

# Synthesis of a New Tetrafunctional Monomer, 1,4-Di(2-hydroxy-3-methacryloyloxypropoxy)phenol, and its Copolymerization

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**ABSTRACT:** The new aromatic tetrafunctional methacrylate monomer, 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol, and its application for the synthesis of porous microspheres have been presented. It was copolymerized with trimethylolpropane trimethacrylate in the presence of pore-forming diluents mixture (chlorobenzene and 1-decanol). The results indicate that composition of diluents mixture influence porous structure of copolymers. The porous structure of the copolymer obtained in the presence

of 50% chlorobenzene was studied in detail. The results show that pore volume and the most probable pore size diameters determined for the copolymer in the dry and in the wetted states are different. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3718–3726, 2008

**Key words:** 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol; trimethylolpropane trimethacrylate copolymerization; polymeric microspheres; porous structure

## INTRODUCTION

Porous polymeric particles are important materials used as column packings in different chromatographic methods. Polymeric materials overcome some of the problems of silica- and carbon-based sorbents. They are stable in through the pH range and compared with carbon-based sorbents, but the compounds adsorbed are easily eluted. On the other hand, their swelling and thermal properties require improvements.

In 1963, Millar et al.<sup>1</sup> described the preparation of porous materials by suspension polymerization of styrene (ST) and divinylbenzene (DVB) in the presence of inert solvent. The first application of such materials as packings for gas chromatography (GC) was reported by Hollis.<sup>2</sup> Since that time porous ST-DVB copolymers have gained popularity in size exclusion chromatography (SEC), high performance liquid chromatography (HPLC), and solid phase extraction (SPE).<sup>3–5</sup> ST-DVB copolymers possess hydrophobic structure; their interactions with the analytes are based on the  $\pi$ - $\pi$  interactions of the aromatic rings.<sup>6</sup> To improve wettability of polymeric sorbents, functional groups were introduced to the existing hydrophobic polymer.<sup>7</sup> In other approaches, monomers possessing polar functional groups are

used in their synthesis.<sup>8–10</sup> An important group of such monomers is formed by methacrylate compounds which can possess carboxyl, ester, hydroxyl, etc. functional groups in their structures. Methacrylate copolymers obtained in this way are less hydrophobic than the traditional ST-DVB stationary phases. The electron-donating ability of these functional groups additionally contributes to the adsorption analytes with electron-withdrawing groups.<sup>11</sup>

In this work, the synthesis of the new aromatic tetrafunctional methacrylate monomer 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol (1,4DMH) and its application for the synthesis of porous microspheres are presented. Porous beads were obtained by suspension-emulsion copolymerization with trimethylolpropane trimethacrylate (TRIM) in the presence of pore-forming diluents. The porous structures of copolymers in dry and swollen states are studied.

## EXPERIMENTAL

### Chemicals and eluents

Bis(2-ethylhexyl) sulfosuccinate sodium salt (DAC, BP),  $n$  = decanol and 2-methacrylic acid were from Fluka AG (Buchs, Switzerland). Trimethylolpropane trimethacrylate and  $\alpha,\alpha'$ -azoisobisbutyronitrile were obtained from Merck (Darmstadt, Germany). Reagent grade acetone, methanol, chlorobenzene, chloroform, propan-2-ol, methylene chloride, toluene, sodium hydroxide, 2-(chloromethyl) oxirane, butan-1-ol, and hydroquinone were from POCh (Gliwice, Poland).

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TABLE I  
Polymerization Recipe of 1,4DMH-TRIM Copolymers

Copolymer	Monomers (g)		Diluents (mL)		Concentration of chlorobenzene in the mixture with <i>n</i> -decanol (%)	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Most probable pore diameter (Å)
	1,4DMH	TRIM	Chlorobenzene	<i>n</i> = Decanol				
1,4DMH-TRIM	8.04	6.96	22.50	–	100	88	0.277	390
	8.04	6.96	19.10	3.40	85	135	0.576	250
	8.04	6.96	11.25	11.25	50	210	0.730	300
	8.04	6.96	3.40	19.10	15	15	0.100	–

THF used in exclusion chromatography (EC) experiments, was HPLC-grade from Merck (Darmstadt, Germany). Alkylphenones and phthalates were laboratory-reagent-grade and were obtained from a number of sources. Polystyrene standards were obtained from Toyo Soda (Tokyo, Japan) and Merck.

#### Preparation of 1,4-di(2,3-epoxypropoxy)phenol

In a 750-cm<sup>3</sup>, round bottomed, three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropper, 3 moles (277.5 g) of 2-(chloromethyl)oxirane, 2.1 moles (120.9 g) of propan-2-ol, and 0.3 mole (33.3 g) of hydroquinone were placed. The mixture was heated to 70°C. Meanwhile, 13.5% solution of NaOH was prepared by dissolving 0.72 mole (28.8 g) NaOH in 180 cm<sup>3</sup> H<sub>2</sub>O. About 15 cm<sup>3</sup> of this solution was added to the stirred mixture into 15 min, and afterwards remaining portions were added. When the whole NaOH solution was added to the flask, the reaction was continued for 10 min. Temperature of the mixture was maintained at 70°C. When the reaction was over, the content of the flask was placed in the dropper, and the organic layer was distilled at low pressure (1.6 kPa) order to separate propan-2-ol and the excess of 2-(chloromethyl)oxirane. The remaining 2-(chloromethyl)oxirane and water were distilled at low pressure after 50 g of toluene was added into it. The epoxide derivative was dissolved in 150 g of chloroform and filtered off. Then the crude product was crystallized from butan-1-ol. The yield of the obtained products was about 80%; its epoxide number equal to 0.9 was the same as the theoretical one.

