

Investigation of the Surface Area and Polarity of Porous Copolymers of Maleic Anhydride and Divinylbenzene

M. Maciejewska, Ł. Szajnecki, B. Gawdzik

Faculty of Chemistry, MCS University, pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland

Received 28 March 2011; accepted 2 September 2011

DOI 10.1002/app.35572

Published online 17 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Porous copolymers of maleic anhydride (MA) and divinylbenzene (DVB) in the form of regular microspheres were prepared by suspension polymerization. During copolymerization the mixture of 1,4-dioxane and *n*-dodecane as a pore-forming diluent was used. It was found that specific surface area of the obtained beads is strongly dependent on the diluent system and polymerization medium and achieves a value from 4 to 535 m²/g. To determine the influence of polymerization medium on

the selectivity and polarity of the copolymers, inverse gas chromatography (IGC) was applied. To determine these parameters, three procedures were applied: overall polarity, the selectivity triangle, and the ΔC method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 300–307, 2012

Key words: polymeric microspheres; porous structure; maleic anhydride; polarity of surface; inverse gas chromatography

INTRODUCTION

Macroporous, crosslinked copolymers in the form of microspheres are effective materials for many separation processes and, therefore, they are widely used as starting material and specific sorbents.^{1–4} The knowledge of structural parameters and chemical properties of these polymers are of paramount importance for their applications. Usually textural characterization has been performed using adsorption of probe molecules (Ar, N₂, CO₂, etc). Among them adsorption of N₂ at low temperature (77K) is most widely applied.^{5–8} Also the polarity and selectivity of the used adsorbents are very important parameters. To determine these parameters, inverse gas chromatography is used. In inverse gas chromatography, the species of interest is the stationary phase.^{9–12} This is in contrast to conventional analytical GC, where the stationary phase is of interest only as far as its ability to separate the injected compounds is concerned. The porosity of solid sorbent and the presence of functional groups at the surface are key factors. The sorbent should be porous in order to offer a large interacting surface area. Its chemical structure is important for its specificity toward the molecules.¹³ Among commercially available sorbent materials, the most popular are non-polar styrene-divinylbenzene copolymers. During the last decades, the copolymerization of various

functional monomers of the acceptor-donor type and synthesis of new functional polymers with given structure and important properties have attracted considerable interest.^{14–17} Maleic anhydride copolymers are used for many purposes according to a detailed summary of their applications by Trivedi et al.¹⁸

Suitable method for the production of microspherical porous copolymers is suspension polymerization. It has been established that the morphology of copolymer obtained by this method is strongly influenced by the polymerization conditions: type and relative molar ratio of monomers, diluent nature, dilution degree of the monomers, crosslinking degree, polymerization temperature, etc.¹⁹

Ogawa et al.²⁰ have reported the preparation of styrene-maleic anhydride-divinylbenzene beads where glycerol was taken as the continuous phase. Sodium chloride has been added to reduce the solubility of MA in glycerol; but even after using excess of MA and very high percentage of DVB (crosslinker) the copolymer beads have a low MA content. The preparation of spherical styrene-maleic anhydride beads in aqueous phase with sodium chloride and magnesium hydroxide as a stabilizer was presented by Annakutty and Pramila.²¹ The suspension polymerization with such stabilizers as poly(vinyl alcohol) and hydroxyethyl cellulose were also tested by this team, but no beads were obtained.

This article reports on the preparation of spherical porous copolymer beads of maleic anhydride (MA)-divinylbenzene (DVB). The copolymer beads were prepared by the suspension polymerization method in both water and glycerol as the dispersing

Correspondence to: M. Maciejewska (mmacieje@umcs.pl).

TABLE I
Polymerization Recipe

Copolymer	Polymerization medium	Abbreviation of diluent system	Porogenic mixture (mL)	
			<i>n</i> -dodecane	1,4-dioxane
MA-DVB _g	glycerol	A	–	22.50
		B	3.40	19.10
		C	11.25	11.25
		D	19.10	3.40
		E	22.50	–
MA-DVB _w	water	A	–	22.50
		B	3.40	19.10
		C	11.25	11.25
		D	19.10	3.40
		E	22.50	–

medium. In order to reduce the solubility of maleic anhydride in the polymerization medium sodium chloride was added. Poly(vinylpyrrolidone) was used as a suspension stabilizer and 1,4-dioxane–*n*-dodecane mixture as the pore-forming diluent (porogen). By careful choice of the diluents' composition, a wide range of porosities was obtained. Such parameters as specific surface areas, pore volumes, pore size distributions, and average pore diameters were determined by the method of nitrogen adsorption on the surface of the studied materials. To complete the study, the polarity and selectivity of the copolymers were determined by IGC. For the chromatographic measurements, copolymers with highly developed surface area were chosen. During IGC investigation, three procedures were applied: the selectivity triangle, the general selectivity, and the ΔC method.

