g values of macroporous methacrylate copolymers by inverse gas chromatography.

EXPERIMENTAL

Materials

Glycidyl methacrylate–ethylene dimethacrylate (G-60) copolymer containing 40 wt.-% of the cross-linking agent was prepared by radical copolymerization using 1-dodecanol and cyclohexanol as porogenic agents[9]. Glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer with bound PEG 2000 polyethylene glycol (0.1 mmol/g) was prepared by the reaction of sodium polyethylene glycol with the above copolymer in dioxan for 12 h under reflux[10]. PEG 2000 polyethylene glycol in an amount 20 wt.-% was also deposited on the surface of the glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer. Synachrom E5 (Lachema, Brno, Czechoslovakia) is a macroporous copolymer of styrene and divinylbenzene.

The properties of the sorbents investigated are summarized in Table I.

The sorbents were extracted with methanol in a Soxhlet apparatus prior to measurement.

Chromatographic measurements

The retention times of methane, pentane, heptane and methanol were measured by gas chromatography on 1 m × 3 mm I.D. columns packed with the above sorbents in amounts of 1.6–2.7 g with ionization detection at 30–180°C. Measurements in the range between −55 and +25°C were performed on 1.2 cm × 3 mm I.D. columns packed with 0.016–0.031 g of the sorbent under investigation and placed in a low-temperature thermostat with ethanol as the cooling medium. The columns were thermostated to the lowest temperature (−55 or +30°C) for at least 2 h; after the first measurement, the temperature was gradually increased by 5–10°C and the retention time of the solutes was again measured after thermostating for 30 min. The retention times of the solutes were corrected for the column resistance, and from these, the known flow-rate of the carrier gas and the weight of the sample, pure

TABLE I

PROPERTIES OF THE SORBENTS

Polymer	Content of cross-linking agent (%, w/w)	S_g (m^2/g)[*]		V_g (cm^3/g)[**]	
		A	B	A	B
Glycidyl methacrylate–ethylene di-methacrylate (G-60)	40	55.5	42.9	1.47	1.04
Glycidyl methacrylate–ethylene di-methacrylate with bound PEG 2000 (G-60-PEG)	40[***]	–	26.9	–	0.88
Glycidyl methacrylate–ethylene di-methacrylate with deposited PEG 2000 (20%, w/w) (G-60 + PEG 2000)	40	–	25.0	–	0.79
Styrene–divinylbenzene (Synachrom E5)	50	350	136.6	–	1.55

[*] Surface area: A, before heating; B, after heating.
[**] Specific pore volume according to cyclohexane retention; A, before heating; B, after heating.
[***] 0.1 mmol g/PEG.

retention volumes were calculated and used in plotting the retention diagrams (Figs. 1–4), *i.e.*, the dependence of log V_g on the reciprocal temperature of the column.

Peak asymmetry $(A = x/y)$ was defined as the ratio of intercepts cut out by a perpendicular drawn from the maximum of the peak to the base at one tenth of the peak height at the baseline[11]. The peak area was determined by integration. Values of the peak asymmetry, width and area were used in plotting other types of retention diagrams, *i.e.*, dependences on reciprocal temperature.

RESULTS AND DISCUSSION

It is generally considered that T_g cannot be determined for macroporous, strongly cross-linked copolymers. A negative result was indeed obtained in the experiments involving DSC.

We therefore used Guillet and co-worker's method of "molecular probes" with methanol and heptane as solutes with respect to the polymers under investigation, in the temperature range between −55 and +180°C. Macroporous and strongly cross-linked (40–50 wt.-%) copolymers of glycidyl methacrylate, styrene and glycidyl methacrylate with attached PEG 2000 polyethylene glycol chains, the expected T_g values of which might differ considerably, were chosen for the determination.