#### Preparation of 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol

The reaction between the epoxide groups of 1,4-di(2,3-epoxypropoxy)phenol (1,4EPH) and the carboxylic ones of 2-methacrylic acid went on at 80–100°C. The synthesis was carried out in a 250-cm<sup>3</sup> round bottomed flask equipped with a thermometer, a mechanical stirrer, and a heater. To the flask, 0.45 mole (100 g) of 1,4EPH, 0.9 mole (77.4 g) of 2-metha-

rylic acid, 1.8 g of TEBA (a catalyst), and 0.02 g hydroquinone (polymerization inhibitor) were added. The progress of the reaction was controlled by determination of the acidic number. The acidic number determined the milligrams of KOH used to neutralize the free acids contained in 1 g of substance. The reaction was considered to be over when the acidic number was below 3. The obtained crude product was purified by crystallization from toluene. The yield of crystallization was about 65%.

The chemical structure of this new methacrylic monomer was confirmed by spectroscopic methods.

#### Preparation of the 1,4DMH-TRIM copolymers

Copolymerization with TRIM (trimethylolpropane trimethacrylate) was made in the aqueous medium.

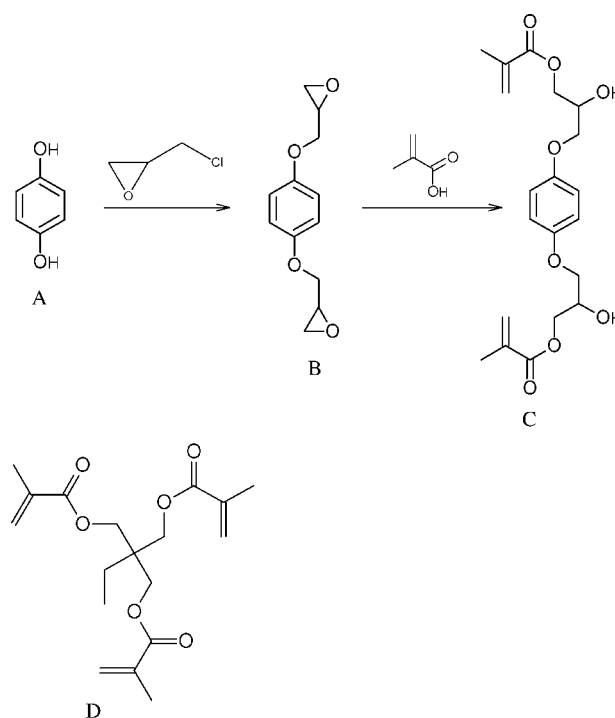


Figure 1 Synthesis and chemical structure of the compounds used for copolymerization: (A) hydroquinone, (B) 1,4-di(2,3-epoxypropoxy)phenol (1,4EPH), (C) 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol (1,4DMH), (D) trimethylolpropane trimethacrylate (TRIM).

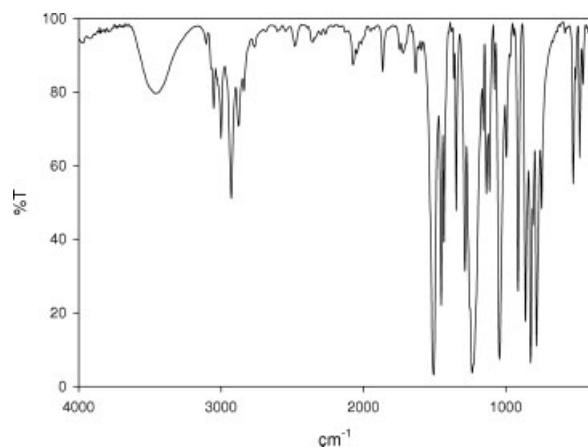


Figure 2 FTIR spectrum of 1,4EPH.

In each case, 195 cm<sup>3</sup> of redistilled water and 2.2 g of bis(2-ethylhexyl) sulfosuccinate sodium salt (surfactant) were stirred for 1 h at 80°C in a three-necked flask fitted with a stirrer, a water condenser, and a thermometer. Then, the solution containing 8.04 g of 1,4EPH and 6.96 g of TRIM (an equivalent mole fraction of monomers), and 0.15 g of  $\alpha,\alpha'$ -azobisisobutyronitrile (initiator) in the solution of pore-forming diluents (chlorobenzene and *n* = decanol) were added while stirring to the aqueous medium (Table I). Copolymerization was performed for 20 h at 80°C. Porous beads that formed in this process were sucked off, washed with distilled water, dried and extracted in a Soxhlet apparatus with boiling acetone, toluene, and methanol. Then, the beads were separated on sieves. Uniform particles (5–15  $\mu\text{m}$ ) used in further studies were isolated by sedimentation and decantation from acetone. The screening procedure was controlled by microscopic examination.

### Characterization

<sup>1</sup>H NMR spectra were recorded on a Bruker 300 MSL instrument (Bruker, Germany) operating at the <sup>1</sup>H resonance frequency of 300 MHz. Chemical shifts were referred to chloroform serving as an internal standard. The <sup>13</sup>C NMR spectrum of the compounds in chloroform was made using the same apparatus.

