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INVESTIGATION OF THE SURFACE STRUCTURE OF POLYMERS BY CHROMATOGRAPHIC METHODS

II. MACROPOROUS POLY(2-HYDROXYETHYL METHACRYLATE–CO-ETHYLENEDIMETHACRYLATES)*

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SUMMARY

Macroporous poly(2-hydroxyethyl methacrylate–co-ethvlenedimethacrylates) are suitable sorbents for gas chromatography. Their polarity, as described by Kováts' indices, is influenced by the ratio of 2-hydroxyethyl methacrylate to ethylenedimethacrylate, and by the ratio of cyclohexanol to dodecanol used in the polymerization. Interactions of these copolymers with low-molecular-weight compounds under chromatographic conditions are predominantly non-specific. The specific interactions are mainly due to the formation of hydrogen bonds. From the dependence of the logarithm of the specific retention volumes of pentane and ethanol on $1/T$, it may be inferred that, up to the glass transition temperature of the polymer (T_g), the low-molecular-weight solute is adsorbed on to the surface of the copolymers, while above T_g its diffusion into the copolymer sets in (especially with Spheron G10B and G50F); this is confirmed by the sorption isotherms of ethanol and pentane on these copolymers at 150 °C.

INTRODUCTION

By appropriate choice of reaction conditions, macroporous poly(2-hydroxyethyl methacrylate–co-ethylenedimethacrylates) (Spheron-type sorbents) can be prepared which possess specific surfaces, porosities, grain sizes and polarities[1–3]. These copolymers have been used as chromatographic sorbents[3,4] because of their ability to fractionate branched hydrocarbons, polar compounds and gases.

The present work is an attempt to elucidate the interaction between the surface of macroporous poly(2-hydroxyethyl methacrylate–co-ethylenedimethacrylates) and low-molecular-weight solutes under gas chromatographic (GC) conditions.

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* Part I: J. Hradil, A. L. Kaganov, J. Štamberg and P. Synek, *J. Polym. Sci., Part C*, Symposium No. 47 (1974) 123. Presented at 13th Prague Microsymposium on Macromolecules, "Transformations of Functional Groups on Polymers", Prague, August, 1973.

EXPERIMENTAL

Macroporous copolymers (extracted with ethanol during 18 h in a Soxhlet apparatus) of grain size 160–200 μm were used as packing in glass columns (100 × 0.32 cm I.D.). After the columns had been conditioned (8 h at 200 °C in a stream of nitrogen), the measurements were carried out on a Perkin-Elmer Model F 11 apparatus equipped with a flame ionization detector and using nitrogen as carrier gas (nitrogen flow-rate, 10–30 ml/min) at column temperatures of 50–175 °C. The samples (0.1–1.0 μl) were injected by use of a Hamilton 7101-NCH syringe.

Poly(2-hydroxyethyl methacrylate) (viscometrically determined molecular weight: 94,000) was coated (0.05 and 4.83 wt. %) from a methanolic solution on to Chromosorb W (grain size 147–175 μm, specific surface area S_g = 1.0 m²/g; Johns-Manville, Denver, Colo., U.S.A.) by evaporation on a rotational vacuum evaporator at room temperature. The sample was not conditioned before measurement. The measurements were performed under the conditions described above.

Kováts' retention indices (I) were calculated[5] using the specific retention volumes (V_g ml/g) of the compounds (Table I) under conditions (sample volume, 0.1 μl) where I is not dependent on the volume of sample injected.

The sorption isotherms[6] of pentane and ethanol at 150 °C were determined from their chromatographic peaks, the dependence of which on the volume of sample in-

TABLE I

PROPERTIES OF MACROPOROUS POLY (2-HYDROXYETHYL METHACRYLATE–CO-ETHYLENEDIMETHACRYLATES)

In the designation of Spheron, the letter G indicates the possibility of using the copolymer in GC, the number give the content of the crosslinking agent (ethylenedimethacrylate) in the starting monomeric mixture (wt. %) and the last letter is related to the ratio of the inert components, cyclohexanol: dodecanol (wt. %), during the polymerization (A = 100:0, B = 91:9, C = 70:30 and F = 54:46).

