Journal of Chromatography, 114 (1975) 335–344

CHROM. 8481

POLAR MACROPOROUS SORBENTS FOR GAS CHROMATOGRAPHY

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(Received April 4th, 1975)

SUMMARY

Macroporous copolymers having a large specific surface area (up to 500 m^2/g) and sufficient thermal stability (up to 300°) have been prepared by copolymerization of monomers of the methacrylate type. The separation efficiency as characterized by Van Deemter's equation is very high ($H_{min.} = 0.12$ cm). The use of these polymers for the separation of various mixtures of compounds is documented for several examples.

INTRODUCTION

Macroporous sorbents of the styrene–divinylbenzene type are well established in gas–solid chromatography (GSC)[1,2]. At present, efforts are concentrated on broadening the range of macroporous copolymers by including sorbents having a higher polarity[3,4] such as the commercially available Porapak N[5,6], Porapak T[5,6] and Chromosorb 104[5]. Macroporous copolymers known under the trade mark as Spheron® (Lachema, Brno, Czechoslovakia)[7] are sorbents of medium polarity. The latter can be varied by chemical transformation[8] or by using monomers of various polarity in the suspension polymerization. The present study concerns the chromatographic properties of multicomponent macroporous copolymers of medium and higher polarity.

EXPERIMENTAL

Preparation of macroporous copolymers

The polymers under investigation were prepared by suspension copolymerization of the cross-linking agent ethylenedimethacrylate with methyl methacrylate (polymer I), methyl methacrylate and 2-hydroxyethyl methacrylate (polymer II), or of acrylonitrile and 2-hydroxyethyl methacrylate (polymer III) (Table I) under the conditions of formation of the macroporous structure[9]. On completion of the polymerization, the polymers were extracted with benzene, dried at reduced pressure and fractionated on molecular sieves. Fractions of 100–200 and 200–300 μm were used for chromatographic measurements.

The specific surface area (S_g in m^2/g) was measured by the method of thermal desorption of nitrogen according to Nelsen and Eggertsen[10] using aluminium oxide ($S_g = 200$ m^2/g) and titanium dioxide ($S_g = 7$ m^2/g) as standards of known specific surface area (Table I). The thermal stability was determined with a DuPont 950 apparatus within a range of 25–480°, at a heating rate of 10°/min. The analyses were made in an inert nitrogen or argon atmosphere, at a flow-rate of 200 ml/min (Table I). Porapak T (Waters Ass., Frankfurt/M, G.F.R.) (particle size, 125–140 μm) was characterized in the same way, for comparison with the other polymers.

Chromatography

Retention times of the homologous paraffin series (C_5–C_9), alcohols (C_1–C_4) and chromatographic standards (benzene, methyl ethyl ketone, nitromethane and pyridine) were measured on glass columns (120 × 0.3 cm I.D.) packed with the macroporous polymers under investigation (Table I) at 100, 125, 150 and 175° using a Pye apparatus (Pye Unicam, Cambridge, Great Britain) provided with an ionization detector (^{90}Sr). Prior to the measurement, the polymers were conditioned by heating to 170° for 24 h in a stream of an inert gas. The carrier gas (argon) flow-rate was varied from 25 to 30 ml/min; the pressure gradient on the column was measured with an open mercury manometer. The retention times thus obtained were used to calculate Kováts' indices[11].

Adsorption isotherms indicating the dependence of the amount sorbed (a in mole/g) on partial pressure (p in Torr) were calculated for hexane and ethanol from the dependences of the amount injected (0.05–0.1 μl) on the shape of the peak, according to Gray and Guillet[12] (Figs. 2 and 3). The asymmetry of the peaks for 0.05–1.0-μl amounts of heptane or ethanol was defined as the ratio of the x and y intercepts cut out from a peak at one tenth of its height by a perpendicular line drawn from the maximum of the peak to the zero line[13] (Table III). The dynamic properties of columns packed with the macroporous polymers were described by Van Deemter's equation[14]. The individual terms of Van Deemter's equation were calculated from the experimental data by using the method of Dubský and Krejčí[15] (Figs. 4 and 5).