EXPERIMENTAL

Synthesis of porous copolymers

Copolymerizations were performed in two different suspension media: water and glycerol. In the first experiment (MA-DVB_w preparation), 195 mL of distilled water, 3 g of poly(vinylpyrrolidone) as a suspension stabilizer, and 5 g of NaCl were stirred for 6 h at 80°C in a three-necked flask fitted with a stirrer, water condenser, and thermometer. Then the solution containing 15 g of monomer (maleic anhydride) and crosslinking agent (divinylbenzene) in the relative molar ratio 1 : 1 and 0.2 g of α,α' -azobisbutyronitrile in 22.5 mL of pore-forming diluents (1,4-dioxane + *n*-dodecane) was prepared and added while stirring to the aqueous medium. Relative ratio of diluents to monomers (mL/g) was 1.5 : 1.0.

In the second experiment (MA-DVB_g preparation), instead of water, 195 mL of glycerol was used. Experimental parameters of the copolymerizations are shown in Table I. Copolymerization was performed for 20 h at 80°C. Porous beads formed in this process were filtered, washed with hot water, and

extracted in a Soxhlet apparatus with acetone, toluene, and methanol. The purified beads were separated into fractions by the sieving.

Characterization of copolymers

Textural characterization of the copolymers was carried out by the low-temperature nitrogen adsorption-desorption method. Nitrogen adsorption-desorption measurements were made at 77K using a volumetric adsorption analyzer ASAP 2405 (Micrometrics Inc., USA). The measurements of the surface properties of the copolymers were preceded by activation of the samples at 140°C for 2 h. The specific surface areas of the investigated beads were calculated by the Brunauer-Emmet-Teller (BET) method for the adsorption data in the range of a relative pressure p/p_0 from 0.05 to 0.25. The total pore volume was estimated from a single point adsorption at p/p_0 equal to 0.985. The pore size distributions (PSD) were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) procedure²² The maximum of PSD was defined as the most probable pore diameter in contrast to the average pore diameter calculated as $D_p = 4V_p/S_{BET}$ (on assumption of a cylindrical shape of pores).

The surface of the obtained beads was also examined using an atomic force microscope (AFM), AFM Nanoscope III (Digital Instruments, USA) operating in contact mode. The images presented in this article contain 512 × 512 data points which were obtained within a few seconds. The typical force applied to obtain these images ranged from 1.0 to 100 nN.

Thermogravimetric analysis (TG) was carried out on a MOM (Budapest, Hungary) derivatograph at a heating rate of 10°C min⁻¹ in air, in the temperature range from 20 to 1000°C with the sample weight of 100 mg. As a reference sample, α -Al₂O₃ was used. The initial decomposition temperature (IDT), $T_{20\%}$, $T_{50\%}$ of weight loss and final decomposition temperature (FDT) were determined.

IGC experiments

Chromatographic measurements were carried out on a Dani GC 1000 gas chromatograph (Dani, Italy) equipped with injector (220°C) a thermal conductivity detector (TCD, 220°C), using stainless-steel columns (100 cm × 1.6 mm I.D.), and helium as carrier gas at a flow-rate of 50 mL/min. The samples were manually injected using a 1-μL syringe (SGE, North Melbourne, Australia).

Chromatographic columns were packed with obtained porous polymers (MA-DVB_w and MA-DVB_g) in the form of spherical beads. The diameter of the sorbent beads was always 0.08–0.12 mm. Before measurements all the columns were conditioned in a stream of helium. The columns were conditioned with temperature programming from 60 to 230°C at 4°C/min and then overnight isothermally at the final temperature.

Polarity

The polarity of the studied copolymers was determined according to procedure propose by Rohrscheider and modified by McReynolds²³ The method based on the measurement of the retention times of the standard substances: benzene (*x*), *n*-butanol (*y*), pentan-2-one (*z*) and calculation of the retention indices (I_x , I_y , I_z , respectively) from the equation proposed by Kovats²⁴:

$$I_x = 100 \left[\frac{\log t'_{R,x} - \log t'_{R,n}}{\log t'_{R,n+1} - \log t'_{R,n} + n} \right]$$

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

Remaining indices (I_y and I_z) were calculated analogically. After determination the retention indices on the studied copolymers, the McReynolds' constants (ΔI) were obtained by calculating the difference between the Kovats' index for benzene, *n*-butanol, pentan-2-one on examined stationary phase and graphitized thermally carbon black (GTCB):

$$\begin{aligned} \text{McReynolds' constant for benzene} &= \Delta I_x \\ &= I_{x,\text{phase}} - I_{x,\text{GTCB}} \end{aligned}$$

McReynolds' constant for *n*-butanol and pentan-2-one were calculated analogically. The sum of the three calculated McReynolds' constant was used to define the overall polarity of the phase under study. The measurements were carried out at 140°C.

