

# Synthesis, Structure, and Properties of New Methacrylic Derivatives of Naphthalene-2,3-Diol

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**ABSTRACT:** The synthesis of a new monomer, 2,3-(2-hydroxy-3-methacryloyloxypropoxy)naphthalene, and its copolymerization with divinylbenzene is presented. This monomer was obtained from naphthalene-2,3-diol in a two-step synthesis. Copolymers in the form of porous microspheres were prepared by a suspension-emulsion polymerization method. As pore-forming diluents, toluene, 1-decanol, benzyl alcohol, and their mixtures were used. In studies of their porous structure, two methods were used: the adsorption of nitrogen at low temperatures, which provided information

about the porous structure of the material in a dry state, and inverse exclusion chromatography, which provided information about the porous structure of the polymer swollen by a good solvent. The obtained results suggest that the porous structures for the dry and swollen polymers were different. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1886–1895, 2006

**Key words:** atomic force microscopy (AFM); copolymerization; surfaces

## INTRODUCTION

Polymer-based packing materials for high-performance liquid chromatography (HPLC) have potential advantages, including chemical stability in their operation over a wide pH range with a broad array of possible surface chemistries.<sup>1</sup> Despite these advantages, polymeric packings have some limitations. The most important is that they do not achieve such efficiencies as alkyl bonded silicas. The next drawback of commercially available polymer-based packing materials is associated with the limited variety of their chemical structures. For many years, the most popular HPLC packings have been macroporous spherical beads of polystyrene crosslinked with divinylbenzene (ST–DVB).<sup>2</sup> As these materials are highly hydrophobic, they have limited application. Recently, the search for more hydrophilic materials has been made. These new materials have been obtained from monomers containing polar functional groups or by the chemical modification of the non-polar ST–DVB polymeric matrix.

Methacrylate-type materials are an important group of less hydrophobic polymeric packing materials. These materials are mainly copolymers of ethylene dimethacrylate. From time to time, applications of other methacrylate derivatives have been reported.<sup>3–5</sup> Azanova and Hradil<sup>6</sup> described the preparation and

sorption properties of methacrylate and functionalized methacrylate macroporous copolymers. Smigol and coworkers<sup>7–9</sup> also used different methacrylic monomers for the preparation of monodisperse macroporous beads for HPLC. A copolymer of di(methacryloyloxymethyl)naphthalene and divinylbenzene (DVB) was successfully used for HPLC packing.<sup>10–12</sup> This chemically stable material had a slight tendency to swell or shrink when the organic solvent was changed. Weak polar ester groups present in its chemical skeleton meant that it could be used for the separation of both polar and nonpolar compounds.

The promising properties of the aforementioned polymer resulted in our attempt to apply another methacrylate derivative of naphthalene as a monomer for the synthesis of HPLC polymeric packing.

This article describes the synthesis of 2,3-(2-hydroxy-3-methacryloyloxypropoxy)naphthalene (NAF-DM) and its use in the preparation of packing in the form of porous microspheres. Monodisperse beads were obtained by suspension-emulsion copolymerization with DVB in the presence of different pore-forming diluents. The influence of the synthesis conditions on the size and porous structure of the final microspheres was studied. Changes in the bead porous structures in dry and wetted (with various organic solvents) conditions were also determined.

## EXPERIMENTAL

### Chemicals and eluents

Naphthalene-2,3-diol, bis(2-ethylhexyl)sulfosuccinate sodium salt, decan-1-ol, tetrahydrofuran (THF), benzyl

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alcohol, and 2-methacrylic acid were from Fluka AG (Buchs, Switzerland). DVB (Fluka) was washed with 3% aqueous sodium hydroxide solution before use.  $\alpha,\alpha'$ -Azobisisobutyronitrile was obtained from Merck (Darmstadt, Germany). Reagent-grade acetone, methanol, chlorobenzene, chloroform, propan-2-ol, methylene chloride, toluene, sodium hydroxide, potassium hydroxide, 2-(chloromethyl)oxirane, and hydroquinone were from POCh (Gliwice, Poland).

### Preparation of 2,3-di(2,3-epoxypropoxy)naphthalene (NAF-EP)

In a 1000-cm<sup>3</sup>, round-bottom, three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropper, 0.3 mol of naphthalene-2,3-diol (48.0 g) was placed together with 3 mol (277.5 g) of 2-(chloromethyl)oxirane and 2.1 mol (120.9 g) of propan-2-ol; the whole mixture was heated over a water bath at 75°C. Then, at the same temperature, 3 g of NaOH (addition catalyst) was added during 10 min; another portion of a 13.5% solution of NaOH was added (0.7 mol or 27.75 g), and stirring was continued for 5 min. When the reaction was over, the contents of the flask were placed into the dropper, the water layer was separated along with the sodium chloride in it, and the organic layer was distilled at low pressure (1.6 kPa) to separate 2-propanol 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. The epoxide derivative was filtered off. The yield of the obtained products was about 88.5%; its epoxide number was close to the theoretical value.