TABLE I

CHARACTERIZATION OF THE MACROPOROUS POLYMERS

MMA = Methyl methacryalate; HEMA = 2-hydroxyethyl methacrylate; AN = acrylonitrile; EDMA = ethylenedimethacrylate.

Polymer	*Composition of mixture (% by wt.)*				*Analysis (%)*		*Granulation (μm)*	*Specific surface area, S_g (m²/g)*	*Temperature of onset of decomposition, t_{PR} (°C)*
	MMA	*HEMA*	*AN*	*EDMA*	*C*	*H*			
I	10	—	—	90	61.47	7.77	200–300	521	243
II	8.4	31.6	—	60	59.41	7.75	100–200	176	226
III	—	40	10	50			100–200	116	300
IV*	—	—	—	—	59.46	7.13	125–149	431	235

* Porapak T; according to the elemental analysis and infrared spectra (band at 1750 cm^{-1}), this polymer is also of the ester type.

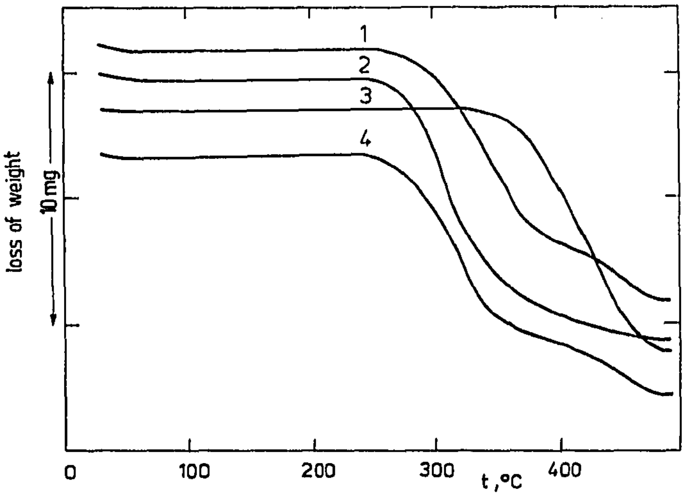


Fig. 1. Differential thermogravimetric analysis of the macroporous polymers. Heating rate, 10°/min. Inert gas (argon) flow-rate, 200 ml/min. Polymers: 1 = I (sample weight, 10.5 mg); 2 = II (11.4 mg); 3 = III (10.8 mg); and 4 = IV (10.2 mg).

RESULTS AND DISCUSSION

By heterogeneous multicomponent copolymerization, macroporous polymers of methyl methacrylate (polymer I), of methyl methacrylate and 2-hydroxyethyl methacrylate (polymer II) and of acrylonitrile and 2-hydroxyethyl methacrylate (polymer III) cross-linked with ethylenedimethacrylate were prepared. The copolymers were perfectly spherical and had a particle size similar to that used in analytical applications. The thermal stability, which is a condition necessary for the

TABLE II

KOVÁTS' INDICES FOR ROHRSCHNEIDER'S STANDARDS AND AN HOMOLOGOUS SERIES OF ALCOHOLS AS DETERMINED FROM THEIR RETENTION TIMES ON THE MACROPOROUS POLYMERS

Column, glass (120 × 0.3 cm I.D.).

Adsorbate	*150°*				*175°*		
	*Polymer I**	*Polymer II**	*Polymer III**	*Polymer IV**	*Porapak N*[5]	*Porapak T*[5]	*Chromosorb 104*[5]
Benzene	638	717	815	691	651	720	845
Ethanol	489	622	725	586	483	564	700
Methyl ethyl ketone	631	737	863	696	624	702	860
Nitromethane	598	734	925	702	596	721	965
Pyridine	725	900	1060	—	748	849	1060
Methanol	392	543	650	514	—	—	—
Propanol	589	709	840	687	—	—	—
Butanol	696	815	959	793	—	—	—

* Carrier gas (argon) flow-rate, 25 ml/min; amount of adsorbate injected, 0.1 μl.

TABLE III

ASYMMETRY* OF THE CHROMATOGRAPHIC PEAKS OF HEXANE AND ETHANOL AS DETERMINED ON POLYMERS AT A COLUMN TEMPERATURE OF 150°

Column as in Table II.

