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Studies on the Selectivity of Porous Polymers Containing Different Functional Groups

BARBARA GAWDZIK AND TADEUSZ MATYNIA
Faculty of Chemistry, MCS University, pl. Marii Curie-Sklodowskiej 3, 20-031 Lublin, Poland

Abstract. Three types of porous polymers containing different functional groups were synthesized as stationary phases for gas chromatography. The influence of functional groups in the copolymer skeletons on their selectivities was studied. To determine the selectivities of these copolymers, two procedures were applied: the selectivity triangle and the general selectivity. As a reference phase Porapak Q which does not contain any functional groups was used.

Keywords: gas chromatography, porous polymer stationary phase, selectivity studies

1. Introduction

Porous polymers are known under various trade names and differ in their chemical and porous structure. Chemical structure of porous polymer depends on the chemical structure of the monomers used whereas the porous structure is mainly dependent on the copolymerization conditions. The chemical structure is responsible for the chromatographic properties of porous polymers, in particular the selectivity.

Among various methods describing the selectivity of stationary phases, that of Rohrchneider (1966), modified by McReynolds (1970) is the most successful. According to Smith et al. (1978) graphitized thermal carbon black (GTCB) is a more suitable reference for classifying solid phases in chromatography than squalane because with this phase none of the modified McReynolds' constants is negative. Using this modification of McReynolds' system it is possible to obtain a good measure of the selectivity of polymeric sorbents. In this method, the selectivity of a phase is characterized by five constants represented by the difference in the Kovats retention indices of test substances (benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine) on the phase under study and on a reference column packed with GTCB, at the same temperature.

Castello and D'Amato (1987) propose to use Porapak Q as a "standard polymeric phase" in the selectivity studies, because it is the least polar porous polymer of those commercially available.

To distinguish the contribution of the common retention mechanism (hydrogen-bond donor, acceptor and dipole interaction) to the selectivity of porous polymers, Hepp and Klee (1987) adopted the selectivity triangle, developed earlier by Snyder (1974) for liquid chromatography. Retention indices of *n*-butanol, 1,4-dioxane and 1-nitropropane, in reference to those obtained on GTCB are used for determining hydrogen-bond donor, hydrogen-bond acceptor and dipole characteristics of porous polymer.

As retention is governed by the total energy of interaction, the extent to which any selectivity is exhibited depends on the amount of polar interaction relative to nonpolar interaction. In order to determine the solute-sorbent dispersive interaction, in this method GTCB was also used as a reference phase.

The aim of this work is to evaluate differences in selectivities and strengths of the polar interactions of polymeric sorbents containing different functional groups in their skeletons. Besides nonpolar Porapak Q (styrene-divinylbenzene type), three other porous copolymers synthesized by us, were used. They are, e.g., di(methacryloyloxymethyl)*m*-xylene-divinylbenzene (DMX-DVB), which contains ester functional groups (Gawdzik and Matynia, 1994a), p,p'-dihydroxydiphenylpropane diglycidyl

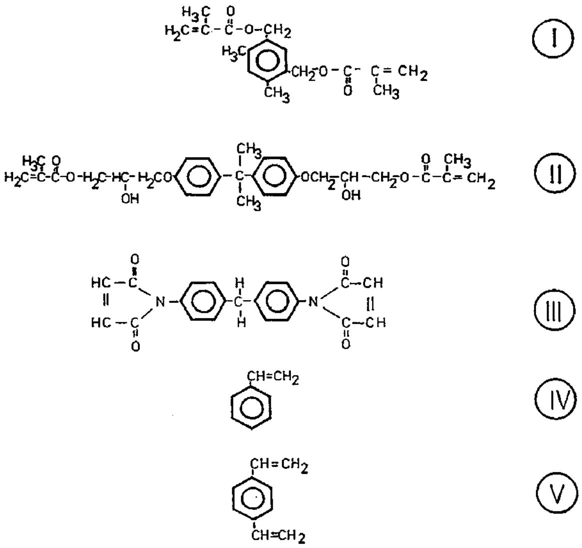

Figure 1. Structure of the monomers used: (I) di(methacryloyloxymethyl)*m*-xylene; (II) methacrylic ester of p,p'dihydroxydiphenylpropane diglycidyl ether; (III) 4,4′-bismaleimidodiphenylmethane; (IV) styrene; (V) divinylbenzene.

ether-divinylbenzene (MEDDE-DVB) with ester and hydroxyl groups (Gawdzik and Matynia, 1994b) and 4,4′-bismaleimidodiphenylmethane-styrene (BM-ST), containing imide functional groups (Matynia et al., 1996). Chemical structures of the monomers used are shown in Fig. 1.