### Preparation of NAF-DM

Triethylbenzylammonia chloride was prepared with a procedure described by Małosza.<sup>13</sup>

The reaction between the epoxide groups of NAF-EP and the carboxylic ones of 2-methacrylic acid

went on at 80–100°C. The synthesis was carried out in a 500-cm<sup>3</sup>, round-bottom flask equipped with a thermometer, a mechanical stirrer, and a heater. To this flask, 0.5 mol (223 g) of NAF-EP, 1 mol (86.09 g) of 2-methacrylic acid, 2 g of triethylbenzylammonia chloride (a catalyst), and 0.02 g of hydroquinone (a polymerization inhibitor) were added. The progress of the reaction was controlled by the determination of the acidic number. The acidic number determines the amount of KOH milligrams used to neutralize the free acids contained in 1 g of a substance. The reaction was considered to be over when the acidic number was below 3. Its rate would be higher if the reaction were carried out at higher temperatures, but a considerable exothermic effect can result in the loss of control of the reaction and the appearance of some products of darker color.

### Copolymerization

Copolymerization with DVB was performed in an aqueous medium. In a typical experiment, 150 mL of redistilled water and 1.4 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 10 g of NAF-DM and 3 g of DVB and 0.18 g of  $\alpha,\alpha'$ -azobisisobutyronitrile (initiator) in the diluent mixture (toluene and decan-1-ol) was added while the aqueous medium was stirred (Table I). Copolymerization was performed for 18 h at 80°C. The obtained copolymers were washed with distilled water, filtered off, dried, and extracted in a Soxhlet apparatus with boiling acetone and methanol. Then, the polymer beads were separated on sieves. Microscopic examination showed that in most cases, particles of perfectly spherical shape with diameters in the range 2–25  $\mu\text{m}$  were obtained.

Uniform particles (5–15  $\mu\text{m}$ ) used in further studies were isolated by sedimentation from acetone-methanol (90 : 10 v/v).

TABLE I  
Experimental Parameters of the Syntheses of the NAF-DVB Copolymers

Synthesis	NAF-DVB (g)	Initiator (g)	Diluent (mL)			Product
			Toluene	1-Decanol	Benzyl alcohol	
1	10/3	0.18	16.00	0	0	Microspheres
2	10/3	0.18	12.00	4.00	0	Microspheres
3	10/3	0.18	8.00	8.00	0	Microspheres
4	10/3	0.18	5.00	11.00	0	Microspheres
5	10/3	0.18	4.00	12.00	0	Microspheres
6	10/3	0.18	0	16	0	Coagulated
7	10/6	0.18	8.00	8.00	0	Microspheres
8	10/3	0.18	3.00	5.00	8.00	Microspheres
9	10/3	0.18	3.00	3.00	10.00	Microspheres
10	10/3	0.18	0	0	16	Coagulated

### Characterization

IR spectra were determined on a PerkinElmer 1700 Fourier transform infrared (FTIR) spectrometer with KBr pallets.  $^1\text{H}$ -NMR spectra were recorded on a Bruker 300 MHz instrument (Bruker, Germany) operating at the  $^1\text{H}$  resonance frequency of 300 MHz. Chemical shifts referred to chloroform serving as an internal standard. The  $^{13}\text{C}$ -NMR spectrum of the NAF-DM in chloroform was obtained with the same apparatus.

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

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

### Chromatographic measurements

The retention volumes ( $V_R$ 's) 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 columns packed with the copolymers. The columns (i.d. = 100 mm  $\times$  4.1 mm) were packed according to a procedure described earlier.<sup>10</sup> They were thermostated at 30°C. The diameter of the polymeric beads packed in the columns was 5–15  $\mu\text{m}$ . The chemical structures of the monomers used for preparation of column packing are presented in Figure 1.

Each substance was injected separately as a 0.1% (v/v) solution in THF. In the HPLC and inverse exclusion chromatography (EC) measurements, THF was the mobile phase at a flow rate 1 mL/min. To determine the swelling propensity (SP) factors, twice-distilled water, at the same flow rate, was used as the mobile phase. The given  $V_R$ 's were always the mean of three determinations.