Amount of sample injected (μl)	*Polymer I*		*Polymer II***		*Polymer III*		*Polymer IV*	
	Hexane	*Ethanol*	*Hexane*	*Ethanol*	*Hexane*	*Ethanol*	*Hexane*	*Ethanol*
0.05	0.38	0.53	— —	0.54 (0.71)	—	—	0.55	0.51
0.1	0.34	0.39	0.59 (0.69)	0.45 (0.67)	—	0.60	0.53	0.50
0.2	0.29	0.34	0.38 (0.64)	0.29 (0.54)	0.30	0.39	0.38	0.38
0.3	0.22	0.34	0.28 (0.60)	0.24 (0.41)	0.31	0.29	0.33	0.32
0.4	0.15	0.25	0.22 (0.57)	0.25 (0.54)	0.29	0.24	—	0.27
0.5	0.15	0.27	0.22 (0.41)	0.24 (0.28)	0.32	0.21	0.22	0.25
0.7	0.11	0.20	0.18 (0.30)	0.22 (0.26)	0.28	0.16	0.19	0.18
1.0	—	0.21	0.15 (0.32)	0.22 (0.25)	0.28	0.16	0.20	0.17

* As defined in the Experimental section.

** The data in parentheses were determined at 175°.

use of polymers in gas chromatography, is generally higher than for Porapak T (polymer IV). Polymer III is much more stable than copolymers of acrylonitrile[3] and its stability approaches that of the styrene–divinylbenzene copolymers[2]. It can be seen from Table I that the polymers thus prepared can be used up to 220°. A small weight loss (1–2%) in the initial stage of thermal analysis (Fig. 1) corresponds to loss of water and of low-molecular-weight compounds adsorbed on the surface of the polymers as a result of their sorption activity.

The chemical structure of the above polymers is reflected in their high polarity (Table II) which can be widely varied by adjusting the concentration and polarity of the monomers (Table I). As indicated by Kováts' indices, polymer I is the least polar; its polarity is similar to Porapak N[5,6], which, according to elemental analysis (68.49% C; 7.64% H; 1.02% N) and to the infrared spectra (band at 1750 cm^{-1}), is a sorbent of the ester type, the polarity being decreased by the co-monomer

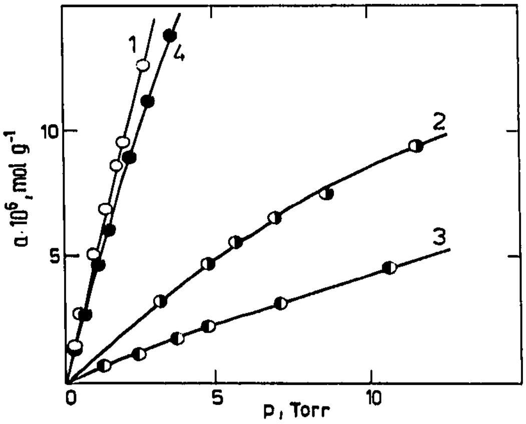


Fig. 2. Adsorption isotherms for hexane on the macroporous polymers at a column temperature of 150°. Column, glass (120 × 0.3 cm I.D.). Carrier gas, argon. Polymers as in Fig. 1.

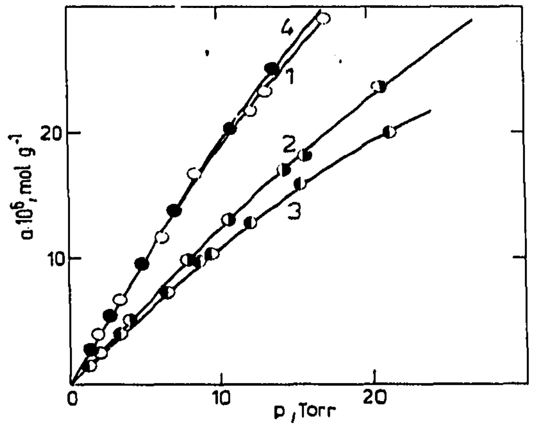


Fig. 3. Adsorption isotherms of ethanol on the macroporous polymers. Column details and polymers as in Fig. 2.

(probably vinylpyrrolidine). The higher polarity of polymer II compared to Porapak T[5,6] can be assigned to the amount (31.6% by wt.) of 2-hydroxyethyl methacrylate present. The most polar macroporous copolymer of all the sorbents described so far is Chromosorb 104 (ref. 5); a similar polarity has also been found for polymer III.