In order to determine the selectivities of these copolymers, two procedures were applied: the selectivity triangle (Snyder, 1974; Hepp and Klee, 1987) and the general selectivity (Smith et al., 1978). To confirm the validity of these methods a test mixture was separeted on each of the copolymer studied.

2. Experimental

Preparation of Copolymers

Porous copolymers of DMX-DVB, MEDDE-DVB and BM-ST were obtained by suspension polymerization from the equivalent mole fraction of monomers. Details of the syntheses conditions were published elswhere (Gawdzik and Matynia, 1994a, 1994b; Matynia et al., 1996).

The shape of the beads was confirmed by microscopic examination. The diameter of the sorbent beads used in chromatographic experiments was always 0.20–0.25 mm. Porapak Q of a similar sieve fraction came from Waters Assoc.

Measurements of Specific Surfaces of Polymers

Measurements of the specific surface areas of the copolymers were carried out by the method of nitrogen adsorption at low temperatures, using a Sorptomatic 1806 instrument (Carlo Erba, Milan, Italy). The specific surface area was calculated by the BET method, assuming that the area of a single nitrogen molecule is 0.162 nm^2 (Ościk, 1979).

Thermogravimetric (TG) Measurements

The measurements were carried on a derivatograph (MOM, Budapest, Hungary) at a heating rate of 5°C/min from 20 to 500°C in air.

The initial decomposition temperature was determined from the course of the TG curve.

Chromatographic Measurements

Chromatographic measurements were carried out on a Chromatron GCHF-18.3 gas chromatograph (Chromatron, Berlin, Germany) equipped with a thermal conductivity detector and stainless-steel columns (100 cm × 4 mm I.D.). Hydrogen at a flow-rate of 50 ml/min was used as carrier gas. Before use all the columns were conditioned with temperature programming from 60 to 240°C (in the case of Porapak Q to 200°C) and then till the retention times for *n*-alkanes were constant. The measurements of retention indices for McReynolds substances (benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine) were carried out at 140°C and those of selectivity parameters (*n*-butanol, 1-nitropropane and 1,4-dioxane) at 200°C. Samples were injected by means of a 1-μl syringe (SGE, North Melbourne, Australia). Each sample was injected separately, dipping the needle (at the zero position of the piston) into the sample. The mixture of polar test solutes (acetonitrile, 2-propanol, triethylamine, 1,2-dichloroethane and octane) and *n*-alkanes were injected as mixtures in an amount of 0.2 μl.

The retention time of the peak of air was considered to be the dead time.

Selectivity Calculations

The selectivity parameters (x_i) were calculated and plotted on the face of the selectivity triangle by using the equation (Hepp and Klee, 1987):

$$x_i = \frac{\Delta I_i}{\Delta I_b + \Delta I_n + \Delta I_d}$$

where ΔI_b, ΔI_n and ΔI_d are the McReynolds constants for n-butanol, 1-nitropropane and 1,4-dioxane, respectively.

The McReynolds constants (ΔI_i) were calculated by substracting the average retention indices of the probe solute on GTCB from those on each of the porous copolymers. The values of the retention indices of n-butanol, 1-nitropropane and 1,4-dioxane on GTCB were taken from the paper by Hepp and Klee [6].