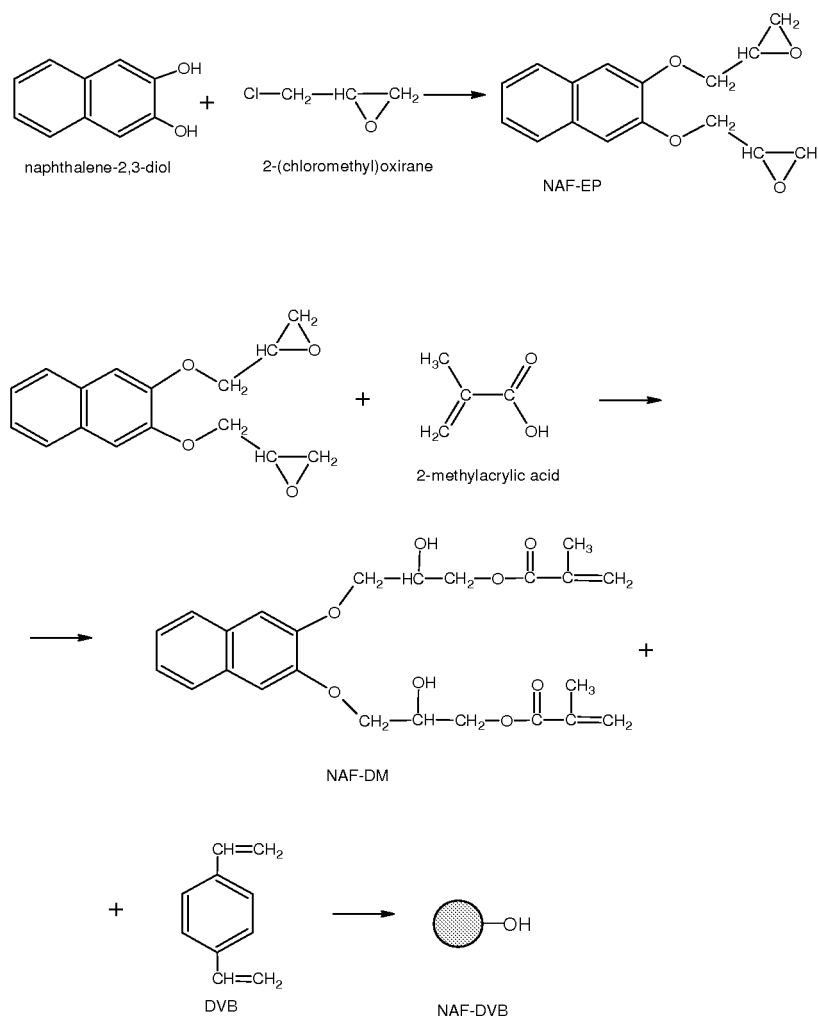


Figure 1 Synthesis and chemical structure of the compound used for copolymerization.

### Characterization of the porous structure

Such parameters as specific surface area ( $S$ ), pore volume ( $V_p$ ), pore-size distribution, and average pore diameter were determined by the method of nitrogen adsorption on the surface of the studied stationary phases in a dry state.  $S$  was calculated by the Brunauer–Emmett–Teller method, with the assumption that the area of a single nitrogen molecule was  $16.2 \text{ \AA}^2$ . These determinations were made with an adsorption analyzer ASAP 2405 (Micrometrics, Inc., Rockport, ME). The measurements of the surface properties of the copolymers were preceded by the activation of the samples at  $200^\circ\text{C}$  for 2 h. The beads were examined with an atomic force microscope (AFM Nanoscope III, Digital Instruments, Santa Barbara, CA) operating in the contact mode. The images presented in this article contain  $512 \times 512$  data points, which were obtained within a few seconds. The typical force applied to obtain these images ranged from 1.0 to 100 nN.

In a swollen state, the beads were characterized by the inverse EC technique introduced by Halász and Martin.<sup>14</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 [ $\Phi$  (Å)] was calculated from the following equation:<sup>15</sup>

$$\Phi = 0.63M_w^{0.59} \quad (1)$$

where  $M_w$  is the gram molecular weight of the probe.

$\Phi$  is associated with a pore diameter that corresponds to the smallest pore, which allows unhindered access for the probe of a given molecular weight. Nevejans and Verzele<sup>16</sup> and Gawdzik and Osypiuk<sup>17</sup> used toluene, alkylphenones, phthalates, and polystyrenes as the pore-size probes.

The cumulative pore-size distribution was determined from the plot of  $1 - K_0(\text{EC})$  versus  $\log \Phi$ , where  $K_0(\text{EC})$  is the distribution constant in exclusion chromatography as calculated from the following equation:<sup>14</sup>

$$K_0(\text{EC}) = \frac{V_R - V_0}{V_p} = \frac{V_R - V_0}{V_i - V_0} \quad (2)$$

where  $V_R$  is the retention volume of the probe;  $V_0$  is the interstitial volume, which is equal to  $V_R$  of a totally excluded molecule;  $V_i$  is the retention volume of a totally included molecule; and  $V_p (= V_i - V_0)$  is the pore volume.

SPs of the copolymers were calculated according to Nevejans and Verzele:<sup>15</sup>

$$\text{SP} = \frac{p(\text{THF}) - p(\text{H}_2\text{O})}{p(\text{H}_2\text{O})} \quad (3)$$

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 the mobile phases, respectively.