A disadvantage of styrene–divinylbenzene copolymers which is only sometimes reported[2] consists in the formation of tails to the chromatographic peaks. This is prevented by silylation of the sorbents. Although the polymers under investigation were not surface-treated, the formation of tails to peaks of both non-polar and polar

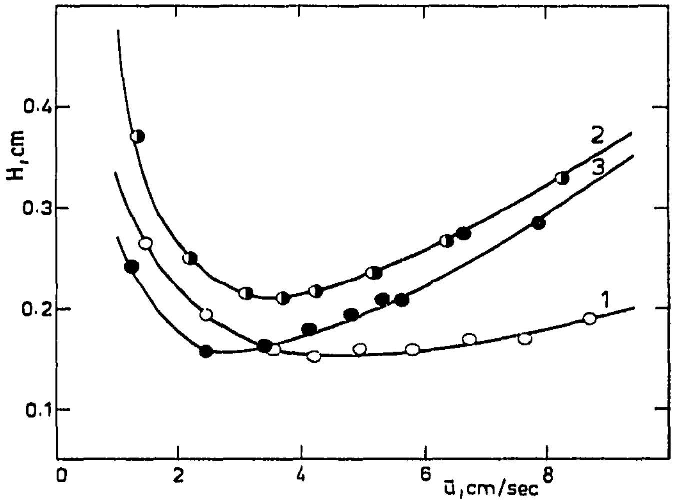


Fig. 4. Dependence of a height equivalent to a theoretical plate (H) on the linear flow-rate ($\bar{u}$) of the carrier gas (argon) for 0.1-μl amounts of heptane at a column temperature of 150°. Other column details as in Fig. 2. Polymers: 1 = I (calculated dependence: $H = 0.024 + 0.289/\bar{u} + 0.015\bar{u}$; $H_{\min.} = 0.15$ cm); 2 = II ($H = 0.092 + 0.539/\bar{u} + 0.043\,\bar{u}$; $H_{\min.} = 0.21$ cm); and 3 = IV ($H = -0.042 + 0.277/\bar{u} + 0.037\,\bar{u}$; $H_{\min.} = 0.16$ cm).

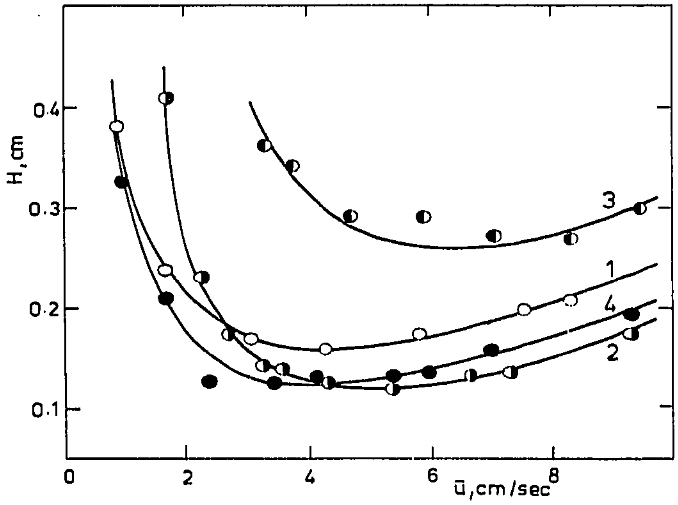


Fig. 5. Dependence of a height equivalent to a theoretical plate (H) on the linear flow-rate ($\bar{u}$) of carrier gas (argon) for 0.1-μl amounts of propanol at a column temperature of 150°. Other column details as in Fig. 2. Polymers: 1 = I (calculated dependence: $H = -0.001 + 0.325/\bar{u} + 0.020\,\bar{u}$; $H_{\text{min.}} = 0.16$ cm); 2 = II ($H = -0.195 + 0.837/\bar{u} + 0.030\,\bar{u}$; $H_{\text{min.}} = 0.12$ cm); 3 = III ($H = -0.432 + 2.289/\bar{u} + 0.052\,\bar{u}$; $H_{\text{min.}} = 0.26$ cm); and 4 = IV ($H = -0.058 + 0.363/\bar{u} + 0.023\,\bar{u}$; $H_{\text{min.}} = 0.13$ cm).