The general selectivity ($\sum I = x + y + z$) was calculated using the reported retention data of GTCB for benzene (x), n-butanol (y) and 2-pentanone (z) (Kalashnikova et al., 1976). Retention indices were calculated from the equation (Kovats, 1958):

$$I_x = 100\,\lg(t'_{R,x}/t'_{R,z})/\lg(t'_{R,z+1}/t'_{R,z}) + 100\mathrm{z}$$

where

$t'_{R,x}$: denotes the reduced retention time of the substance x;
$t'_{R,z}$: the reduced retention time of the homologous alkane with the nearest shortest retention time;
$t'_{R,z+1}$: the reduced retention time of the next higher homologue eluted after homologue z;
z: denotes the number of carbon atoms in the n-alkane molecule

3. Results and Discussion

From the data given in Table 1 it appears that specific surface areas of synthesized by us copolymers are rather low in comparison with those of Porapak Q. Their initial decomposition temperatures determined from the TG curves are significantly higher. Among the studied copolymers DMX-DVB and MEDDE-DVB are formed from two tetrafunctional monomers, so their cross-linkage is very high. Copolymer BM-ST possessing a smaller degree of cross-linking indicates the highest thermal resistance. In this case imide functional groups are responsible for excellent thermal stability of this copolymer. In Table 2 retention indices, modified McReynolds constants and the general selectivities ($\sum I$) for the studied copolymers are presented. The general selectivity indices $\sum I$, defined as a measure of the polarity of the copolymer, indicate that all porous copolymers synthesized by us have a polar character. The MEDDE-DVB porous copolymer which contains hydroxyl and ester functional groups in its skeleton has the highest polarity. Values of $\sum I$ and McReynolds constants on Porapak Q which does not contain any functional groups are the lowest. Comparing retention indices for the McReynolds test substances it can be seen that 1-nitropropane and

Table 1. Properties of the copolymers used.

Copolymer	Mole fraction of monomers	Specific surface area (m^2/g)	Initial decomposition temperature (°C)
MEDDE-DVB	0.5 : 0.5	71	270
BM-ST	0.5 : 0.5	70	360
DMX-DVB	0.5 : 0.5	180	250
Porapak Q	Unknown	660	200

Table 2. Kovats retention indices for the McReynolds test substances and general selectivities ($\sum I$) for the porous copolymers (140°C).

	I								
Copolymer	Benzene	n-Butanol	2-Pentanone	1-Nitropropane	Pyridine	x	y	z	$\sum I = x + y + z$
MEDDE-DVB	824	900	892	1022	1110	250	411	327	988
BM-ST	685	756	809	862	835	111	267	244	622
DMX-DVB	640	678	792	750	718	66	189	227	482
Porapak Q	617	607	651	654	660	43	118	86	247

Table 3. Kovats retention indices for *n*-butanol, 1-nitropropane and 1,4-dioxane and porous copolymers selectivity parameters (200°C).

	I									
Copolymer	*n*-Butanol	1-Nitropropane	1,4-Dioxane	ΔI_b	ΔI_n	ΔI_d	$\sum \Delta I_i$	x_{acc}	x_{dip}	x_{don}
MEDDE-DVB	907	1028	981	421	522	497	1440	0.292	0.363	0.345
BM-ST	788	878	826	302	372	342	1016	0.297	0.366	0.337
DMX-DVB	689	762	720	203	256	236	695	0.292	0.368	0.340
Porapak Q	636	683	648	127	168	164	459	0.276	0.366	0.358

pyridine are strongly retained on the MEDDE-DVB copolymer.

It must be stressed that every polar molecule is capable of several polar interactions and that retention on any particular stationary phase depend on the total interaction. It is possible to evaluate relative interactions between any particular stationary phase and polar probes providing that they have identifiable polar characteristics which predominates. In Table 3, $\sum \Delta I_i$, describing the relative polar contributions to retention and selectivity parameters (x_i) for *n*-butanol, 1,4-dioxane and 1-nitropropane are summarized. In this study *n*-butanol (hydrogen-bond donor) is used to measure hydrogen-bond acceptor characteristics, 1,4-dioxane (hydrogen-bond acceptor) to measure hydrogen-bond donor characteristics and 1-nitropropane to measure dipole characteristics of the polymer.

According to Hepp and Klee, phase with $\sum \Delta I_i$ values close to or exceeding 1000 exhibit inherent selectivity. Compared with Porapak Q all the copolymers studied have stronger hydrogen-bond acceptor properties. This is undoubtedly associated with the presence of lone electron pairs on oxygen and nitrogen atoms in the DMX, MEDDE and BM monomers. Values of selectivity parameters x_i indicate that all the studied copolymers interact with molecules of large dipole moments in a similar way. The location of the copolymers on the selectivity triangle is presented in Fig. 2. As all the copolymers are situated further away from the dipole-corner of the triangle, they would be expected to show little affinity towards dipole-molecules.