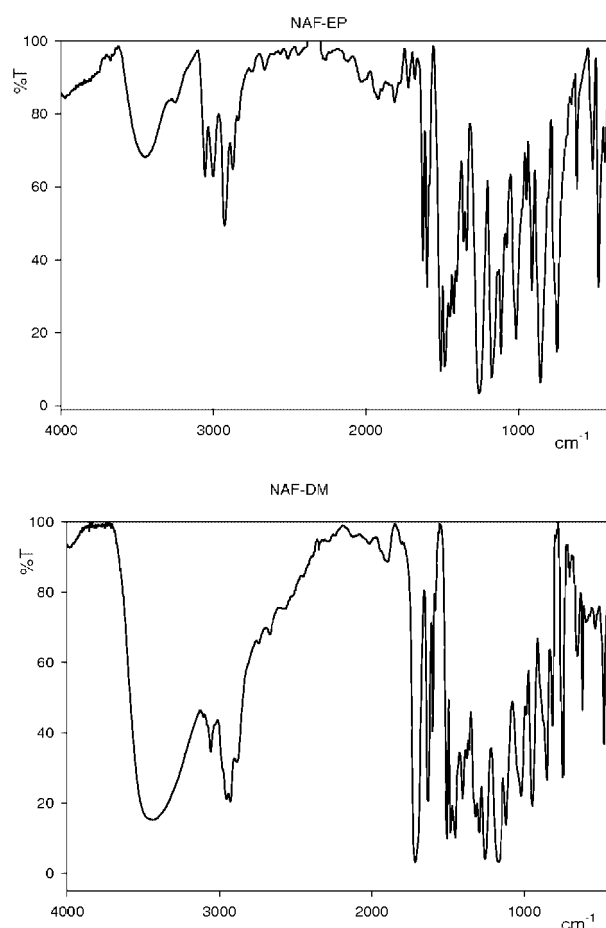
The swellability coefficients ( $B$ 's) were determined by equilibrium swelling in acetone, methanol, 1,4-dioxane, dichloromethane, isopropyl alcohol, and *n*-heptane with the centrifugation method.<sup>18,19</sup>  $B$  is expressed as

$$B = \frac{V_s - V_d}{V_d} \times 100\% \quad (4)$$

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

## RESULTS AND DISCUSSION

Scheme 1 presents the synthesis of NAF-DM and its copolymerization with DVB. The obtained monomer possessed ester and secondary hydroxyl groups of hydrophilic character in its chemical structure. The chemical structure of this monomer was confirmed by spectroscopic methods.



**Figure 2** FTIR spectra of the NAF-EP and NAF-DM compounds. % T is % transmission.

### IR spectroscopy

The FTIR spectra of NAF-DM and its precursor (NAF-EP) are shown in Figure 2. In the spectrum of NAF-EP, C—H stretching vibrations of the aromatic ring backbone methylene and methyl groups were observed at 3065 and 2931  $\text{cm}^{-1}$ . The epoxide group gave a shape signal at 916  $\text{cm}^{-1}$ . The aromatic skeletal absorption was observed at 1603  $\text{cm}^{-1}$ . In the NAF-DM spectrum, vibrations of the —OH group were visible at 3426  $\text{cm}^{-1}$ . The signal of the C=O group occurred at 1717  $\text{cm}^{-1}$  and that of =C—H occurred at 947  $\text{cm}^{-1}$ .

### NMR spectroscopy

In the  $^1\text{H-NMR}$  spectrum of NAF-EP, the protons in the methylene group (—CH<sub>2</sub>) connected with a skel-

eton gave a shape bands at  $\delta = 3.436\text{--}3.494$ , whereas protons from the terminal methylene group (—CH<sub>2</sub>) showed signal at  $\delta = 2.784\text{--}2.854$  and 2.927–2.958. The bands at  $\delta = 7.176$ , 7.290–7.339, and 7.654–7.690 corresponded to the phenyl ring. In the  $^1\text{H-NMR}$  spectrum of NAF-DM in chloroform, the protons of the methylene group (—CH<sub>2</sub>) gave signals at  $\delta = 4.144\text{--}4.4232$  and 4.411, the proton in the hydroxyl group (—OH) gave a signal at  $\delta = 3.539\text{--}3.695$ , and the protons near the double bond (—CH=CH<sub>2</sub>) gave signals at  $\delta = 5.554\text{--}5.562$  and 6.120–6.176.

Figure 3 presents the  $^{13}\text{C-NMR}$  spectra of NAF-EP and NAF-DM. Both spectra showed a set of three peaks at 76.7, 77.1, and 77.6 ppm. These peaks came from the solvent chloroform and could be neglected in the interpretation of the spectra. In the spectrum of NAF-EP, eight peaks were visible. The carbon