compounds was low (Table III). The symmetry of the peaks of the polar compounds (*e.g.*, ethanol) on less polar sorbents (polymer I) was higher than that of the non-polar compounds (*e.g.*, hexane); on the other hand, the symmetry of the peaks of the non-polar compounds on polar sorbents (polymer III) was higher than that of the polar compounds. The symmetry of the peaks generally decreased on increasing the amount

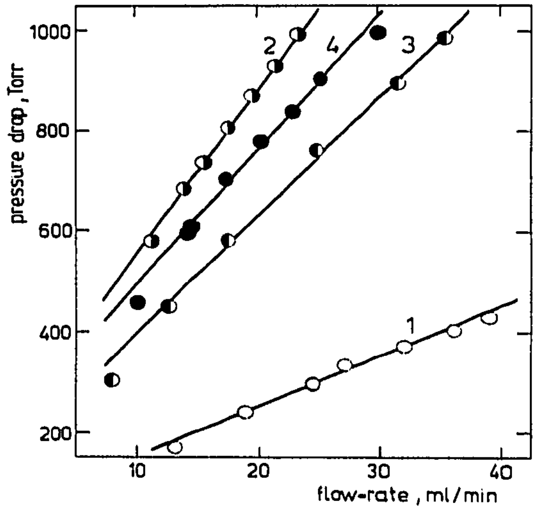


Fig. 6. Effect of the carrier gas flow-rate on the pressure gradient in the column at a column temperature of 150°. Other column details as in Fig. 2. Polymers: 1 = I (granulation, 200–300 μm); 2 = II (100–200 μm); 3 = III (100–200 μm); 4 = IV (125–149 μm).

of sample injected due to the higher sensitivity of the sorbents towards overloading, but it was considerably improved by increasing the working temperature (Table III). At 175°, the value reached for ethanol was 0.71, compared with 0.54 at 150°.

The macroporous structure of the polymers is reflected in their specific surface area (Table I). We obtained polymers of high specific surface area, which is a condition of the successful application of polymers in adsorption chromatography. All the specific surface areas of the polymers were larger than those of similar types prepared so far[3]. The specific surface area is reflected in the amount of the adsorbate sorbed by the polymer, as can be seen from the adsorption isotherms (Figs. 2 and 3). The isotherms are of type I according to Brunauer's classification, as is usual for polymeric sorbents[16]. Adsorption isotherms for the polar and non-polar compounds (ethanol and hexane) were almost linear for all the types of copolymers under investigation, even at a comparatively low temperature (150°), in agreement with the high symmetry of peaks as discussed above.

The dynamic conditions on the columns packed with the polymers used throughout this work were studied by following the dependence of a height equivalent to a theoretical plate (H) on the linear flow-rate ($\bar{u}$) of the carrier gas and characterized by the calculated form of Van Deemter's equation. The experimentally determined points and constants of the calculated dependence for heptane and propanol are given in Figs. 4 and 5. The course of the graphs in the region of the minimum height equivalent to a theoretical plate ($H_{\text{min.}}$) is very flat, from which one may deduce that columns packed with the polymers have a constant efficiency over a broad range of carrier gas flow-rate. Values of $H_{\text{min.}}$ are usually very low (heptane, 0.15–0.21 cm; propanol, 0.12–0.26 cm).

The influences of the carrier gas flow-rate (Fig. 6) and of the column temperature (Fig. 7) on the pressure gradient in the column were investigated with respect to the higher resistances of polymeric sorbent packings. The dependences thus ob-