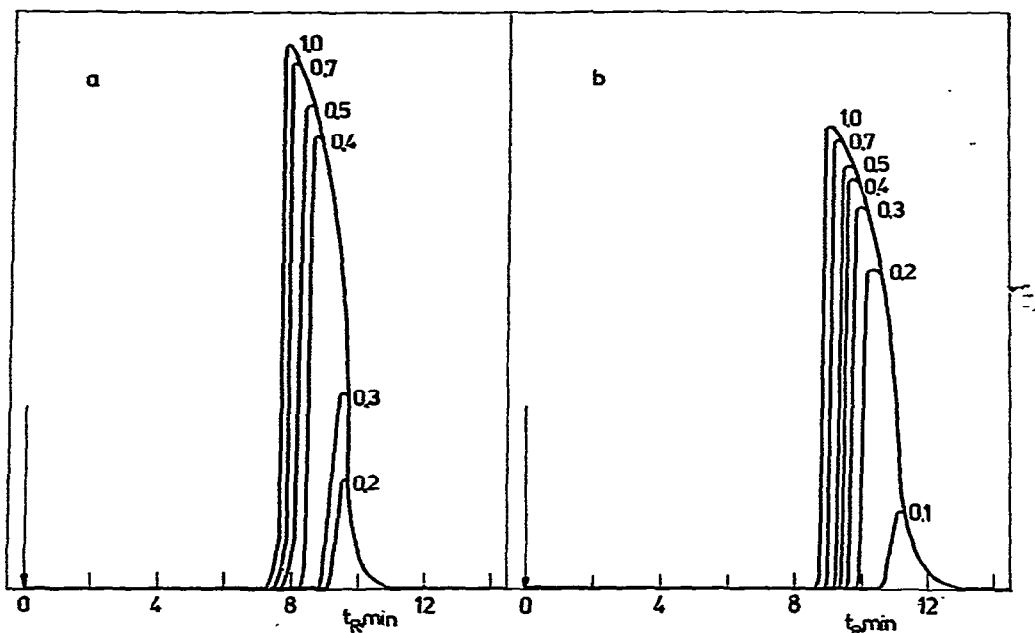| | Spheron | | | | | | | | | |
	G10B	G24B	G39B	G50B	G50F	G75F	G90F	G100F	G50A	G50C
Specific area, S_g (m²/g)	1.5	17	78	97	41	160	209	170	146	109
Composition of copolymers	55.5	56.2	56.6	58.0	57.6	58.4	59.3	60.4	58.0	56.8
(%C ± 0.1%), found (calc.)	(55.9)	(56.6)	(57.4)	(58.0)	(58.0)	(59.3)	(60.0)	(60.6)	(58.0)	(58.0)
Kováts' indices at 150°C										
Nitromethane	1025	1167	908	748	757	683	690	657	710	766
Ethanol	900	996	802	644	654	560	552	530	631	663
Acetone	—	—	—	701	—	—	563*	—	—	—
Propanol	—	1127	835	778	—	—	621*	—	638	790*
2-Propanol	—	1033	811	727	—	—	581*	596	491	721*
2-Butanone	833	1019	884	759	759	702	651	670	715	771
1,2-Dichloroethane	—	1041	819	720	—	—	671*	452	700	792*
Chloroform	—	—	—	—	—	—	625*	—	—	—
Ethyl acetate	—	975	821	753	—	—	652*	596	701	777*
tert.-Butyl alcohol	—	1041	827	770	—	—	770*	597	710	774*
Pyridine	1403	1360	1120	948	985	804	—	678	—	—
Benzene	860	935	832	719	722	686	660	677	701	739
Carbon tetrachloride	—	854	754	704	—	—	636*	646	754	692*
Cyclohexane	—	913	684	670	—	—	628*	638	669	645*

* Kováts' indices determined at 175 °C.

Fig. 1. Chromatographic peaks as a function of the volume of the sample injected for pentane (a) and ethanol (b) on Spheron G90F at 150 °C. The volumes are given in μl.

jected (0.05–$1.0\ \mu l$) can be seen in Fig. 1. The partial pressure, p in Pa, was calculated from

$$p = (mqRT/AF)h \qquad (1)$$

where m is the amount in moles of pentane or ethanol injected, q is the chart speed of the recorder in min^{-1}, R (= 8.3143 J/°K·mole) is the gas constant, T is the column temperature in °K, A is the peak area in m^2, F is the flow-rate of the carrier gas (nitrogen) in kl/min and h is the peak height in metres. The amount of the compound, a in mole/m^2, sorbed at the above partial pressure is given by

$$a = mA_a/wAS_g \qquad (2)$$

in which A_a is the chromatogram area between the point of injection, the zero line and the diffusion profile of the peak having a height h in m^2, w is the weight of the copolymer in grams and S_g is the specific surface area of the copolymer in m^2/g. The individual sorption isotherms are given in Fig. 2. The dependence of the logarithm of the specific retention volume, log V_g, of pentane and ethanol on temperature for a sample volume of 0.1 μl was determined for the temperature range 50–170 °C.