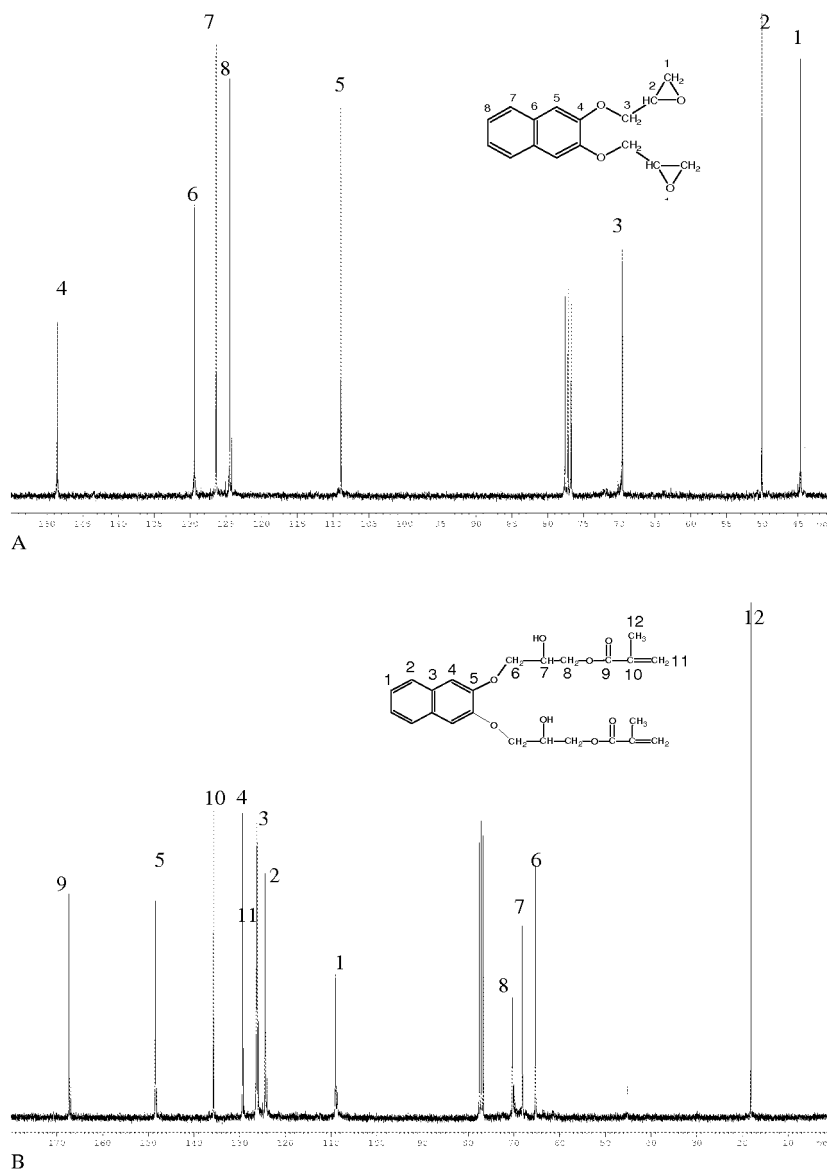


Figure 3  $^{13}\text{C-NMR}$  spectra of (A) NAF-EP and (B) NAF-DM.

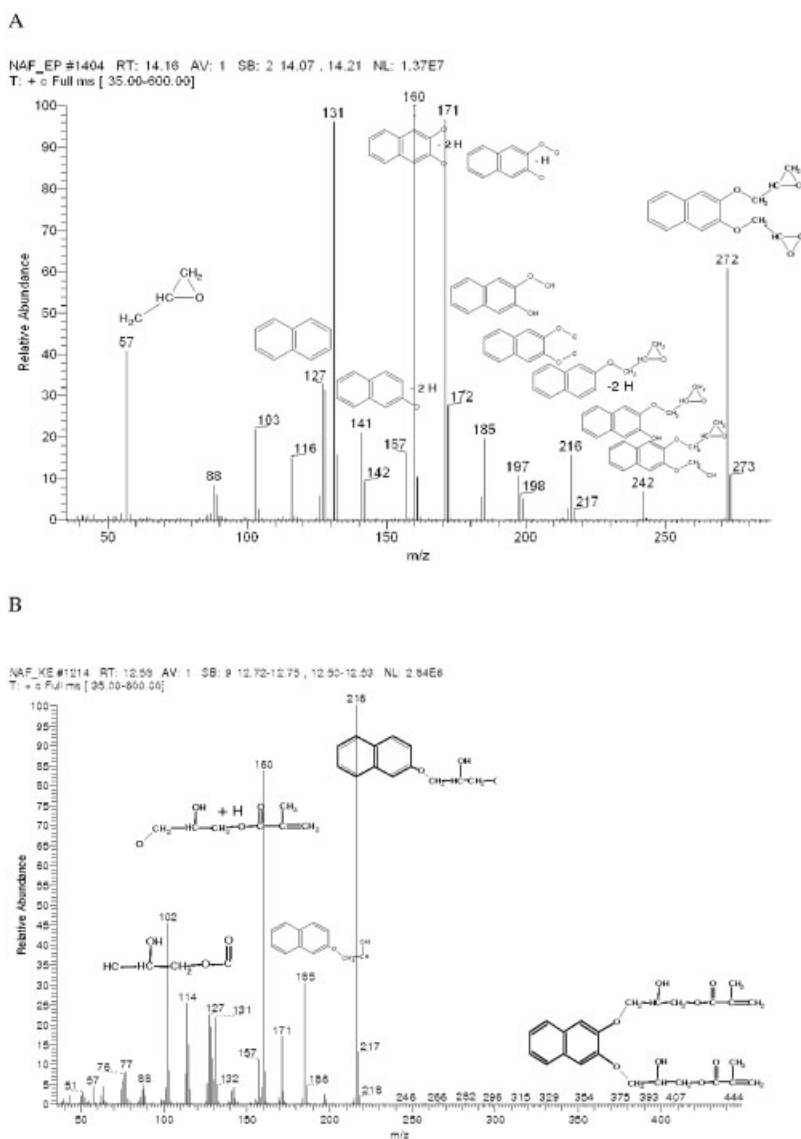
atom in the terminal methylene group ( $-\text{CH}_2$ ) gave a signal at 44.6 ppm, the carbon in the methylene group ( $-\text{O}-\text{CH}_2-$ ) connected with oxygen at 69.6 ppm, and the carbon of the epoxide group ( $-\text{CH}-$ ) showed a signal at 50.1 ppm. The signals at 108.9, 124.4, 126.4, and 148.6 ppm came from five different types of carbon atoms of the aromatic ring.