As suggested by the retention diagrams, which show the logarithmic dependence of retention volumes on reciprocal temperature, methanol and heptane provided, for all copolymers under investigation, evidence of a change in the surface properties of these copolymers with temperature (Figs. 1–4). The deviation from linearity of the retention diagram, although not as marked as with linear copolymers[1–7], nevertheless bears sufficient evidence and is reproducible. Moreover, there is a slight increase in the retention volume of methanol with glycidyl methacrylate copolymers. The lowest response was observed for the styrene–divinylbenzene copolymer, owing to the higher degree of cross-linking of the latter and to the poorer
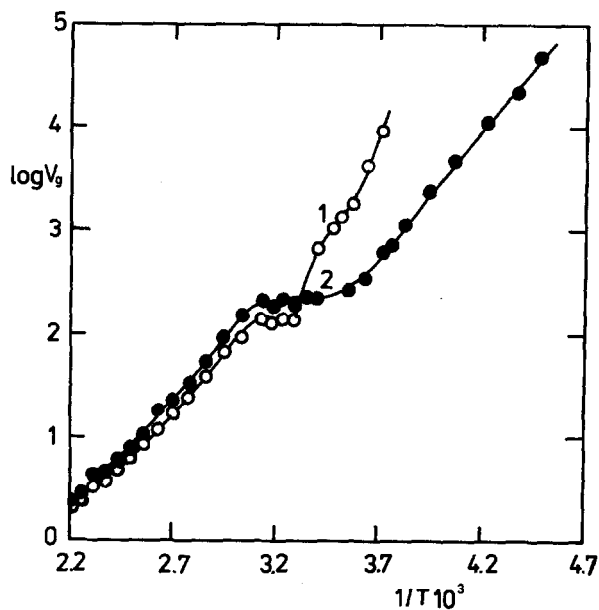
Fig. 1. Retention diagram of methanol (1) and heptane (2) on glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer.
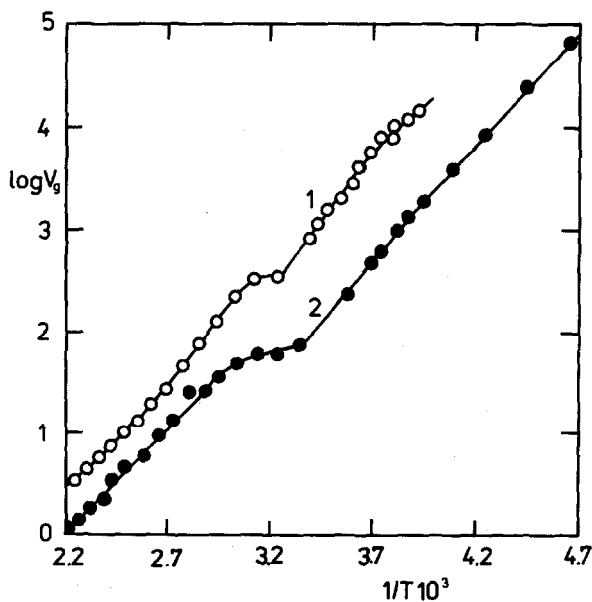