Gas chromatography/mass spectrometry (GC-MS) was made on a Thermo-Finnigan DSQ spectrometer (Finnigan, USA) hyphenated with a Trace GC-Ultra gas chromatograph equipped with a fused-silica RTX-5 capillary column (20 m  $\times$  0.18 mm I.D., film thickness 0.20  $\mu\text{m}$ ). The conditions were as follows: injector PTV-split 1:20, a temperature program of 35–320°C at a rate 20°C min<sup>-1</sup>; MS electron ionization at 70 eV, ion volume temperature 220°C.

IR spectra were determined on a PerkinElmer 1700 Fourier transform infrared (FTIR) spectrometer with KBr pellets.

The beads were examined using an atomic force (AFM) and scanning electron microscopes (SEM). The images presented in this article were obtained from AFM Nanoscope III (Digital Instruments, USA) operating in contact mode. They contain 512  $\times$  512 data points which were obtained within a few seconds. Copolymers were also imaged using a BS-301 numerical scanning electron microscope (Czech Republic) with Satellite system digital picture detection.

Thermograms were run on a Paulik Erdey derivatograph (MOM, Budapest, Hungary).

### Chromatographic measurements

Retention volumes of toluene, alkylphenones, phthalates, and polystyrene standards were determined with a Hewlett-Packard HP-1050 liquid chromatograph equipped with a diode array UV detector, a Rheodyne 7125 injection valve with 20  $\mu\text{L}$  sample loop and column packed with the copolymer. The column (100 mm  $\times$  4.1mm I.D.) was packed according to the procedure described previously.<sup>12</sup>

In the EC measurements, THF was the mobile phase at a flow rate of 1 mL/min. Each substance was injected separately as a 0.1% (v/v) solution in THF. The given retention volumes were always the mean of three measurement.

To determine the swelling propensity (SP factors), twice distilled water, at the same flow rate was used as the mobile phase. SP factor was calculated according to the method of Nevejan and Verzele<sup>13</sup>

$$SP = \frac{p(\text{THF}) - p(\text{H}_2\text{O})}{p(\text{H}_2\text{O})}$$

where  $p = P/\eta$ , is the pressure relative to the mobile phase viscosity,  $\eta$ , and  $P$  is the column inlet pressure when THF and water were used as mobile phase, respectively.

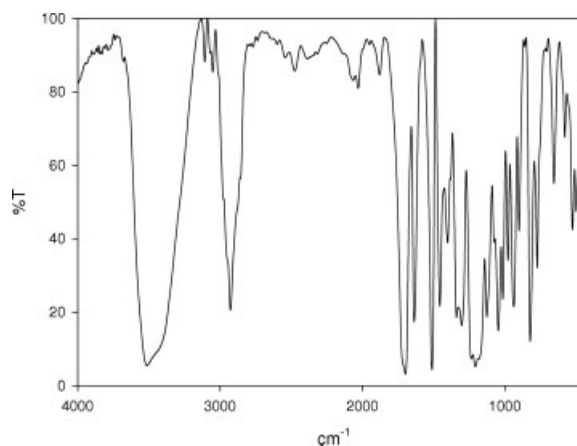


Figure 3 FTIR spectrum of 1,4DMH.