In the spectrum of NAF-DM, 12 peaks were visible. Two of  $\text{sp}^2$ -hybridized carbon atoms of the double bond were much more deshielded than the  $\text{sp}^3$ -hybridized carbon atoms. The terminal carbon atom of the double bond absorbed at 126.6 ppm, and the more highly substituted one absorbed at 135.8 ppm. The carbon of the methyl group absorbed at 18.1 ppm. The signal for the carbonyl group of ester appeared at 167.3 ppm. The carbon of the methylene groups absorbed at 65.2 and 70.3 ppm. The most highly deshielded carbon atom (68.2 ppm) was bonded to the

oxygen atom in the hydroxyl group ( $-\text{OH}$ ). Five different types of carbon atoms of the aromatic ring gave signals at 109.2, 124.4, 126.2, and 148.5 ppm.

### GC-MS

The chemical structures of NAF-DM and its precursor NAF-EP were also confirmed by GC-MS analysis. As their spectra were not available in the library, identification was achieved the analysis of molecular and fragmentary ions. As shown in the spectra presented in Figure 4, the molecular ions corresponding to the calculated molecular weight of NAF-EP (272) and 2,3-(2-hydroxy-3-methacryloyloxypropoxy) naphthalene (444) were well visible. A large number of fragmentary ions were also visible. The most important were identified, and their meanings are presented in both spectra.



**Figure 4** Mass spectrometer spectra of the (A) NAF-EP and (B) NAF-DM.

TABLE II  
Characterization of the Porous Structure of the Obtained Porous Beads

Synthesis	S (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	Volume of the micropores (cm <sup>3</sup> /g)	Average pore diameter (Å)
1	3	0.00	0	0
2	22	0.04	0	77
3	40	0.12	0	120
4	70	0.24	0	133
5	28	0.09	0	126
6	—	—	—	—
7	38	0.11	0	110
8	19	0.10	0	212
9	31	0.12	0	138
10	—	—	—	—

### Porous structure characterization

The new monomer (NAF-DM), whose structure and properties were discussed previously, was applied for the preparation of porous microspheres. It was copolymerized with DVB through suspension-emulsion polymerization. All syntheses were carried out in the presence of pore-forming diluents: toluene, 1-decanol, benzyl alcohol, or their mixtures. Independent of diluent composition, the diameter of the obtained microspheres was almost the same: 2–25 μm. Detailed information about the experimental parameters of all of the syntheses are summarized in Table I.

In Table II, the characterization of the porous structure of the obtained microspheres is presented. From these data, one can see that the obtained beads were

characterized by rather low porosities. In their porous structures, no micropores were present. The microspheres obtained in synthesis 4 possessed the largest V<sub>p</sub> and S values. The value of their average pore diameter suggests that this material had a mezoporous structure. As such properties of porous structure are desirable from a chromatographic point of view, this copolymer was chosen for detailed studies.

All of the studied microspheres were examined by the adsorption/desorption method in a dry state. In a dry copolymer, micropores are not accessible for the nitrogen molecule because their diameters are smaller than that of the nitrogen molecule.<sup>20</sup>

The situation changes when the polymer is wetted by a good solvent. In Table III, the V<sub>R</sub>'s of the compounds used as the pore probes obtained from the inverse EC measurements are presented. From these data and the weights of the copolymer in the chromatographic columns, V<sub>p</sub> and volume of micropores for the studied copolymer are determined (Table IV). According to Nevejans and Verzele,<sup>15</sup> the term *microporosity* defines pores with a diameter smaller than 20 Å. In the studies presented here, the differences between the V<sub>R</sub>'s of toluene (Φ = 9 Å) and the molecule of dinonyl phthalate (Φ = 22 Å) indicated the contribution of micropores to the internal structure of the copolymer.<sup>17</sup>