Fig. 2. Retention diagram of methanol (1) and heptane (2) on glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer with chemically bound PEG 2000 polyethylene glycol.
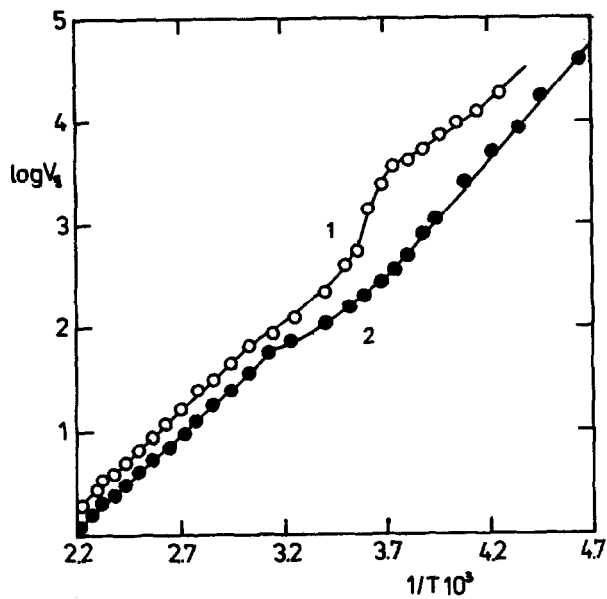
Fig. 3. Retention diagram of methanol (1) and heptane (2) on glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer with deposited PEG 2000 polyethylene glycol.
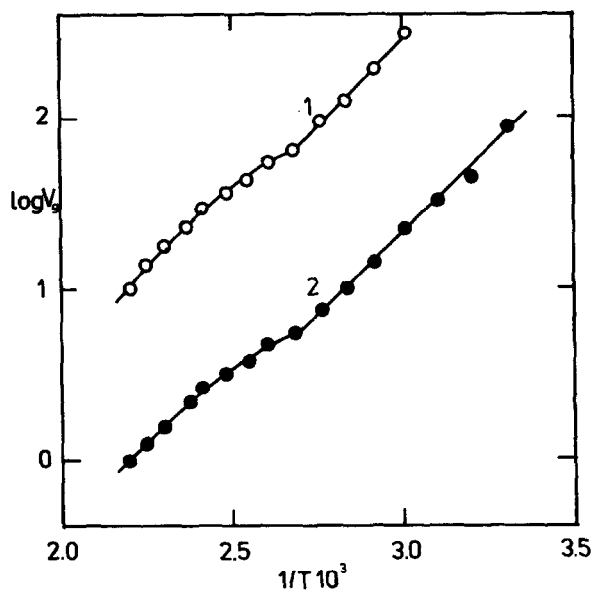

Fig. 4. Retention diagram of methanol (1) and heptane (2) on the styrene–divinylbenzene (Synachrom E5) macroporous copolymer.

suitability of methanol and heptane as detection solutes. Owing to the too small size of their molecules, neither pentane nor methane is able to detect changes in the polymer properties. Moreover, the retention of methane indicates the absence of any interactions with the polymer, being proportional to the flow-rate of the carrier gas (nitrogen). The effect depends on kinetics but reproducible results were obtained after thermostating the column for 30 min (Fig. 1).

The linear dependence on reciprocal temperature is also disturbed in the case of peak asymmetry (Fig. 5a), width (Fig. 5b) and area (Fig. 5c), which is proportional to the solute concentration in the vapour phase; a disturbance has also been observed for the logarithm of the ratio of the retention volumes of heptane and methanol (Fig. 6), which has not previously been reported. Changes in the diagrams, although less pronounced than for the retention volumes, in the case of fractions provide more information on the polarity of the polymers, which is discussed below.
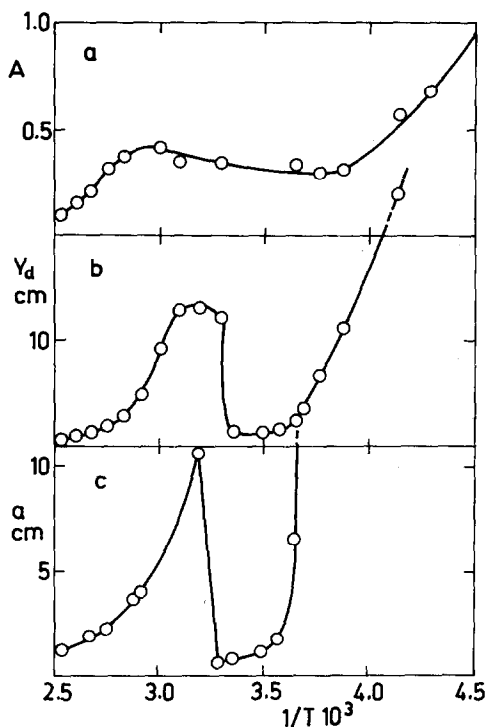

Fig. 5. Dependences of the characteristics of the peaks of heptane on the temperature of the column packed with glycidyl methacrylate–ethylene dimethacrylate copolymer. (a) Peak asymmetry $(A = x/y)$; (b) peak widths at zero line (Y_d); (c) peak areas (a).

Deviations in the retention diagrams of the individual copolymers are interpreted as the glass transition temperatures, and are compared with reported data for the homopolymers in Table II.