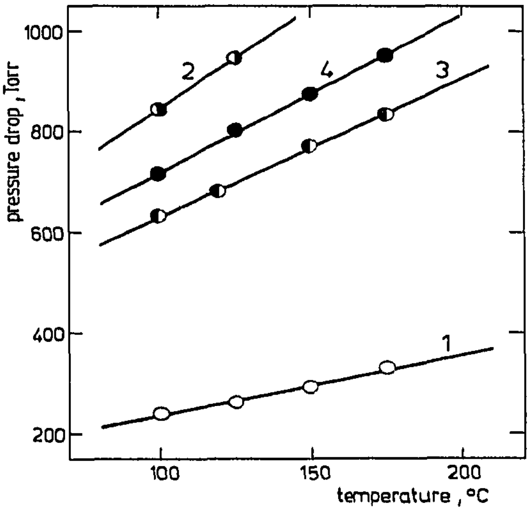
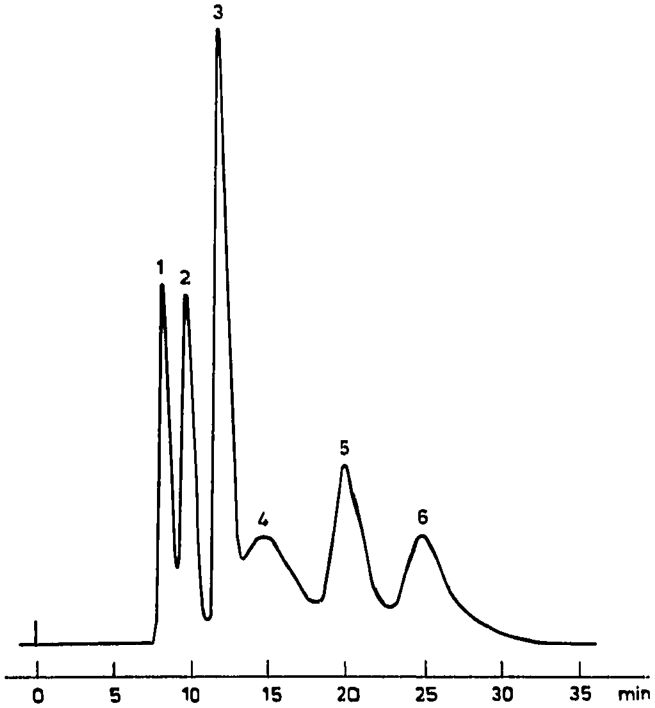


Fig. 7. Effect of the column temperature on the pressure gradient in the column during a carrier gas flow-rate of 25 ml/min. Other column details as in Fig. 2. Polymers as in Fig. 6.



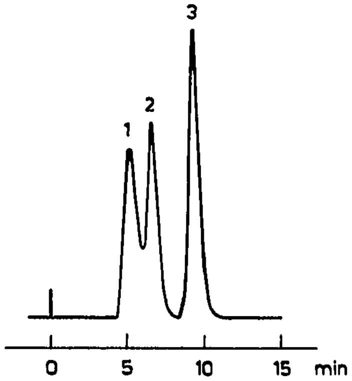


Fig. 8. Gas chromatographic separation of olefins on a glass column (120 × 0.3 cm I.D.) packed with polymer I. Column temperature, 125°. Carrier gas (argon) flow-rate, 25 ml/min. Amount of sample injected, 0.15 μl. Peaks: 1 = 1-pentene; 2 = cyclopentene; 3 = *trans*-1,3-pentadiene; 4 = 3,3-dimethyl-1-butene; 5 = *cis*-4-methyl-2-pentene; and 6 = 1-hexene.

Fig. 9. Gas chromatographic separation of cyclohexane (1), cyclohexene (2) and benzene (3) on a glass column (120 × 0.3 cm I.D.) packed with polymer II. Column temperature, 154°. Carrier gas (argon) flow-rate, 26 ml/min. Amount of sample injected, 0.1 μl.

tained allow us to conclude that column packings consisting of polymers II and III have resistances similar to those of Porapak T. With increasing particle size, the pressure gradient on the column markedly decreased (polymer I). Work at higher temperatures would require a sorbent having a higher granulation. Because of the dependence of the pressure gradient on the carrier gas flow-rate and of the optimum column efficiency at lower flow-rates (Figs. 4 and 5), it was possible to work at lower carrier gas flow-rates than is usual with macroporous sorbents.