Selectivity triangle

Selectivity triangle method was introduced by Snyder.²⁵ This method based on determination of the retention indices of the standard substances: 1,4-dioxane (*d*), *n*-butanol (*b*), and 1-nitropropane (*n*) at 200°C. The retention indices of those substances (I_d , I_b , and I_n) can be used for evaluation of H-donor, H-acceptor, and dipole characteristic of the examined stationary phase. For this purpose the McReynolds' constant for 1,4-dioxane (ΔI_d), *n*-butanol (ΔI_b), and 1-nitropropane (ΔI_n) have to be calculated as described above. On the basis of the determined McReynolds' constants, the contribution of each type of interactions (selectivity parameters: x_{acc} , x_{don} , x_{dip}) can be calculated using the equations²⁶:

$$x_{\text{acc}} = \frac{\Delta I_b}{\Sigma \Delta I}, \quad x_{\text{don}} = \frac{\Delta I_d}{\Sigma \Delta I}, \quad x_{\text{dip}} = \frac{\Delta I_n}{\Sigma \Delta I},$$

where $\Sigma \Delta I = \Delta I_b + \Delta I_d + \Delta I_n$

The values of the retention indices of *n*-butanol, 1-nitropropane, and 1,4-dioxane on GTCB were from the paper by Hepp and Klee.²⁷

ΔC method

Castello²⁸ proposed the ΔC method as a polarity indicator of gas chromatographic columns. ΔC can be considered as a measure of the difference in the behavior of the non-polar and the polar homologous series. This method based on the difference in apparent carbon number of *n*-alkanes and *n*-alcohols with the same retention.²⁹ ΔC can be regarded as a number of methylene groups that should be theoretically added to a linear alkane with *Z* carbon atoms to obtain a hypothetical *n*-alkane with the same retention time of a linear alcohol with *Z* carbon atoms.

The ΔC method evaluates the relative contribution of dispersion forces, the hydrogen bonds, and dipole moment to the retention. According to Castello,³⁰ if the ΔC does not change with temperature, the elution order of all compounds, independent of their polarity, remains unchanged at different isotherms and in programmed temperature analyses. The change of ΔC with temperature or with ageing of the column is a measure of the rate of decrease in polar interactions compared to the rate of decrease in dispersive interaction. Both interactions decrease as the temperature increases. If the dispersive interactions drop at lower rate with respect to polar interaction, a negative ΔC trend is expected. However, if the dispersive interactions decrease at a greater rate than polar ones, positive trend will be observed. The value of polarity determined on the basis of ΔC methods is in accordance with values of polarity indicators obtained from other methods and

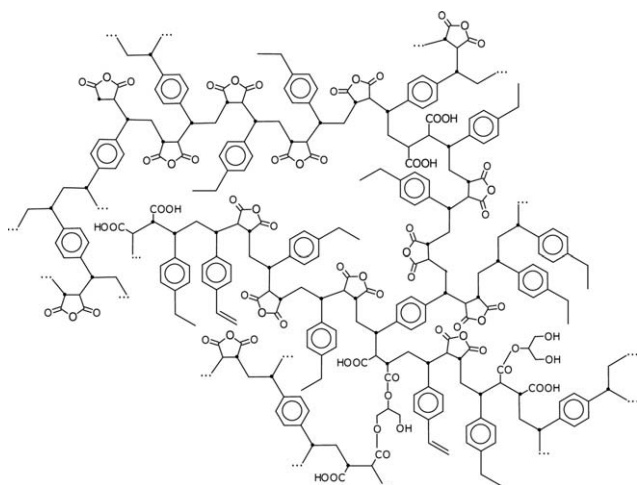


Figure 1 Chemical structure of the synthesized copolymer (marked anhydride that hydrolyzed to carboxylic ones in water medium and possible esterification product in glycerol medium).