The specific surface area of the macroporous copolymers was determined from the thermal desorption of nitrogen[7].

RESULTS AND DISCUSSION

The specific surface areas of macroporous poly(2-hydroxyethyl methacrylate–co-ethylenedimethacrylates) vary from 1.5 to 209 m^2/g (Table I), increasing with the
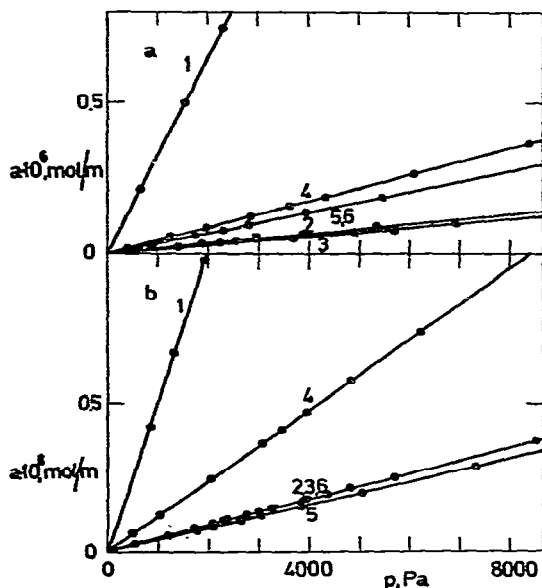
Fig. 2. Sorption isotherms of pentane (a) and ethanol (b) on macroporous poly(2-hydroxyethyl methacrylate–co–ethylenedimethacrylates) at 150 °C. Polymers: 1 = Spheron G10B, 2 = G39B 3 = G50B, 4 = G50F, 5 = G90F and 6 = G100F.

content of the crosslinking agent (ethylenedimethacrylate) in the monomeric mixture used in the copolymerization.

Copolymers suitable for GC are those which exhibit a considerable range of polarity. The polarity of the copolymers studied (Table I) increases with the content of 2-hydroxyethyl methacrylate in the starting monomeric mixture, and is also affected by the ratio of cyclohexanol to dodecanol used in the copolymerization. The decrease in the specific surface area and in the elementary carbon content (Table I) of copolymers in the series Spheron G50A–G50F indicates that a higher dodecanol content in the reaction mixture leads to depletion of the crosslinking agent in the polymer. Thus, the changes in polarity with changes in the cyclohexanol:dodecanol ratio can be explained by a change in the composition of the 2-hydroxyethyl methacrylate copolymers. The polarity of 2-hydroxyethyl methacrylate copolymers can also be influenced by inhomogeneities in the copolymer composition and by the changing orientation of polymer chains on the copolymer surface.

Table I shows that the Kováts' indices of polar compounds injected on to macroporous poly(2-hydroxyethyl methacrylate–co–ethylenedimethacrylate) are generally higher than those of hydrocarbons. This is why the above copolymers exhibit specific interactions with low-molecular-weight compounds, together with non-specific interactions due to London forces. The differences between the Kováts' indices of polar compounds and hydrocarbons are largest in the case of alcohols, i.e., compounds which are able to form hydrogen bonds with 2-hydroxyethyl methacrylate copolymers.

An estimate of the extent to which specific and non-specific interactions become operative can also be derived from the sorption isotherms of ethanol and pentane. The amount of ethanol sorbed by 2-hydroxyethyl methacrylate macroporous

copolymers is comparable with that of pentane. Hence, the sorption is predominantly due to non-specific interactions between the injected compound and the macroporous copolymer, bearing in mind that the pentane molecule is larger than that of ethanol, and also considering the higher intensity of specific interactions. The sorption isotherms of pentane and ethanol on the copolymers studied are quite linear in the range measured ($0 < p/p_0 < 0.085$). Linear sorption isotherms are essential for quantitative analysis.