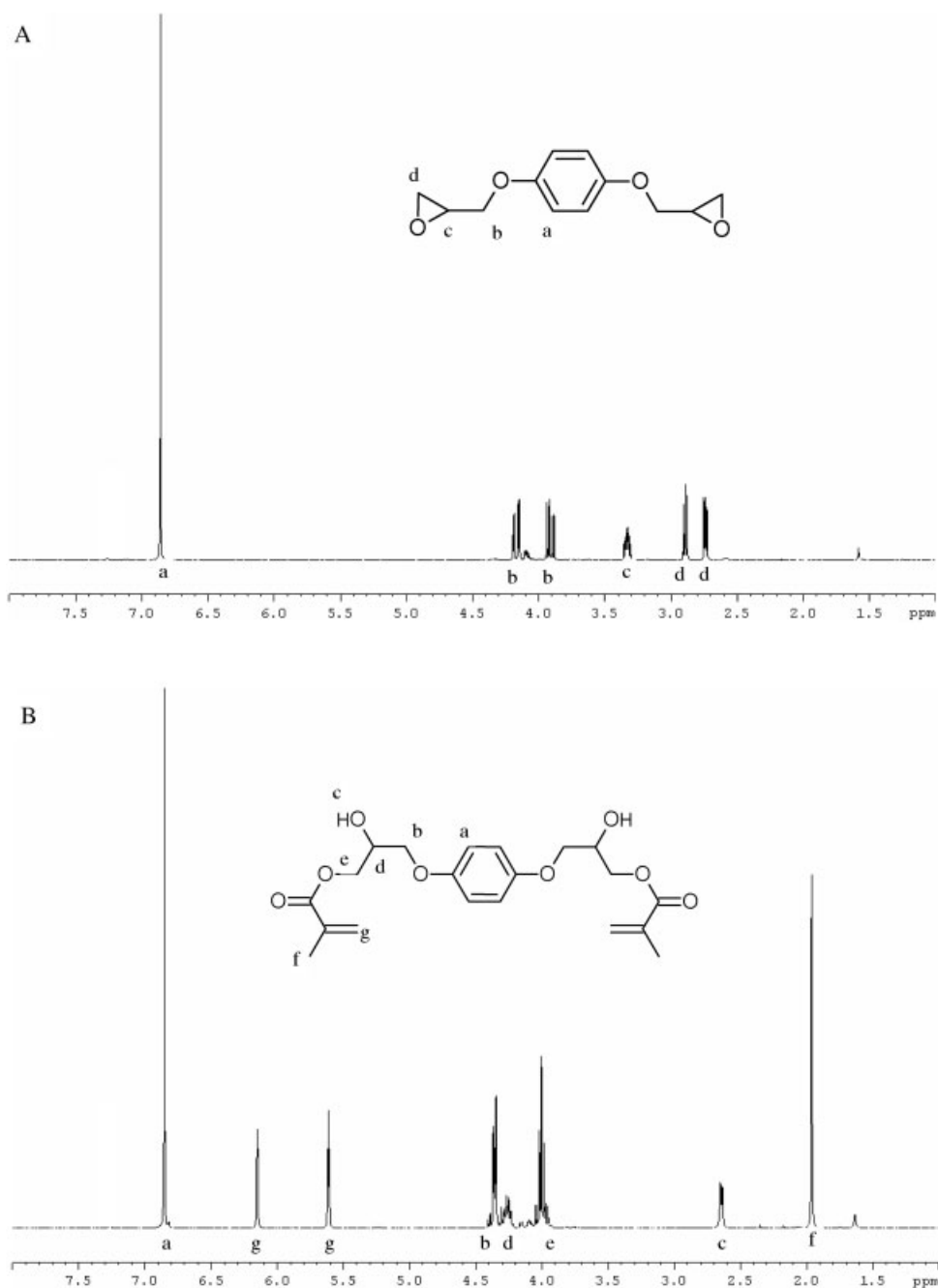


Figure 4  $^1\text{H}$  NMR spectra for 1,4EPH (A), and 1,4DMH (B) compounds

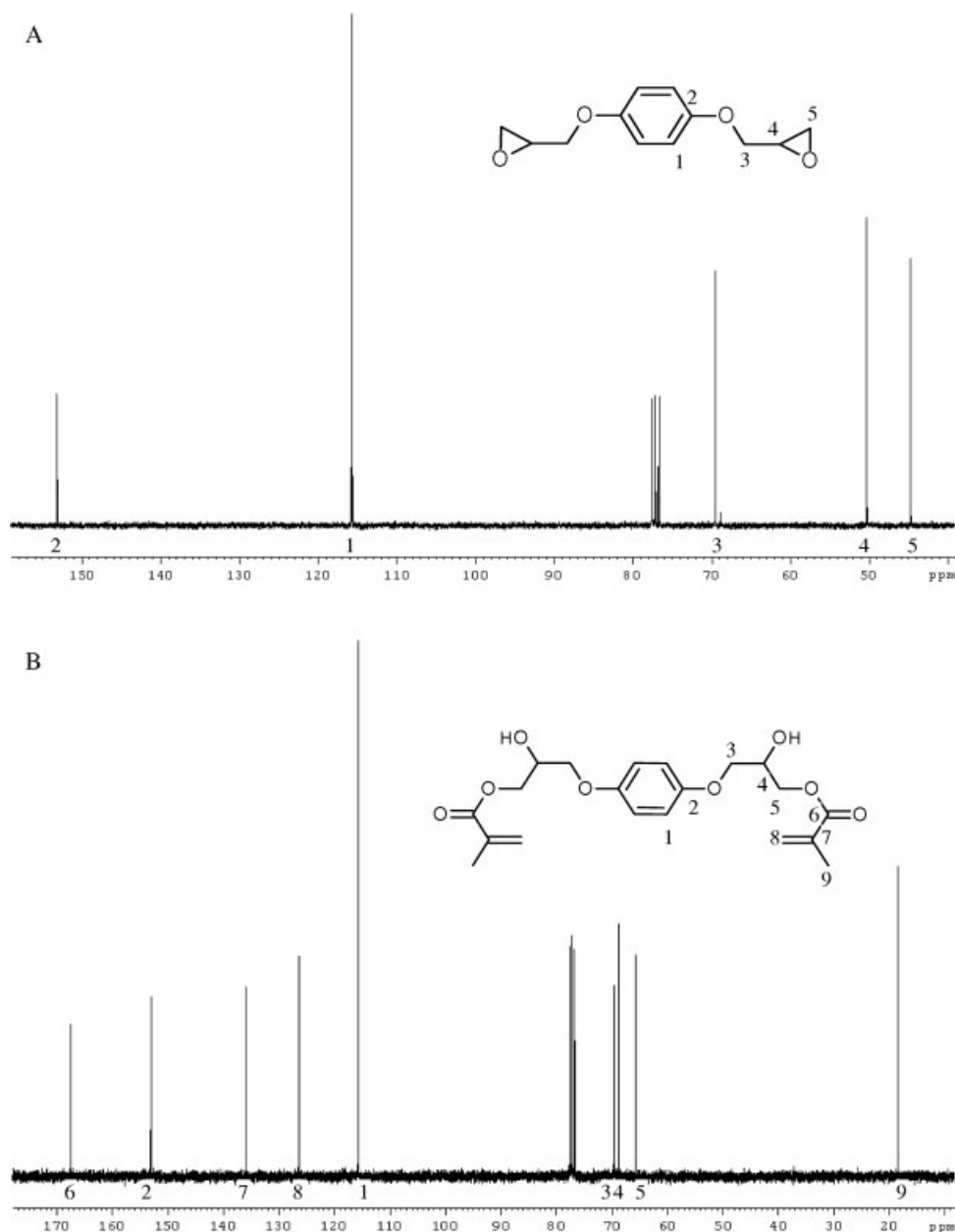
### Porous structure characterization

Porous structure of 1,4DMH-TRIM copolymers was characterized by using inverse exclusion chromatography (EC) and nitrogen adsorption–desorption measurements. In dry state, the copolymers were characterized by means of an adsorption analyzer ASAP 2405 (Micrometrics, USA). Determinations were based on the measurements of adsorption and desorption of nitrogen on the surface of studied copolymer while cooling it with liquid nitrogen. The specific surface areas were calculated by the BET method (based on the

theory of Brunauer, Emmet, and Teller), assuming that the area of a single nitrogen molecule is  $16.2 \text{ \AA}^2$ .<sup>14</sup>

In a swollen state the copolymers were characterized by EC technique introduced by Halasz and Martin.<sup>15</sup> The main assumption in this method is that in the good solvent chains of macromolecules form coils of a diameter corresponding to the polymer molecular weights. The diameter of the probe molecules ( $\Phi$ , in  $\text{\AA}$ ) was calculated from the equation<sup>13</sup>:

$$\Phi = 0.62 M_w^{0.59}$$



**Figure 5**  $^{13}\text{C}$  NMR spectra for 1,4EPH (A), and 1,4DMH (B) compounds

where  $M_w$  is the gram-molecular weight of the probe. The diameter of the probe molecule is associated with a pore diameter ( $\Phi$ ) which corresponds to the smallest pore allowing unhindered access for the probe of a given molecular weight.

As pore-size probes, toluene, alkylphenones, phthalates, and polystyrenes were used.<sup>16,17</sup>