Separations of the test mixture proposed by Hepp and Klee are presented in Fig. 3. The test mixture is composed of a proton donor (2-propanol), a proton acceptor (triethylamine), a weak dipole (1,2-dichloroethane), a strong dipole (acetonitrile) and octane which has no polar functionality. The retention of these substances on GTCB is almost due to dispersive interaction, hence they elute in the following order according to their boiling points and molar volumes: (1) acetonitrile; (2) 2-propanol; (3) 1,2-dichloroethane; (4) triethylamine; (5) octane. On all the copolymers 2-propanol (hydrogen-bond donor) is retained longer than acetonitrile (dipole). Insignificantly better affinity towards dipole molecules indicates only DMX-DVB porous polymer. On this phase acetonitrile is retained in similar strenth as 2-propanol. Additionally on the MEDDE-DVB porous polymer triethylamine is eluted after octane what means that this copolymer has stronger hydrogen-bond properties.

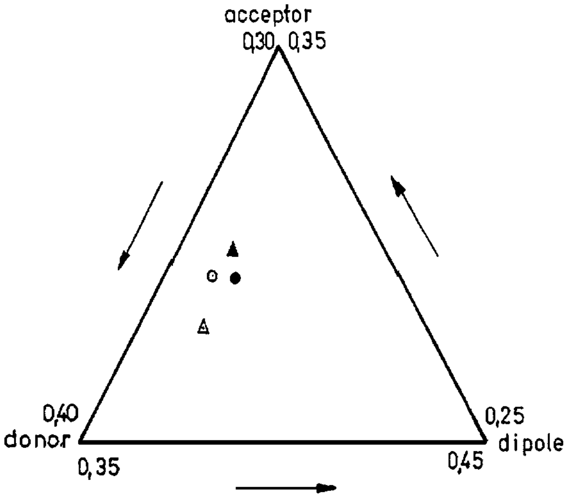

Figure 2. Selectivity triangle showing relative selectivities of the porous polymers: ● = DMX-DVB; ○ = MEDDE-DVB; ▲ = BM-ST; △ = Porapak Q.

It should be noted that on all copolymers synthesized by us peak of triethylamine is more symmetrical than that obtained on less polar Porapak Q.

The results presented here indicate that the selectivity of polymeric sorbents mainly depends upon the chemical nature of functional groups existing in the copolymer skeleton. Choice of proper monomers in the synthesis of porous polymers allows for obtaining phases with unique selectivities.