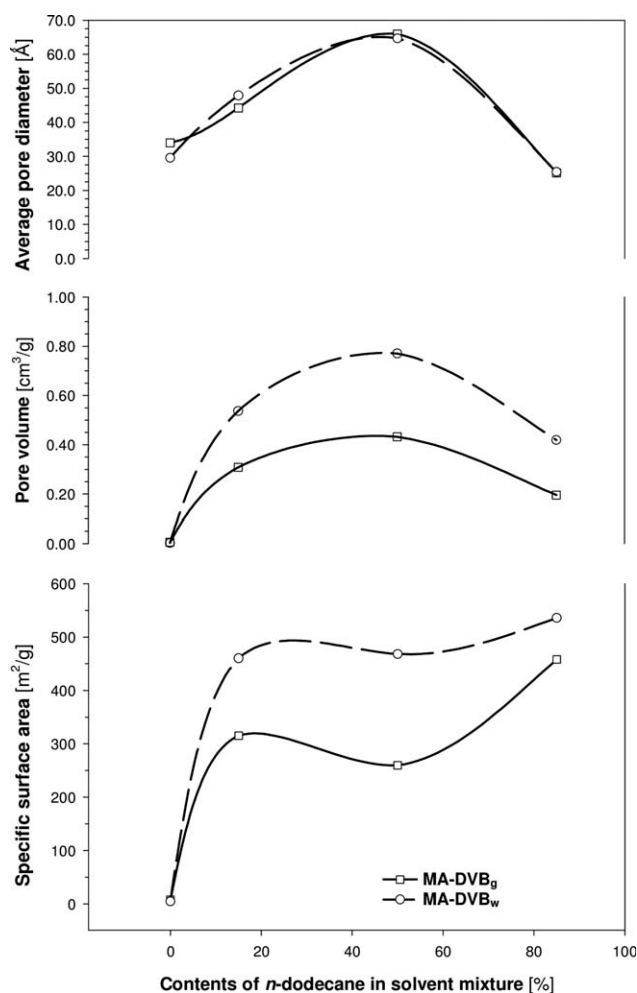


Figure 2 An influence of *n*-dodecane concentration in the diluent mixture on the porous structure parameters of the studied copolymers.

TABLE II
Characterization of Porous Structure of Copolymers Synthesized at B Diluent System

Copolymer	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
MA-DVB _g	315	0.308	44.22
MA-DVB _w	460	0.537	47.84

therefore it offers a fast procedure for the evaluation of the behavior of GC columns.³¹

The ΔC parameter can be defined as the horizontal distance between the two straight lines having the equation $\ln t'_R = a + bZ$ obtained by plotting $\ln t'_R$ as a function of carbon atoms, Z for *n*-alkanes and *n*-alcohols, respectively. ΔC can be also mathematically calculated on the basis of the following equation:

$$\Delta C = \frac{a_{OH} - a_P}{(b_{OH} - b_P)/2}$$

The a and b parameters are derived from the equations:

$\ln t'_R = a_P + b_P Z$ for *n*-alkanes and $\ln t'_{OH} = a_{OH} + b_{OH} Z$ for *n*-alcohols where Z is the number of carbon atoms.³¹

RESULTS AND DISCUSSION

The suspension polymerization technique in water and glycerol as the dispersing media was successfully applied for synthesis of porous crosslinked

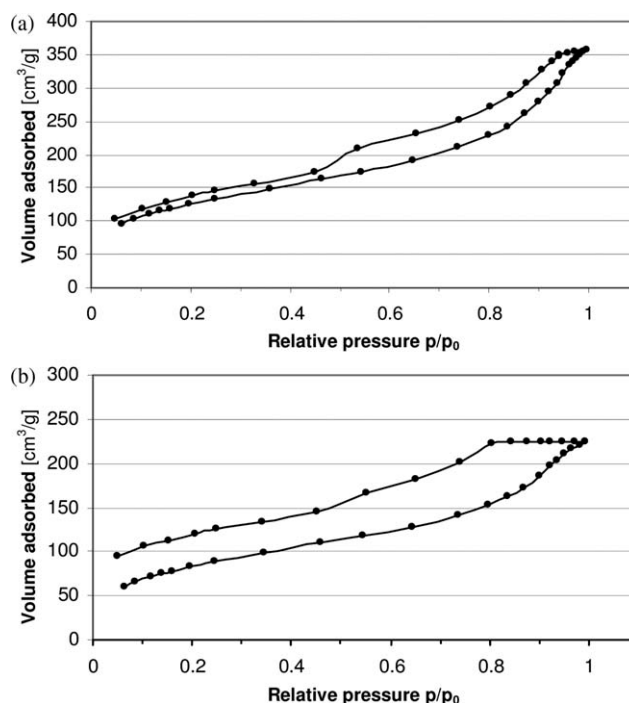


Figure 3 Adsorption/desorption isotherms of nitrogen at 77K: (a) MA-DVB_w and (b) MA-DVB_g

