

Synthesis, Modification, and Porous Properties of New Glycidyl Methacrylate Copolymers

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ABSTRACT: Synthesis, copolymerization, and physicochemical properties of new, of different degrees of crosslinker tetrafunctional bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide and glycidyl methacrylate copolymers are presented. The monomers were used for the synthesis of porous microspheres in the presence of pore-forming diluents, decan-1-ol, and toluene. Influence of diluents composition on their porous structures was studied. Porous structure of the obtained microspheres in dry (from nitrogen adsorption-desorption measurements) states was studied. Their chemical structures

were studied by the use of Fourier transform infrared. The number of epoxy groups of the obtained copolymers, their thermal properties (thermogravimetric analysis), and swelling characteristics in 10 solvents of different chemical nature were examined. Selected copolymers were modified by amines in the epoxide ring-opening reaction. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3020–3026, 2011

Key words: glycidyl methacrylate; copolymerization; microspheres; surfaces; swelling

INTRODUCTION

Specific properties of polymers like hydrophobic/hydrophilic character, presence of various functional groups, ability for modifications, make these materials very attractive from the biochemical point of view. Crosslinked polymeric systems based on derivatives of styrene-divinylbenzene, hydroxyalkyl methacrylate, glycidyl methacrylate (GMA), and acrylamide have generated considerable interest.^{1–3}

In the group of the mentioned monomers, GMA is of special interest because this compound has not only a double bond but also an epoxy group. Its copolymerization with conventional vinyl monomers enables introduction of reactive functional groups into the structure of polymers produced on an industrial scale. In recent years, copolymers based on GMA have attracted increasing interest. The attention paid to these copolymers is largely because of the ability of pendent epoxide groups to enter into a large number of chemical modifications of the initial polymer.^{4–8} First, copolymers based on GMA have been used as supports for enzymes⁹ and as sorbents for chromatography.^{10–12} Second, they can also be used in removing metal ions (e.g., mercuric ions)^{13,14} or even as biomaterials.¹⁵ Recently, functional polymers have attached increasing interest as copolymers^{16–20} or terpolymers^{21–23} with other methacrylates.

Synthesis of polymeric microspheres based on (meth)acrylate derivatives of aromatic diols and their practical use as column packing in high performance liquid chromatography (HPLC) and solid phase extraction (SPE) technique has been the subject of our previous research works.^{24–26} As a comonomer, divinylbenzene was used. The obtained copolymers had high degree of crosslinking and weakly reactive secondary hydroxyl groups in their chemical structure. Current studies are aimed at obtaining polymeric microspheres with reactive functional groups on the surface capable of extensive modifications.

In this article, the new two component, of different degree of crosslinker bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide (BES.DM) and GMA copolymers are described. Porous microspheres were obtained by suspension-emulsion copolymerization in the presence of pore-forming diluents: toluene and decan-1-ol. In their syntheses, different concentrations of toluene in the mixture with decan-1-ol were used. The selected microspheres were modified by amines in the epoxide ring-opening reaction. The products before and after modification were studied in detail.

EXPERIMENTAL

Chemicals and eluents

GMA, decan-1-ol, tetrahydrofuran (THF), and bis(2-ethylhexyl)sulfosuccinate sodium salt (DAC, BP) were from Fluka AG (Buchs, Switzerland). α,α' -Azoiso-bis-

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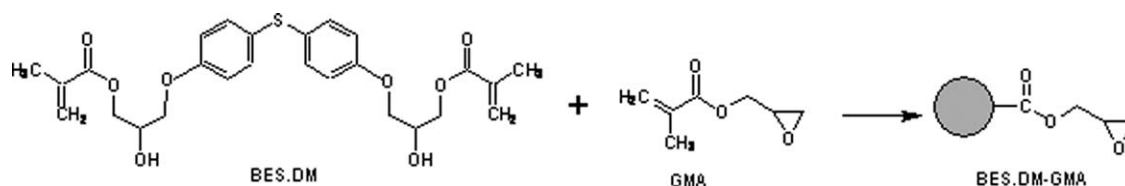


Figure 1 Scheme of synthesis and chemical structure of the monomers used for copolymerization.

butyronitrile (AIBN) and were obtained from Merck (Darmstadt, Germany). Reagent grade acetone, methanol, propan-2-ol, chlorobenzene, chloroform, hexane, toluene, and methyl methylene 1,4-dioxane were from POCh (Gliwice, Poland). BES.DM was obtained by the procedure described in our previous works.^{27,28}

Synthesis of copolymers

Copolymers containing GMA and BES.DM were obtained in a suspension-emulsion copolymerization procedure.²⁹ Synthesis was carried out in a three-necked flask equipped with a stirrer, a water condenser, and a thermometer. The initiator AIBN (1 wt %) was dissolved in monomers, and then the mixture was diluted with a mixed solvent (toluene/decan-1-ol) taken in different proportions. Different concentrations of toluene in the mixture with decan-1-ol were used to qualify the effect of the diluent character on the microsphere properties. The dispersion medium was prepared through the dissolution of 1 wt % DAC, BP in deionized water, and it was used in a 1/5 (w/w) ratio according to the organic phase. The reaction mixture was stirred at 600 rpm for 18 h at 80°C. After cooling, a purification procedure was applied to remove the diluents and unreacted monomers from the products. The obtained copolymers were washed with distilled water, filtered off, dried, and then extracted in a Soxhlet apparatus by different solvents (with boiling acetone and methanol).