The cumulative pore size distribution was determined from the plot  $1 - K_o(\text{EC})$  versus  $\log \Phi$ , where  $K_o(\text{EC})$  is the distribution constant in exclusion chromatography calculated as follows<sup>13</sup>:

$$K_o(\text{EC}) = \frac{V_R - V_0}{V_p} = \frac{V_R - V_0}{V_i - V_0}$$

where:  $V_R$  the retention volume of the probe;  $V_0$  the interstitial volume equal to the retention volume of a totally excluded molecule;  $V_i$  the retention volume of a totally included molecule;  $V_p = V_i - V_0$  the pore volume.

Swellability coefficients,  $B$ , were determined by equilibrium swelling in acetone, methanol, acetonitrile, THF, dichloromethane, using the centrifugation method.  $B$  is expressed as<sup>18</sup>:

$$B = \frac{V_s - V_d}{V_d} \times 100\%$$

where  $V_s$  is the volume of the copolymer after swelling,  $V_d$  is the volume of the dry copolymer.

## RESULTS AND DISCUSSION

Figure 1 presents the synthesis of the new aromatic tetrafunctional methacrylate monomer 1,4DMH and its copolymerization with TRIM. The obtained monomer possesses ester and secondary hydroxyl groups of hydrophilic character in its chemical structure. Chemical structure of this compound was confirmed by spectroscopic methods.

### IR spectroscopy

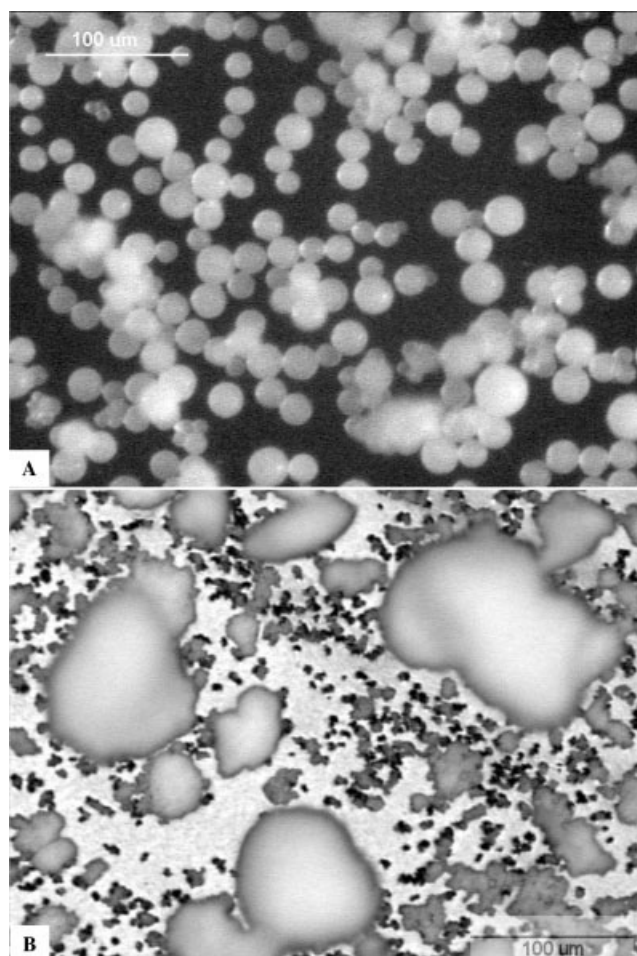
The FTIR spectra of the 1,4DMH and its precursor 1,4EPH were studied. In the spectrum of 1,4EPH (Fig. 2), C—H stretching vibrations of the aromatic ring backbone methylene and methyl groups were observed at 2928 and 3051  $\text{cm}^{-1}$ . The aromatic skeletal absorption was observed at 1506  $\text{cm}^{-1}$ . The epoxide group gave shape signals at 914 and 1236  $\text{cm}^{-1}$ . In the 1,4DMH spectrum (Fig. 3), vibrations of the —OH groups were visible at 3522  $\text{cm}^{-1}$ . The signal of the C=O group occurred at 1698  $\text{cm}^{-1}$ , and that of =C—H at 938  $\text{cm}^{-1}$ .