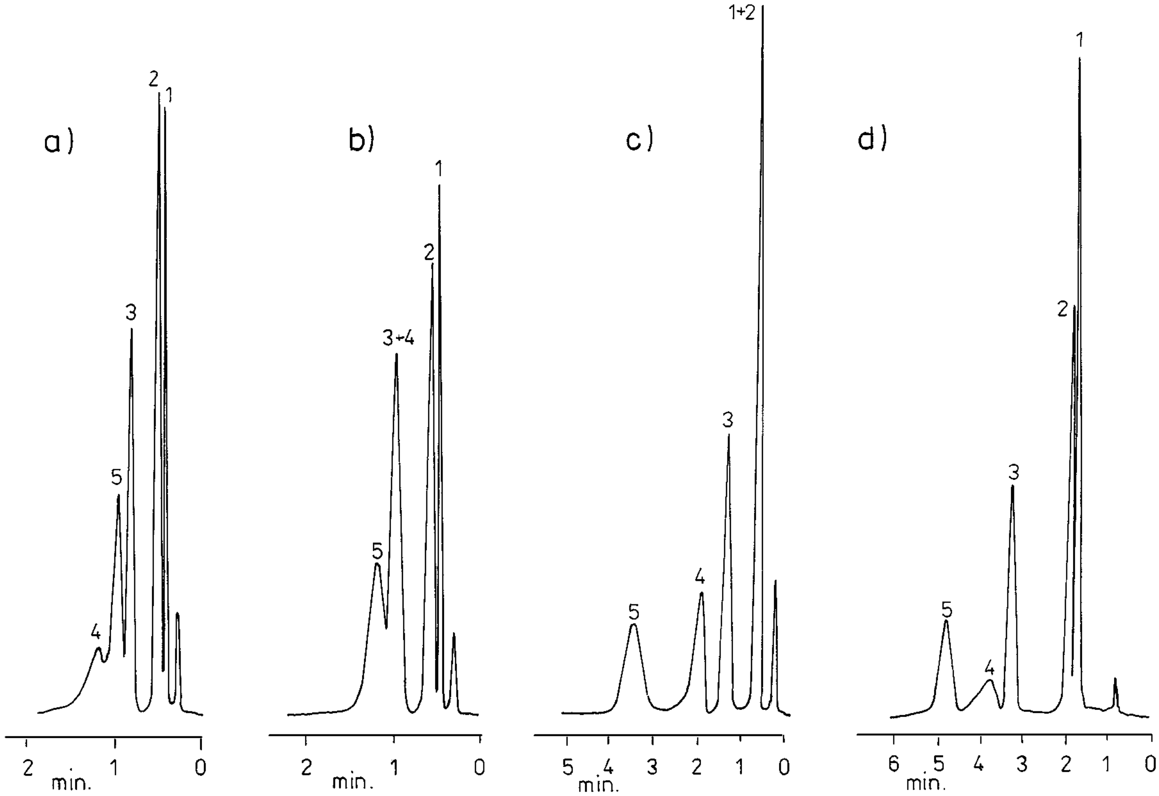

Figure 3. Chromatograms of the test mixture obtained on copolymers: (a) MEDDE-DVB; (b) BM-ST; (c) DMX-DVB; (d) Porapak Q. Peaks: 1 = acetonitrile; 2 = 2-propanol; 3 = 1,2-dichloroethane; 4 = triethylamine; 5 = octane.

References

Castello, G. and G. D'Amato, "Effect of Solute Polarity on the Performance of Porapak Q Type Porous Polymers," *Chromatographia,* **23**, 839 (1987).

Gawdzik, B. and T. Matynia, "Studies of the Selectivity of Di(Methacryloyloxymethyl)*m*-Xylene-Divinylbenzene Porous Copolymers for Gas Chromatography," *Chem. Anal. (Warsaw).*, **39**, 161 (1994a).

Gawdzik, B. and T. Matynia, "Characterization of Methacrylic Ester of p,p'-Dihydroxydiphenylpropane Diglycidyl Ether-Divinylbenzene Porous Copolymers for GC," *Chromatographia,* **38**, 643 (1994b).

Hepp, M.A. and M.S. Klee, "Characterization of Porous Polymers by Polar Strength and Selectivity," *J. Chromatogr.*, **404**, 145 (1987).

Kalashnikova, E.V., A.V. Kisielev, D.P. Poshkus, and K.D. Shcherbakova, "Retention Indices in Gas-Solid Chromatography," *J. Chromatogr.*, **119**, 233 (1976).

Kovats E., *Helvet. Chim. Acta.* **41**, 1915 (1958).

Matynia, T., B. Gawdzik, and E. Chmielewska, "Synthesis and Properties of Porous Copolymers of 4,4′-Bismaleimidodiphenyl methane and Styrene," *J. Appl. Polym. Sci.* **60**, 1971 (1996).

McReynolds, W.O., "Characterization of Some Liquid Phases," *J. Chromatogr. Sci.*, **8**, 685 (1970).

Ościk J., "Adsorpcja," *PWN*, Warsaw, p. 77 (1979).

Rohrchneider, L., "Eine Methode zur Charakterisierung von Gaschromatographishen Trennflüssigkeiten," *J. Chromatogr.*, **22**, 6 (1966).

Smith, J.R.L., A.H.H. Tameesh, and D.J. Waddington, "Porous Polyaromatic Beads III. A Method for Classifying the Selectivity of Porous Polyaromatic Beads," *J. Chromatogr.*, **151**, 21 (1978).

Snyder, L.R., "Classification of the Solvent Properties of Common Liquids," *J. Chromatogr.*, **92**, 223 (1974).