Microscopic examination showed that in most cases, particles of perfect spherical shapes with diameters in the range 5–30 μm were obtained.

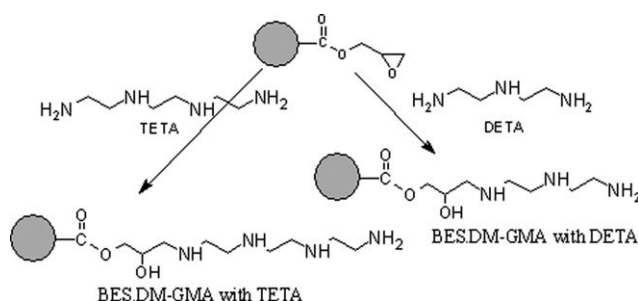


Figure 2 Scheme of chemical modification of obtained copolymers with DETA and TETA.

Uniform particles (5–15 μm) used in further studies were isolated by sedimentation from acetone-methanol mixture (90 : 10, v/v). The screening procedure was controlled by microscopic examination. Chemical structure of the obtained copolymers was confirmed by Fourier transform infrared (FTIR) and elemental analyses.

Modification

The selected copolymers were modified with some amines in the epoxide ring-opening reaction. In a 250-cm³ round-bottomed two-necked flask equipped with a mechanical stirrer, a thermometer, 10 g of selected microspheres were placed together with diethylenetetramine (DETA) or triethylenetetramine (TETA; 10 excess to epoxide groups) and 200 mL of toluene. The whole content was heated over a water bath at 80°C for 24 h. The obtained modified beads were washed with distilled water, filtered off, dried, and extracted in a Soxhlet apparatus with boiling toluene for 5 h. Next, the product was dried under reduced pressure at 30°C and their FTIR and elemental analyses were carried out.

Characterization

Elemental analysis of the parent and modified copolymers was carried out using the Perkin-Elmer CHN 2400 apparatus.





FTIR spectra were recorded using a Perkin-Elmer 1725 X spectrophotometer in the 400–4000 cm^{-1} wave number range using KBr pallets.

Thermogravimetric analysis was carried out by means of a Paulik and Erdey derivatograph

TABLE I
Experimental Parameters of the Synthesis

Synthesis No.	Ratio of monomers (mol %)		Number of epoxy groups (mmol/g)	
	GMA	BES.DM	Calculated	Determined
1	33.3	66.7	0.87	0.73
2	50	50	1.56	1.40
3	66.7	33.3	2.55	1.78
4	75	25	3.23	2.11
5	80	20	3.75	2.37
6	85.8	14.2	4.44	2.79

TABLE II
FTIR Spectra of the Obtained Copolymers (Table I, Synthesis No. 2) Before (BES.DM-GMA) and After Modification with DETA and TETA

Copolymer	cm ⁻¹				
					-CH ₂ -; -CH ₃
BES.DM-GMA	1592	3481	905	1728	3059; 2925
BES.DM-GMA with DETA	1592	3475	-	1731	3050; 2928
BES.DM-GMA with TETA	1596	3481	-	1725	3058; 2922

(Budapest, Hungary) at a heating rate of 10°C/min in air, in the temperature range of 20–1000°C with the sample weight of 100 mg. As a reference, α -Al₂O₃ was used. The initial decomposition temperature (IDT), $T_{20\%}$, $T_{50\%}$ of weight loss, final decomposition temperature (T_{end}), and temperature of the maximum rate of weight loss (T_{max}) were determined.

The beads were also examined using an atomic force microscope (AFM), AFM Nanoscope III (Digital Instruments) operating in the 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.

The HCl/dioxane method (PN-74/C-89085) was used to determine the number of epoxy groups. The epoxide content was calculated from the difference between the blank and that found for the titration of the sample reaction mixture.

Porous structure characterization

Porous structure of copolymers was investigated by nitrogen adsorption at 77 K using adsorption analyzer ASAP 2405 (Micrometrics). Before measurements, the copolymers were outgassed at 150°C for 2 h. 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 in the adsorbed state is 16.2 Å². Pore volumes and pore size distributions were determined by the Barrett, Joyner and Halenda theory (BJH) method.