### NMR spectroscopy

In Figure 4,  $^1\text{H}$  NMR spectra of 1,4EPH and 1,4DMH are presented. In the  $^1\text{H}$ NMR spectrum of 1,4EPH, protons in the methylene group (— $\text{CH}_2$ ) connected with a skeleton give shape bands at  $\delta = 4.150$ – $4.192$  ppm and  $\delta = 3.903$ – $3.940$  ppm, whereas protons from the terminal methylene groups (— $\text{CH}_2$ ) give bands at  $\delta = 2.907$ – $2.891$  ppm and  $\delta = 2.752$ – $2.736$  ppm. Protons from the — $\text{CH—O—}$  group give bands at  $\delta = 3.332$ – $3.337$  ppm. The band at  $\delta = 6.851$  ppm corresponds to the phenyl ring.

In the  $^1\text{H}$  NMR spectrum of 1,4DMH in chloroform, protons of the methylene group (— $\text{CH}_2$ ) give signals at  $\delta = 4.004$ – $4.051$  ppm and  $\delta = 4.392$ – $4.405$  ppm. Proton in the hydroxyl group (—OH) gives signal at  $\delta = 2.634$  ppm while proton connected with the carbon atom connected with the hydroxyl group gives a signal at  $\delta = 4.257$  ppm. Signals of the protons of the methyl group (— $\text{CH}_3$ ) are at  $\delta = 1.959$ – $1.966$  ppm. Protons near the double bonds (— $\text{CH}_2$ ) give signals at  $\delta = 5.602$ – $5.622$  ppm and  $\delta = 6.145$ – $6.153$  ppm. The bands at  $\delta = 6.819$ – $6.854$  ppm correspond to the phenyl ring.

Figure 5 presents the  $^{13}\text{C}$  NMR spectra of these compounds. Both spectra show a set of three peaks at 77.6, 77.2, and 76.7 ppm which should be neglected because they came from the solvent-chloroform. In the spectrum of 1,4EPH, five peaks are visible. The carbon atom in the terminal methylene group (— $\text{CH}_2$ ) gives a signal at 44.7 ppm, the carbon of the epoxide group (— $\text{CH—}$ ) at 50.3 ppm, and the carbon of the methylene group connected with oxy-



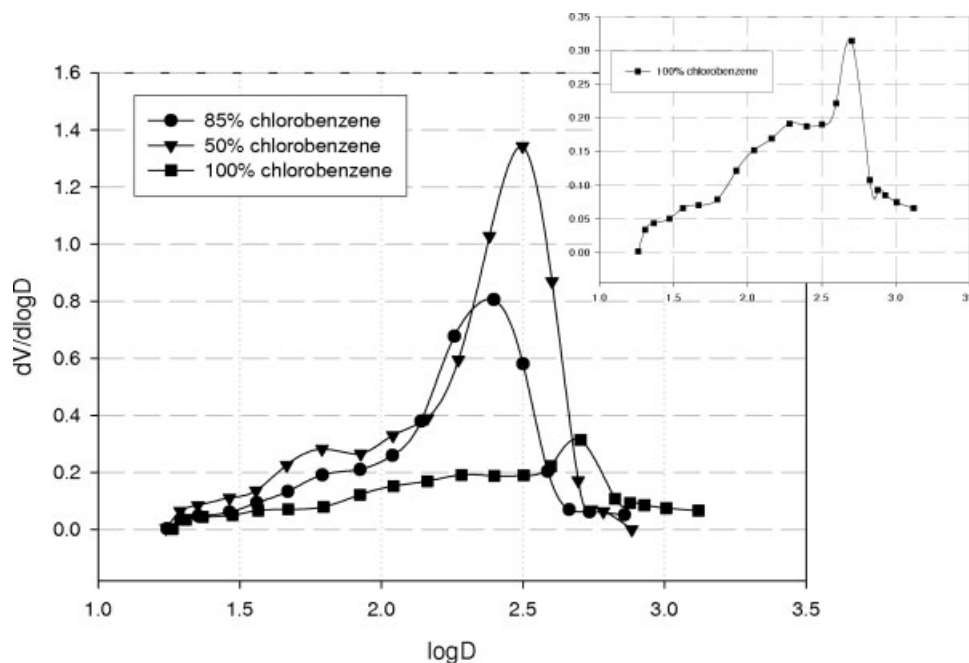
**Figure 6** Scanning electron micrographs of 1,4DMH-TRIM copolymers obtained in the presence: (A) 50% chlorobenzene; (B) 15% chlorobenzene; magnification  $\times 100$ .

gen (— $\text{O—CH}_2$ —) gives a signal at 69.5 ppm. The signals at 115.8 and 153.2 ppm came from two different types of carbon atoms of the aromatic ring.