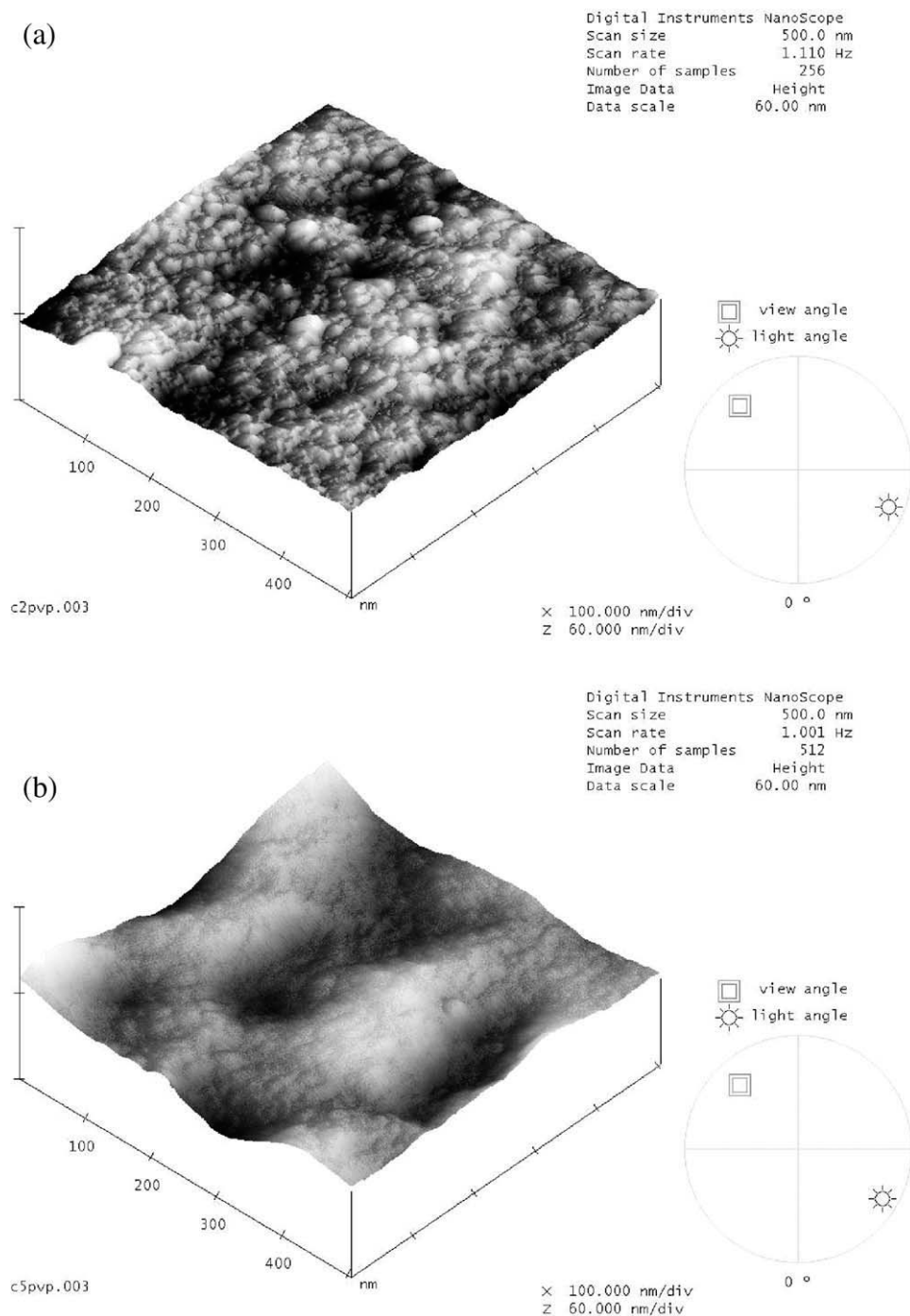


Figure 4 AFM micrographs of the MA-DVB copolymers obtained in (a) glycerol and (b) water media.

copolymers of maleic anhydride and divinylbenzene in the form microspheres. Synthesis of porous particles requires the presence of inert diluent which leads to the formation of permanent pores in the material after removal of diluents. Stable structure of microspheres is caused by high cross-linking degree. All copolymers were synthesized from the equivalent mole ratio of monomers. The proposed chemical structure of the obtained copolymer is presented in Figure 1. It has been established that porous struc-

ture of polymeric materials is determined by the concentration of pore-forming diluent.³² For each pair of monomers, the mixture of 1,4-dioxane and *n*-

TABLE III
Thermal Stability of the Copolymers

Copolymer	IDT (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	FDT (°C)
MA-DVB _g	270	380	470	905
MA-DVB _w	260	380	520	945

TABLE IV
Kovats' Retention Indices for the McReynolds' Test Substances and Overall Polarity ($\Sigma\Delta I$) for the Porous Copolymers (140°C)

Copolymer	Kovats' retention indices			McReynolds' constants			
	I_x (benzene)	I_y (<i>n</i> -butanol)	I_z (pentan-2-one)	ΔI_x	ΔI_y	ΔI_z	$\Sigma\Delta I$
MA-DVB _g	618	618	657	44	129	92	265
MA-DVB _w	620	638	679	46	149	114	309
GTCB	574	489	565	–	–	–	–

dodecane as a pore-forming diluent was employed. The volume/mass ratio of diluents to monomers was constant. Concentrations of *n*-dodecane in the mixture with 1,4-dioxane changed from 0 to 100%. Unfortunately the product of copolymerization in the presence of pure *n*-dodecane was irregular in shape and coagulated. In Figure 2, the influence of *n*-dodecane concentration in the mixture on the porous structure of the studied copolymers is presented. Copolymers obtained in water as well as obtained in glycerol medium follow the same pattern. An increase of amount of *n*-dodecane concentration leads to increase of specific surface areas. The largest specific surface area is observed for the copolymers obtained in presence of 85% (v/v) *n*-dodecane. The diluent mixture composition also influences the pore volume and the average pore diameter. The maximum of the pore volumes is observed for the copolymers prepared in the presence of 50% of *n*-dodecane. For higher concentration of *n*-dodecane, pore volume and average pores diameters decrease.