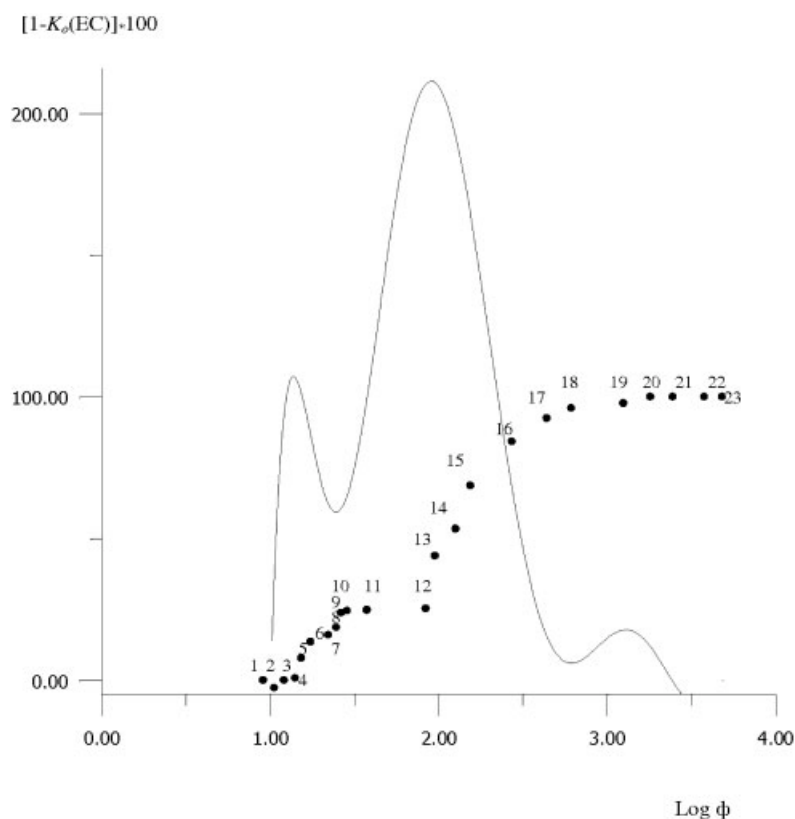
In the bimodal pore-size distribution of the NAF-DVB copolymer (Fig. 5), one can see that in its porous structure, in addition to mezopores and macropores with diameters of 20–500 Å, some micropores (9–22 Å) were present. Changes in its porous structure in comparison to that of the dry copolymer

TABLE III  
Φ and V<sub>R</sub> Values of the Probes on the Porous Copolymer NAF-DVB-4

Probe	Molecular weight (g)	Φ (Å)	V <sub>R</sub> (mL)
1. Toluene	92.14	9.1	1.046
2. Acetophenone	120.15	10.6	1.060
3. Butyrophenone	148.20	12.0	1.046
4. Dimethyl phthalate	194.19	14.1	1.042
5. Diethyl phthalate	222.24	15.3	1.005
6. Dipropyl phthalate	250.30	16.3	0.975
7. Dibutyl phthalate	278.35	17.4	0.962
8. Dipentyl phthalate	306.41	18.5	0.948
9. Dioctyl phthalate	390.57	21.3	0.921
10. Dinonyl phthalate	418.62	22.2	0.917
11. Dilauryl phthalate	502.78	24.7	0.916
12. Polystyrene	580	26.9	0.913
13. Polystyrene	2450	62.9	0.815
14. Polystyrene	5100	97.0	0.765
15. Polystyrene	11,600	157.5	0.685
16. Polystyrene	30,300	277.6	0.603
17. Polystyrene	68,000	447.2	0.560
18. Polystyrene	120,000	625.3	0.541
19. Polystyrene	390,000	1253.3	0.532
20. Polystyrene	750,000	1843.4	0.520
21. Polystyrene	1,260,000	2503.6	0.520
22. Polystyrene	2,750,000	3847.3	0.520
23. Polystyrene	3,840,000	4831.7	0.520

TABLE IV  
Properties of the Studied Copolymer

Copolymer	Weight of copolymer in the column (g)	S (m <sup>2</sup> /g)	Surface area of the copolymer in the column (m <sup>2</sup> )
NAF-DVB-4	0.6006	70	42



**Figure 5** Cumulative and differential pore-size distribution curves for the studied polymer. The numbers correspond to the probe compounds from Table III.

were caused by interactions of its net with THF. This good solvent swells the polymeric net. As a consequence, some micropores became detectable. Additionally, the results from inverse EC indicate that  $V_p$  of the studied copolymer was significantly larger than that obtained from the nitrogen adsorption measurements (Table V). Similar results were reported for other synthetic polymers used as HPLC packings.<sup>16,17</sup> Simultaneously, SP for the naphthalene-DVB copolymer was rather small. This means that the porous structure of this copolymer changed in contact with a good solvent such as THF, but the high degree of crosslinking characterizing this copolymer counteracted swelling.

### Swelling studies

To investigate the swelling behavior of the NAF-DVB copolymer more precisely, microspheres were swollen in acetone, methanol, THF, dichloromethane, and hexane. The resulting  $B$  values are summarized in Table VI. From these data, one can see that in all polar solvents, the  $B$  values varied from 28 to 35%. For such behavior, polar functional groups present in the chemical structure were responsible. In nonpolar hexane, this copolymer had a significantly smaller  $B$  value.

### Atomic force microscopy (AFM)

The surface texture of the studied polymer NAF-DVB is shown in Figure 6. Figure 6 presents the contact-mode AFM images of the obtained material in three photos: the section analysis and fragment of its surface, the fragment surface, and the three-dimensional space. The magnification of all photos is 135,000 $\times$ . From the photos made by the atomic force microscope, one can see that the NAF copolymer - DVB had a regular porous structure.