In the spectrum of 1,4DMH, nine peaks are visible. The carbon of the methyl group absorbs at 18.5 ppm, while the carbons from methylene groups at 65.8 and 69.6 ppm. The carbon connected with oxygen of hydroxyl group absorbs at 68.9 ppm. The terminal carbon atom of the double bond absorbs at 126.4 ppm, and connected with it the more highly substituted one absorbs at 136 ppm. The carbon atom of the carbonyl group absorbs at 167.6 ppm. Signals at 115.8 ppm, and at 153.1 ppm came from two different types of carbon atoms of the aromatic ring.

### GC-MS

Chemical structures of 1,4DMH and its precursor 1,4EPH were also confirmed by the GC-MS analysis. In both spectra, molecular ions corresponding to the calculated molecular weight of 1,4-di(2,3-epoxypro-



**Figure 7** Differential pore size distributions as a function of the logarithm of the pore diameter,  $D$ , for the studied copolymers obtained from nitrogen adsorption/desorption isotherms.

poxy)phenol (222), and 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol (394) were well visible.

### Preparation of porous microspheres

The obtained new monomer (1,4DMH) was applied for preparation of porous microspheres. It was copolymerized with TRIM, using the method of suspension-emulsion polymerization. The aim of this undertaking was to prepare material of diameter and porous structure suitable for chromatographic purposes. All syntheses were carried out in the presence of pore-forming diluents: chlorobenzene and *n*-decanol. In this mixture chlorobenzene was as a good solvent for the polymer while *n*-decanol a nonsolvent. The nonsolvent was responsible for the formation of mesopores and macropores in the internal structure of the polymeric material, whereas the good solvent for its microporous structure.<sup>19</sup> In the syntheses of 1,4DMH-TRIM microspheres, different concentrations of chlorobenzene in the mixture with *n*-decanol were used. Other parameters, such as volume ratios of diluents to the monomers were maintained constant. In Figure 6, SEM micrographs of 1,4DMH-TRIM copolymers obtained in the presence of 50 and 15% chlorobenzene are presented.

### Porous structure characterization

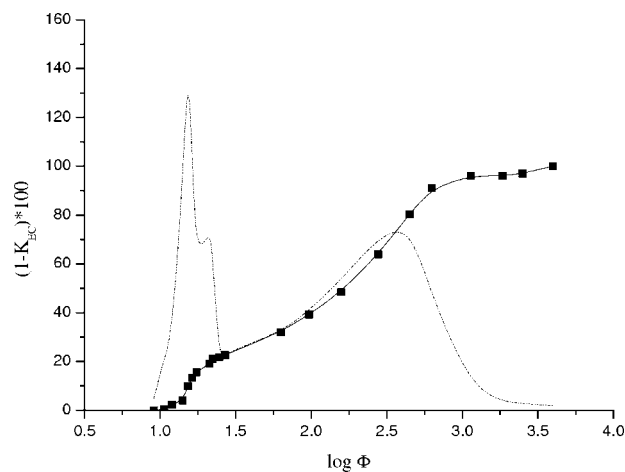
From the data presented in Table I, one can see that different concentrations of chlorobenzene in the mixture with *n*-decanol influence porosity of the

obtained materials. The copolymer prepared in the presence of pure chlorobenzene had the smallest pore volume. A decrease in a chlorobenzene concentration caused an increase in the specific surface areas. The largest specific surface area is obtained for the copolymer synthesized in the presence of 50% (v/v) chlorobenzene. Pore size distributions for copolymers obtained in the presence of 85 and 50% chlorobenzene are monodisperse (Fig. 7). Copolymer obtained in the presence of 15% (v/v) chlorobenzene has no spherical shape and is not taken into further consideration [Fig. 6(B)].

Table II contains the information about the porous structure of the 1,4DMH-TRIM copolymer obtained in the presence of the diluent mixture containing 50% of chlorobenzene, determined in dry (calculated by the BET method from nitrogen adsorption-desorption measurements) and swollen (calculated from the inverse EC method) states. From this data, one can see that the parameters characterizing

**TABLE II**  
Parameters of the Porous Structure for the Copolymer Synthesized in the Presence of 50% Chlorobenzene Obtained with BET and EC Methods

	Specific surface area (m <sup>2</sup> /g)	Pore volume (mL/g)	Volume of micropores (mL/g)	Most probable pore diameter (Å)
BET	210	0.730	0	300
EC	–	1.487	0.324	13/320

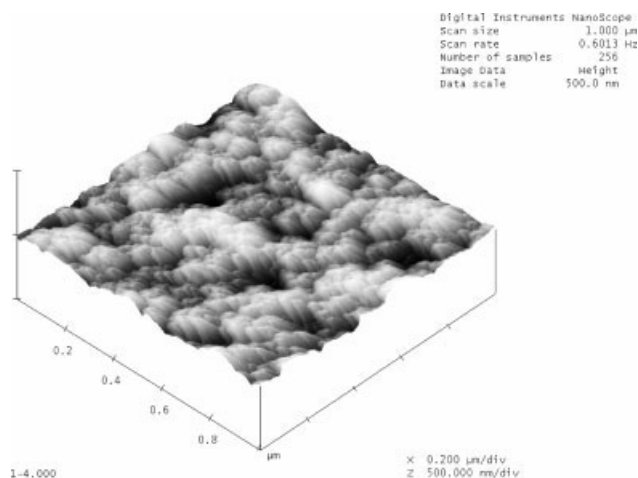


**Figure 8** Cumulative (-), and differential (--) pore size distribution curves obtained from inverse EC measurements for the copolymer obtained in the presence of 50% chlorobenzene.

porous structure in both states are different. In a dry state, when the copolymer was examined by the nitrogen adsorption-desorption method, micropores present in its internal structure were not accessible for the nitrogen molecules.<sup>20</sup> It is different when the polymer is wetted by a good solvent-THF. Its porous structure after swelling is different: pore volume and the most probable pore diameter are larger and micropores appear. Contribution of the micropores to its internal structure exceeds 20%, whereas for the dry copolymer no micropores are revealed.