With increasing temperature of the polymer in the chromatographic column, at a certain point there is an increase in or plateau of the retention volume, which under the usual circumstances continuously decreases, thus indicating a loosening of polymer chains at this temperature and above.
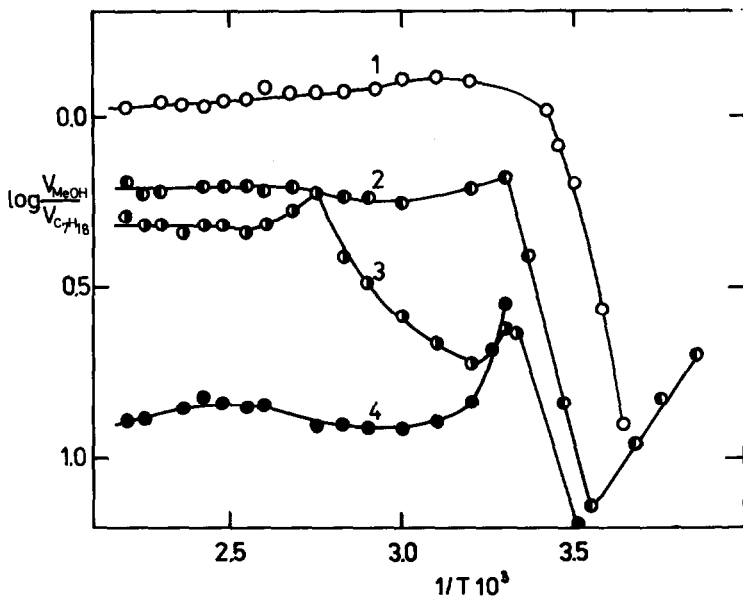
Fig. 6. Dependence of the logarithm of ratio of the retention volumes of heptane and methanol on the temperature of the column packed with the glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer (1), glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer with deposited PEG 2000 (2), glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer with chemically bound PEG 2000 (3), and styrene–divinylbenzene (Synachrom E5) macroporous copolymer (4).

For the glycidyl copolymer glycidyl methacrylate–ethylene dimethacrylate copolymer, the glass transition temperature (40°C) was read from Fig. 1; the value is in good agreement with both that for poly(glycidyl methacrylate)[12] (T_g = 46°C) and that for poly(ethylene dimethacrylate)[13] (T_g = 25°C). Polyethylene glycol deposited on the glycidyl methacrylate–ethylene dimethacrylate macroporous copolymer showed a change at −16°C, in good agreement with the reported data[14] (−28°C for PEG 1540 and −17°C for PEG 6000), and which was particularly distinct with methanol. The change in the retention volume at 40°C corresponding to the methacrylate structure was suppressed by the deposited polyethylene glycol, but could still be observed. This finding confirms that detection of the phenomenon occurs in the surface layer. With polyethyleneglycol bound on the glycidyl methacrylate macroporous copolymer, a smaller change in the retention volumes can be observed with respect to the lower concentration of the introduced polyethylene glycol chains. The response at 40°C is almost analogous to that of the starting glycidyl methacrylate macroporous copolymer. The styrene–divinylbenzene macroporous copolymer (Synachrom E5) produced a plateau of lower intensity at 100°C, i.e., a temperature corresponding to T_g of amorphous polystyrene[15]. It is known that T_g depends on the degree of cross-linking, but the observed values cannot be discussed because of the lower intensity of the plateau.

As indicated above, the diagrams of fractions of the retention volumes of heptane and methanol may provide information on the polarity of the copolymers under study. At low temperatures, these fractions determined for methacrylate copolymers