### Thermogravimetric analysis

The thermal resistance of the NAF-DVB copolymer was also studied. The results from thermogravimetric analysis confirm that this material had a stability that is suitable for chromatographic purposes. The initial decomposition temperature of this copolymer

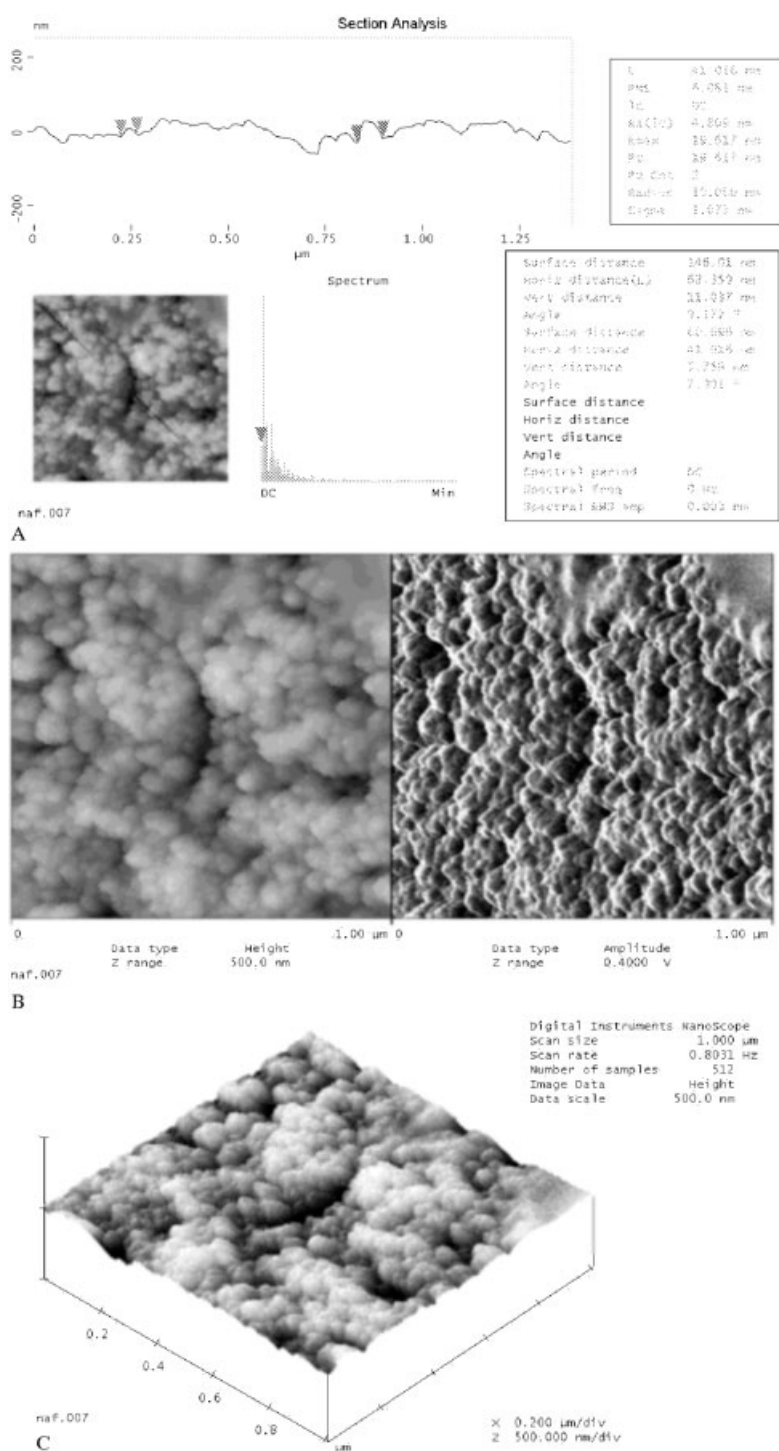
**TABLE V**  
Properties of the Studied Copolymer in the Swollen State

Copolymer	$V_p$ (cm <sup>3</sup> /g)	Contribution of micropores (cm <sup>3</sup> /g)	SP factor
NAF-DVB-4	0.525	0.129	1.4



TABLE VI  
Swelling Studies

Copolymer	B (%)				
	Acetone	Methanol	THF	Dichloromethane	Hexane
NAF-DVB-4	30	35	35	28	15



**Figure 6** Contact-mode AFM images for the copolymer NAF-DVB-4: (A) section analysis and fragment of its surface, (B) fragment surface, and (C) three-dimensional space. Magnification = 135,000 $\times$ .

was recorded at 280°C. The final decomposition temperature was 900°C. The NAF-DVB copolymer decomposed in two stages. The first stage of decomposition was observed in the range of 280–430°C, and the second stage took place between 430 and 900°C.

### CONCLUSIONS

The synthesis of the new monomer NAF-DM and its copolymerization with DVB was presented. The obtained monomer possessed ester and secondary hydroxyl groups of hydrophilic character in its chemical structure.

Its copolymers with DVB in the form of porous microspheres were prepared by a suspension-emulsion polymerization method. As pore-forming diluents, toluene, 1-decanol, benzyl alcohol, and their mixtures were used.

The results indicate that the composition of diluents had a significant influence on the final product of this reaction; for example, in the presence of pure 1-decanol or benzyl alcohol, microspheres were not formed. The most regular porous structure was copolymer 4 obtained in the presence of the mixture of toluene and 1-decanol. This copolymer can be used directly as polymeric packing in HPLC or, thanks to presence of functional groups in

its chemical structure, as a matrix for further chemical modifications.

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