To determine of polarity and selectivity of the obtained copolymers the inverse gas chromatography was applied. Microbeads for gas chromatography should be rigid, thermally stable, and porous to offer a large interacting surface area. Microspheres with a high specific surface area and the pore diameters suitable for chromatography purposes were obtained in the presence of the diluent containing 85% of *n*-dodecane. Thus, such composition of diluents was used in further synthesis of polymeric packing for GC columns. The parameters of the porous structure of the studied copolymers are listed in Table II. The presented data show that not only diluent but also polymerization medium plays an

important role in the porous structure formation. The MA-DVB copolymer obtained in water medium (MA-DVB_w) exhibit larger specific surface area and pore volume comparing with its counterpart obtained in glycerol (MA-DVB_g). More information to complete the study of porous structure can be evaluated on the basis of nitrogen adsorption-desorption isotherms at 77K. Figure 3 shows the N₂ adsorption-desorption isotherms of the investigated samples. The isotherms of both copolymers show hysteresis loops that can be attributed to capillary condensation. According to the IUPAC, they can be classified as type IV that characterizes mesoporous adsorbents.³³ Hysteresis loops may exhibit different shapes. As regards the discussed samples, the hysteresis loops are broad and can be classified as H2 type. Type H2 can be found in many porous adsorbent and is believed to occur in systems where the distribution of pore size and pore shapes are broad. According to Sangwichien et al.,³⁴ this kind of loop occurs when there is a difference in mechanism between condensation and evaporation. This phenomenon takes place in pores with narrow necks and wide bodies (ink-bottle shape) or when the porous material has an interconnected pore network. Figure 4 shows AFM images of the surface of the discussed samples. AFM studies provided direct evidence of the differences in the surface texture of the copolymers obtained in water and glycerol media.

The thermal stabilities of the MA-DVB_w and MA-DVB_g copolymers were assessed by comparing the initial decomposition temperatures (IDT), 20% weight loss, 50% weight loss, and final decomposition temperature (FDT). The results of thermal behavior are summarized in Table III. The presented data indicate that IDT for both studied copolymers

TABLE V
Kovats' Retention Indices for *n*-Butanol (I_b), 1-Nitropropane (I_n), 1,4-Dioxane (I_d), and Porous Copolymers Selectivity Parameters (200°C)

Copolymer	Kovats' retention indices			McReynolds' constants				Selectivity parameters		
	I_b	I_n	I_d	ΔI_b	ΔI_n	ΔI_d	$\Sigma\Delta I$	x_{acc}	x_{dip}	x_{don}
MA-DVB _g	617	675	652	131	169	168	468	0.280	0.361	0.359
MA-DVB _w	638	711	678	152	205	194	551	0.276	0.372	0.352
GTCB	486	506	484	–	–	–	–	–	–	–

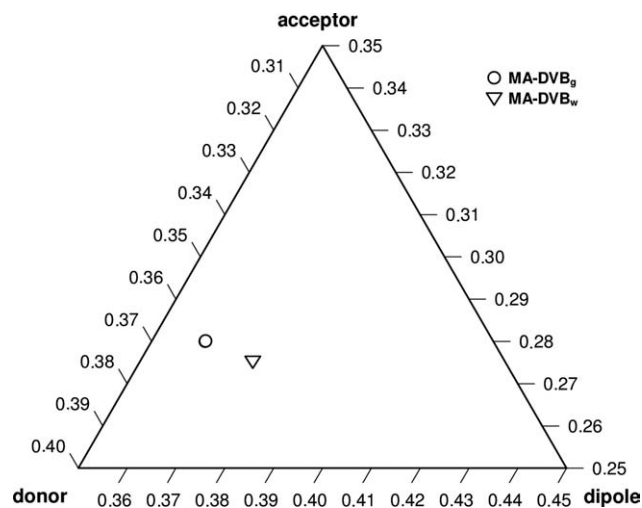


Figure 5 Selectivity triangle showing relative selectivities of the examined porous polymers.

was above 250°C, and consequently they could be used in the inverse gas chromatography investigation.