TABLE II

GLASS TRANSITION TEMPERATURES AND THERMODYNAMIC PARAMETERS OF THE COPOLYMERS

Copolymer	T_g (°C)			Ref.	Methanol		Heptane	
	Methanol	Heptane	Other methods		$\Delta H_s - \Delta H_v$ (kJ/mole)	$\Delta H_s - \Delta H_v$ (kJ/mole)	$\Delta H_s - \Delta H_v$ (kJ/mole)	$\Delta H_s - \Delta H_v$ (kJ/mole)
G-60	40	40	46, −25	12, 13	9.2	–	9.9	14.4
G-60-PEG	40, −16	40, −16	46, −28	12, 14	10.9	11.0	9.8	9.3
G-60 + PEG 2000	40, −16	40, −16	46, −28	12, 14	8.4	6.3	8.1	10.0
Synachrom E5	100	100	100	15	8.2	8.5	8.1	14.0

approach values for the non-polar styrene–divinylbenzene copolymer (Fig. 6). The fractions increase with temperature, and the curve has a maximum in the T_g region of the polymer. Above T_g, the fraction assumes constant values which may be correlated with the polarity of the copolymer, which decreases in the order G-60 > G-60 + PEG 2000 > G60–PEG 2000 > Synachrom E5. An interesting situation is seen for G-60, for which at lower temperatures the retention of methanol is higher and at temperatures above T_g the retention of heptane exceeds that of methanol.

Using the retention diagrams, it is also possible to determine the enthalpy of adsorption and solution of the solutes into polymers. Their calculated values suffer, however, from considerable inaccuracy in the determination of the heat of vaporization of the solutes. For this reason, overall values ($\Delta H_a - \Delta H_v$ or $\Delta H_s - \Delta H_v$) are given in the Table II which are in agreement with the polarities of the sorbents under investigation as given above. The sensitivities of these enthalpy differences to changes in polarity are, however, lower than the differences in the retention, in accordance with earlier observations[16].

Heating of the macroporous copolymers above T_g brings about sintering of the porous structure, especially in the domain of the micropores, which is reflected not only in a decrease in the specific surface area of the polymers after heating, but also in a lower specific pore volume. Surprisingly, the macroporous glycidyl methacrylate copolymer with either chemically bound or deposited PEG 2000 has the same specific surface area and specific pore volume. As a result of the introduction of chemical chains, by chemical binding or by mere deposition, both the specific surface area and the specific volume of the pores decrease considerably compared with the initial copolymer. Even so, however, it is surprising that at 20 wt.-% of the deposited or introduced polymer the sorbent still remains porous.

Owing to its high sensitivity, the "molecular probe" method of inverse gas chromatography extends our knowledge about the properties of macroporous, strongly cross-linked copolymers.

REFERENCES

1 O. Smidsrød and J. E. Guillet, *Macromolecules*, 2 (1969) 272.
2 A. Lavoie and J. E. Guillet, *Macromolecules*, 2 (1969) 443.
3 J. E. Guillet and A. N. Stein, *Macromolecules*, 3 (1970) 102.
4 D. G. Gray and J. E. Guillet, *Macromolecules*, 4 (1971) 129.
5 A. N. Stein, D. G. Gray and J. E. Guillet, *Brit. Polym. J.*, 3 (1971) 175.
6 N. F. Brockmeier, R. W. McCoy and J. A. Meyer, *Macromolecules*, 5 (1972) 464.
7 J. E. Guillet and M. Galin, *J. Polym. Sci., Polym. Lett. Ed.*, 11 (1973) 233.
8 J. Biroš and J. Hradil, unpublished results.
9 F. Švec, J. Hradil, J. Čoupek and J. Kálal, *Angew. Macromol. Chem.*, 48 (1975) 135.
10 J. Kahovec, F. Švec, F. Šebesta and M. Pražský, *23rd Prague Microsymposium on Macromolecules, Selective Polymeric Sorbents, Prague, July 19–22, 1982*, paper M28.
11 T. A. Gough and C. F. Simpson, *J. Chromatogr.*, 51 (1970) 129.
12 I. A. Arbuzova and V. N. Efremova, *Vysokomol. Soedin.*, 1 (1959) 455.

13 M. Ilavský, J. Hasa, V. Vojta and J. Janáček, *J. Polym. Sci., Polym. Phys. Ed.*, 14 (1976) 285.
14 J. A. Foucher, J. V. Koleske, E. R. Sartee, J. J. Stratta and C. W. Wilson, *J. Appl. Phys.*, 37 (1966) 3962.
15 J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1975.
16 J. Hradil and J. Lukáš, *J. Chromatogr.*, 172 (1979) 85.