**TABLE III**  
Diameters ( $\Phi$ ) and Retention Volume of the Probes on the Studied 1,4DMH-TRIM Copolymer

S. No.	Probe	Molecular weight (g)	$\Phi$ (Å)	Retention volume (mL)
1	Toluene	92.14	9.1	1.067
2	Acetophenone	120.15	10.6	1.065
3	Butyrophenone	148.20	12.0	1.001
4	Dimethyl phthalate	194.19	14.1	1.041
5	Diethyl phthalate	222.24	15.3	1.004
6	Dipropyl phthalate	250.30	16.3	0.982
7	Dibutyl phthalate	278.35	17.4	0.967
8	Diethyl phthalate	390.57	21.3	0.945
9	Dinonyl phthalate	418.62	22.2	0.931
10	Dilauryl phthalate	502.78	24.7	0.908
11	Polystyrene	580	26.9	0.922
12	Polystyrene	2,450	62.9	0.862
13	Polystyrene	5,100	97.0	0.816
14	Polystyrene	11,600	157.5	0.757
15	Polystyrene	30,300	277.6	0.658
16	Polystyrene	68,000	447.2	0.553
17	Polystyrene	120,000	625.3	0.484
18	Polystyrene	330,000	1135.7	0.452
19	Polystyrene	750,000	1843.4	0.452
20	Polytyrene	1,260,000	2503.6	0.446
21	Polystyrene	2,750,000	3967.8	0.427



**Figure 9** Contact-mode AFM image for the 1,4DMH-TRIM copolymer (three-dimensional space; magnification  $\times 135,000$ ).

In Figure 8, cumulative and differential pore size distribution curves of the studied copolymer are presented. These curves (based on the data of Table III) resemble porous structure of the polymer after swelling. In comparison with Figure 7, in which the copolymer had monodisperse pore size distribution, it has bimodal pore size distribution with two maxima at  $\sim 16$  Å and 320 Å.

The surface texture of this copolymer is shown in Figure 9. It presents contact mode AFM image of the fragment of the surface of 1,4DMH-TRIM microsphere. It confirms earlier studies.

In Table IV, the results of swelling determination for 1,4DMH-TRIM copolymers in hexane, toluene, THF, acetone, and methanol are presented. The results of the swellability coefficients vary from 2 to 50%. In the nonpolar hexane studied, copolymers have a small swellability coefficient, whereas in the polar solvents their swellability coefficients are significantly larger. In acetone, the volume of the studied microspheres increased up to 50%.

Simultaneously, the swelling propensity (SP factor determined in chromatographic measurements) for this copolymer is very small. Its value is comparable with that obtained for spherical bonded octadecyl silica gel.<sup>13</sup> According to Nevejans and Verzele, this polymer should be treated as material nonswelling

**TABLE IV**  
Copolymer Swelling Studies

<i>n</i> -Hexane	Swellability coefficient (%)				Swelling propensity (SP factor)
	Toluene	Acetone	methanol	THF	
2	30	40	50	34	0.05



in THF (instead of not high reproducibility of SP factor measurements-typically, with the standard deviation 20–25%).<sup>13</sup> Basing on the value of SP factor in this case can lead to misunderstanding. One can take into account swellability coefficients presented in Table IV. For THF it is equal to 34%, what means that this copolymer swells in this solvent. Its small SP factor is caused by the fact that this material swells both in THF and water, but SP factor was introduced for polymeric stationary phases of ST and DVB type that swelled in THF and shrank in water.

The data in Table IV also show that larger swelling appear when polymeric net can interact with the solvents containing special polar groups (hydroxyl or carbonyl). In other cases, the interactions between polymeric and solvent functional groups are not strong enough and high degree of polymer crosslinking counteracts its swelling.

#### Thermogravimetric analysis

The thermal resistance of 1,4DMH-TRIM microspheres was also studied. The initial decomposition temperature of this copolymer is recorded at 230°C. The final decomposition temperature is 660°C. That result indicates that this material has thermal stability suitable for chromatographic purposes.

#### CONCLUSIONS

The synthesis of the new aromatic tetrafunctional methacrylate monomer, 1,4DMH, has been presented. The obtained monomer was copolymerized with TRIM in the presence of pore-forming diluents (chlorobenzene and 1-decanol) to obtain highly cross-linked porous microspheres. The results indicate that composition of diluents mixture influences

porous structure of copolymers. The porous structure for the copolymer obtained in the presence of 50% chlorobenzene was studied in detail. The results show that pore volume and the most probable pore size diameters determined for the copolymer in the dry and in the wetted states are different. The swelling propensity (SP factor) for this copolymer has the value comparable to that of alkyl bonded silica HPLC phases. On the other hand, it swells significantly in acetone and methanol.

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