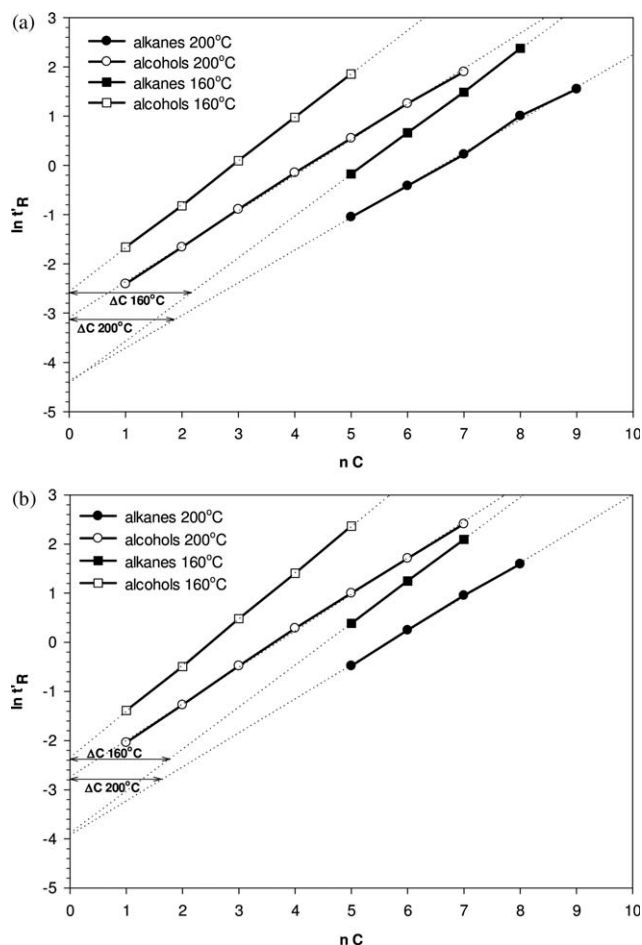


Figure 6 Values of the $\ln t'_R$ for alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol) and alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane) as a function of the number of carbon atoms on the MA-DVB_w (a) and MA-DVB_g (b) columns.

Table IV presents the results of the overall polarity of the phases under studies. Due to the presence of anhydride groups in the MA-DVB copolymers, these materials are slightly more polar than Porapak Q (ST-DVB type). It is noteworthy that the copolymer obtained in the water medium has higher polarity compared to the copolymer from glycerol. Probably some anhydride groups presented in its chemical structure hydrolyzed to more polar carboxylic ones. In the glycerol medium, spontaneous reaction of esterification can take place. The structures formed in both mentioned processes are presented in Figure 1.

The values of selectivity parameters are listed in Table V. MA-DVB_w and MA-DVB_g copolymers exhibits similar hydrogen-acceptor properties. More significant differences can be observed in the case of hydrogen-donor properties. The highest divergence refers to dipole interactions—MA-DVB_w shows stronger dipole character. The location of these copolymers on the selectivity triangle is displayed in Figure 5.

To complete the study, the investigation of ΔC were undertaken. The values of $\ln t'_R$ on MA-DVB_w and MA-DVB_g columns for *n*-alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol) and *n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane) as a function of the number of carbon atom were plotted (Fig. 6), and the ΔC was schematically represent by the length of the arrows. On the basis of the coefficients of the linear regression equations of the experimental data, ΔC parameter was also mathematically calculated. Figure 7 shows the dependence of the ΔC value on temperature for MA-DVB_w and MA-DVB_g columns. The obtained results indicate that ΔC parameter has lower value at higher temperature.

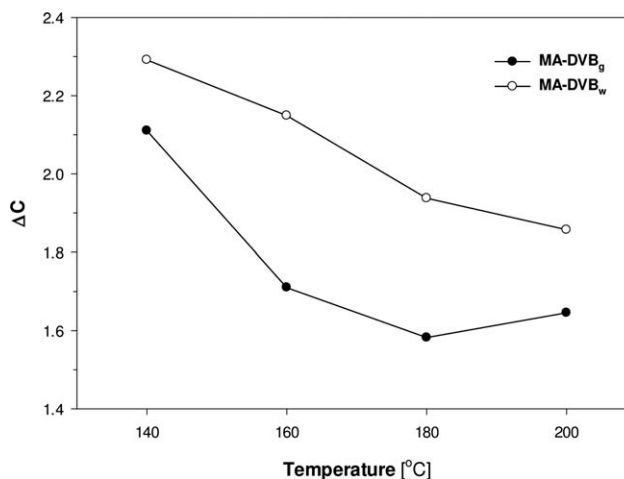


Figure 7 ΔC values of columns packed with the MA-DVB_g and MA-DVB_w porous polymer beads at different temperatures.