The application of the above sorbents in gas chromatography requires knowledge of the distribution of a mixture of compounds. From Kováts' indices, polymer I is the least polar of the series prepared in this work and is convenient for the separation of non-polar and low-polarity compounds. Fig. 8 shows the successful separation of some olefins (1-pentene, cyclopentene, *trans*-1,3-pentadiene, 3,3-dimethyl-1-butene, *cis*-4-methyl-2-pentene and 1-hexene). Polymer II is a sorbent of medium polarity with a wide range of application. Fig. 9 shows the separation of cyclohexane, cyclohexene and benzene, which is not feasible on styrene–divinylbenzene copolymers[2], and Fig. 10 illustrates the separation of alcohols C_1–C_5. Polymer III is a

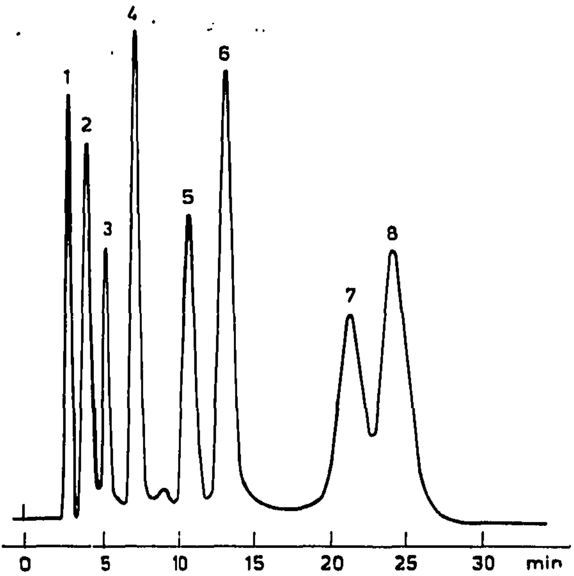


Fig. 10. Gas chromatographic separation of alcohols C_1–C_5 on a glass column (120 × 0.3 cm I.D.) packed with polymer II. Column temperature, 175°. Carrier gas (argon) flow-rate, 25 ml/min. Amount of sample injected, 0.1 μl. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = propanol; 5 = isobutanol; 6 = butanol; 7 = 3-methylbutanol; and 8 = pentanol.

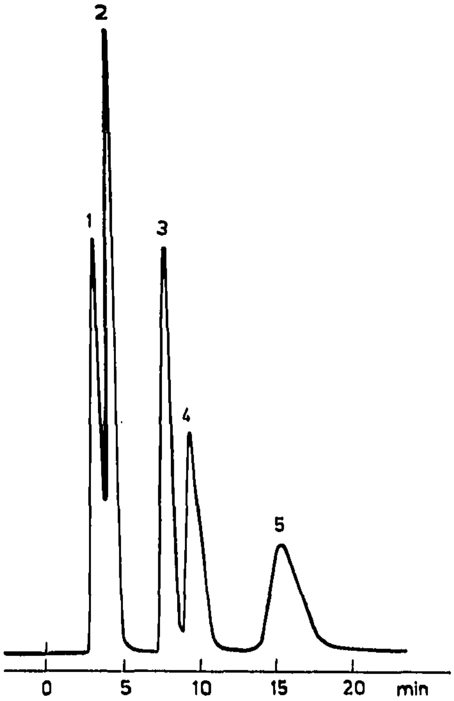


Fig. 11. Gas chromatographic separation of polar compounds on a glass column (120 × 0.3 cm I.D.) packed with polymer III. Column temperature, 125°. Carrier gas (argon) flow-rate, 25 ml/min. Amount of sample injected, 0.1 μl. Peaks: 1 = diethyl ether; 2 = methanol; 3 = ethanol; 4 = acetone; and 5 = ethyl acetate.

sorbent of high polarity suitable for the separation of polar compounds. Fig. 11 shows the separation of diethyl ether, methanol, ethanol, acetone and ethyl acetate. Retention times of compounds on this polymer are considerably shorter than on the other polymeric sorbents. This makes it possible to work at lower temperatures and to separate higher-boiling compounds.

The above survey of the properties of macroporous polymers of the methacrylate type demonstrates their applicability in gas chromatography. The properties of the polymers are generally superior to those of the commercially available types, particularly in polarity (a broader range of sorbents), thermal stability (up to 300°) and column efficiency (H_{min}. for heptane, 0.15 cm).

ACKNOWLEDGEMENT

The authors thank Mrs. E. Votavová, Mrs. V. Slavíková and Mrs. H. Jandová for technical assistance.

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