In the case of macroporous copolymers it is assumed[8] that the injected compound is exclusively adsorbed on the polymer surface. However, Smidsrød and Guillet[9] showed that the injected compound might also be absorbed in the bulk of the linear polymer. I established that the dependence of the logarithm of the specific retention volume on $1/T$ (Fig. 3) for both pentane and ethanol on macroporous poly(2-hydroxyethyl methacrylate–co-ethylenedimethacrylates) exhibited an inflexion* at temperatures ranging from 116 to 132 °C.
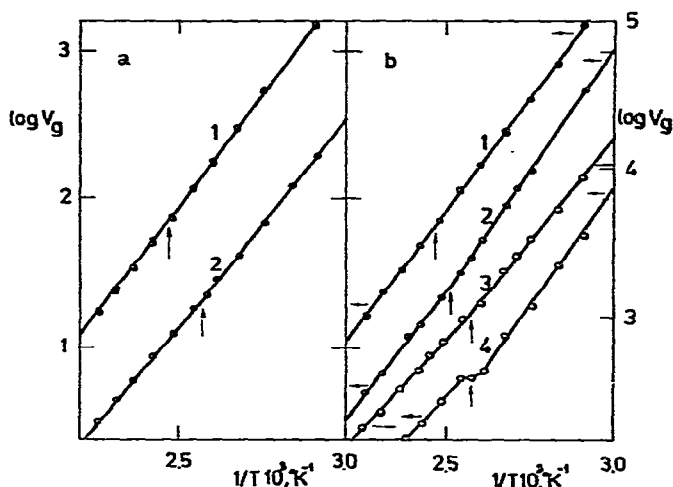

Fig. 3. Dependence of the logarithm of the specific retention volume (log V_g) of pentane (a) and ethanol (b) on $1/T$. Polymers: 1 = Spheron G90F, 2 = G39F, 3 = Chromosorb W with 0.05 wt.% poly(2-hydroxyethyl methacrylate), 4 = the same sorbent with 4.83 wt.% poly(2-hydroxyethyl methacrylate). The dependences were plotted by the least-squares method.

Since the inflexion has been observed both with ethanol and with pentane, which does not take part in associative bonding, and it occurs at a much higher temperature than the boiling points of the injected compounds, the inflexion point can be explained only by a change in the properties of the copolymer. The position of the inflexion corresponds to the glass transition temperature (T_g) of poly(2-hydroxyethyl methacrylate–co-ethylenedimethacrylates) (for 51.4 wt.% of the crosslinking agent, $T_g = 114.5$ °C; for 66.8 wt.% of the crosslinking agent, $T_g = 121.5$ °C)[11], and

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* A similar inflexion has also been observed in the case of Porapak R, macroporous poly(vinyl-pyrrolidine–co-divinylbenzene), and was interpreted in terms of association of water injected onto the copolymer[10]. The inflexion found at 109–122 °C for Porapak R corresponds to T_g of the above copolymer.

is affected by the polarity of the injected compound and by the degree of crosslinking of the copolymer, as established in the dilatometric determination of T_g (ref. 11).

Therefore, at temperatures below T_g, the injected compound is adsorbed on to the surface of the macroporous copolymer, while above T_g absorption sets in. The inflexion point for macroporous copolymers (Fig. 3) is less pronounced than with a linear polymer (4.83 wt.% coated on an inert carrier), but is fully comparable with the inflexion point determined for 0.05 or 0.07 wt.% of poly(2-hydroxyethyl methacrylate)[12]. Also, the transition region near the inflexion point is less pronounced.

Bearing in mind that poly(2-hydroxyethyl methacrylate) coated (0.05 wt.%) on Chromosorb W ($S_g = 1.0$ m²/g) may form a polymer layer with an average thickness of 0.5 nm, which is the longest dimension of the 2-hydroxyethyl methacrylate structure unit, it may be concluded that interactions between the injected compound and the macroporous, strongly crosslinked, copolymer (with >50 wt.% of the crosslinking agent) above T_g take place mainly in the surface layers of the polymer. In the case of less crosslinked macroporous copolymers (with <50 wt.% of the crosslinking agent), the inflexion point is more pronounced because diffusion into the bulk of the copolymer takes place.

The sorption isotherms also indicate, by the greater quantities of ethanol and pentane sorbed on Spheron G10B and G50F, a diffusion of low-molecular-weight compounds into the polymer bulk, and consequently their absorption. On the other hand, the quantity of ethanol sorbed on the other copolymers also above T_g is proportional to the specific surface area of the copolymers.

ACKNOWLEDGEMENT

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