For both discussed copolymers, a significant drop of ΔC parameter with temperature was observed. This phenomenon indicates that at higher temperatures polar interactions weaken. Similar dependence was observed by Castello²⁸ in case of polar columns. In our investigation, the effect is less visible for the copolymer obtained in glycerol.

CONCLUSION

Copolymers of maleic anhydride and divinylbenzene can be obtained in the form of regular microspheres using suspension polymerization. The presence of the inert diluent in the polymerization mixture is responsible for highly developed porous structure of the MA-DVB copolymers. It was found that specific surface area of the obtained beads is strongly dependent on the diluent system and polymerization medium. Polymerization medium (water or glycerol) influences also the chemical character of the surface. The differences into chemical structure of the final copolymers were confirmed by applied procedures (overall polarity, the selectivity triangle, and the ΔC method).

References

1. Okay, G. *Prog Polym Sci* 2000, 25, 711–779.
2. Zhou, W. Q.; Gu, T. Y.; Su, Z. G.; Ma, G. H. *Eur Polym J* 2007, 43, 4493.
3. Bratkowska, D.; Fontanals, N.; Borrull, F.; Cormack, P. A. G.; Sherrington, D. C.; Marce, R. M. *J Chromatogr A* 2010, 1217, 3238.
4. Hentze, H. P.; Antonietti, M. *Rev Mol Biotech* 2002, 90, 27.
5. Trochimczuk, A. W.; Strat, M.; Kolarz, B. N. *React Funct Polym* 2001, 46, 259.
6. Zaleski, R.; Stefaniak, W.; Maciejewska, M.; Goworek, J. *J Porous Mater* 2009, 16, 691.
7. Zaleski, R.; Stefaniak, W.; Maciejewska, M.; Goworek, J. *J Coll Interf Sci* 2010, 343, 134.
8. Maciejewska, M. *J Appl Polym Sci* 2012, DOI: 10.1002/app.34952.
9. Voelkel, A.; Milczewska, K.; Heberger, K. *Anal Chim Acta* 2006, 59, 221.
10. Ourdani, S.; Marani, F. *J Chromatogr A* 2002, 969, 287.
11. Nastasovic, A. B.; Onjia, A. E.; Milonjic, S. K.; Jovanovic, S. M. *Eur Polym J* 2005, 41, 1234.
12. Onjia, A.; Milonjic, S. K.; Jovanovic, N. N.; Jovanovic, S. M. *React Funct Polym* 2000, 43, 269.
13. Thielmann, F. *J Chromatogr* 2004, 1037, 115.
14. Maciejewska, M.; Osypiuk, J.; Gawdzik, B. *J Polym Sci A* 2005, 43, 3049.
15. Maciejewska, M.; Gawdzik, B. *J Appl Polym Sci* 2005, 95, 863.
16. Gawdzik, B.; Maciejewska, M. *J Appl Polym Sci* 2004, 91, 2008.
17. Grochowicz, M.; Gawdzik, B. *React Funct Polym* 2011, 71, 625.
18. Trivedi, B. C.; Culberston, B. M. *Maleic Anhydride*; Plenum Press: New York, 1984.
19. Maciejewska, M.; Gawdzik, B.; Grochowicz, M. *Polish J Chem* 2008, 82, 235.
20. Ogawa, K.; Honmyo, K.; Harada, K. *J Appl Polym Sci* 1984, 29, 2851.
21. Annakutty, M.; Promil, C. *J Appl Polym Sci* 1996, 34, 1605.
22. Ościk, J. *Adsorption*; PWN: Warsaw, Poland, 1974.
23. McReynolds, W.; O. *J Chromatogr Sci* 1970, 8, 685.
24. Kovats, E. *Helvet Chim Acta* 1958, 41, 1915.
25. Snyder, L. R. *J Chromatogr* 1974, 92, 223.
26. Castello, G.; Timossi, A.; Gerbino T. C. *J Chromatogr* 1990, 582, 329.
27. Hepp, M. A.; Klee, M. S. *J Chromatogr* 1987, 404, 145.
28. Castello, G.; Venzani, S.; D'Amato, G. *J Chromatogr A* 1997, 779, 275.
29. Castello, G.; Venzani, S.; Gardella, L. *J Chromatogr A* 1999, 837, 153.
30. Castello, G.; Venzani, S.; Gardella, L. *J Chromatogr A* 1999, 842, 51.
31. Castello, G.; D'Amato, G. *J Chromatogr* 1992, 623, 289.
32. Gawdzik, B.; Maciejewska, M. *J Polym Sci* 2002, 40, 3079.
33. Sing, K.; Everet, D. H.; Haul, R. A. *Pure Appl Chem* 1985, 57, 603.
34. Sangwichien, C.; Aranovich, G. L.; Donohue, M. D. *Colloid Surf A Physicochem Eng Aspect* 2002, 2006, 313.