Swelling

The swellability coefficients, B , were determined by equilibrium swelling in acetone, methanol, propan-2-ol, chlorobenzene, acetonitrile, chloroform, toluene, hexane, THF, and 1,4-dioxane using the centrifugation method.^{30,31} B is expressed as:

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

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

RESULTS AND DISCUSSION

New copolymers of different degrees of crosslinking obtained from GMA and BES.DM as crosslinkers were obtained according to reaction shown in Figure 1. Chemical modification of the obtained copolymers with amines is presented in Figure 2. Experimental parameters of the syntheses are presented in Table I. The obtained copolymers have different number of epoxy groups ranging from 0.73 to 2.79 mmol/g. The closest epoxy groups numbers to theoretical values are characteristic for microspheres containing 1 : 1 and 1 : 2 (mol %) GMA : BES.DM. In these cases, high reactivity of GMA toward BES.DM are visible. According to Brandrup et al.,³² reactivity ratios of GMA toward different methacrylates have similar values, e.g., for the pair GMA and methyl methacrylate they are 0.932 and 0.726 whereas for GMA and buthyl methacrylate 0.94 and 0.85, respectively. Copolymer obtained in synthesis No. 2 (bold in the

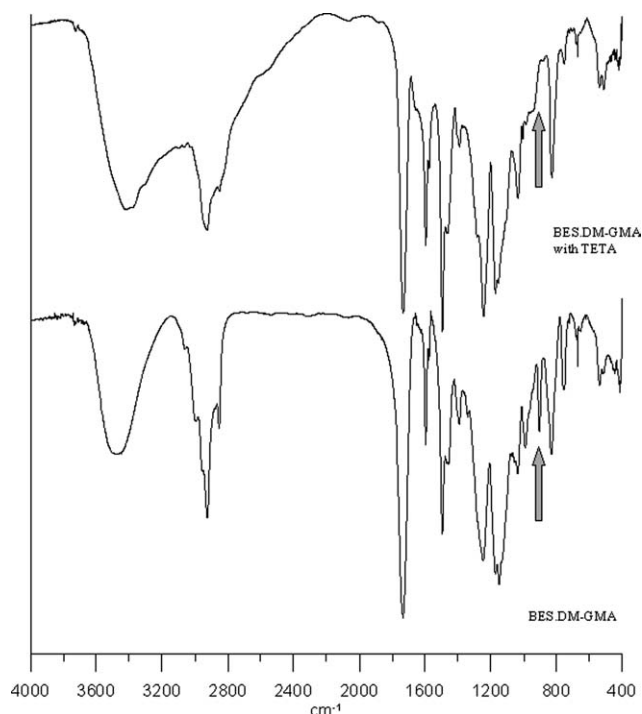


Figure 3 FTIR spectra of the parent (BES.DM-GMA) and modified (BES.DM-GMA with TETA) copolymers.

TABLE III
TG and DTG Data of the Thermal Copolymers Degradation

Copolymer	°C						
	IDT	$T_{20\%}$	$T_{50\%}$	T_{end}	T_{max1}	T_{max2}	T_{max3}
BES.DM-GMA	220	320	380	700	220	360	560
BES.DM-GMA with DETA	220	320	440	740	–	340	595
BES.DM-GMA with TETA	230	320	430	710	–	340	565

Table I) was chosen for further studies and modification. The selection was made taking into account the number of epoxy groups and microspheres porous structure. Chemical structures and properties of the parent and modified copolymers are studied in detail.

FTIR

FTIR of the parent copolymers

The results of FTIR analysis of the new copolymers are presented in Table II. In the spectrum of the BES.DM and GMA copolymers, C–H stretching vibrations of aromatic ring backbone methylene and methyl groups are observed at 3059 and 2923 cm^{-1} . The epoxide group gives a shape signal at 905 cm^{-1} . The aromatic skeletal absorption is observed at 1592 cm^{-1} . In the spectrum, the vibrations of –OH group are visible at 3481 cm^{-1} . The signal of C=O group occurs at 1728 cm^{-1} .

FTIR of the modified copolymers

Most signals observed in the spectra of the modified copolymers are the same. Only disappearance of the bands characteristic of absorption of epoxy groups

TABLE IV
Swelling Studies

Solvent	Swellability coefficient, B (%)						
	Copolymer No. (Table I)						Copolymer No. 2 modified DETA
	1	2	3	4	5	6	
Acetone	22	20	18	16	15	15	8
Methanol	15	14	13	13	11	10	6
Propan-2-ol	14	12	12	11	9	8	5
Chlorobenzene	2	0	0	0	0	0	2
Acetonitrile	18	22	23	25	28	30	9
Chloroform	23	22	17	10	7	3	10
Toluene	5	3	1	0	0	0	0
Hexane	0	0	0	0	0	0	0
THF	42	40	35	27	15	8	12
1,4-Dioxane	31	29	23	16	12	9	10

TABLE V
Characterization of the Porous Structure of the Obtained Porous Microspheres

Copolymer No. (Table I)	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
1	85	0.43	200
2	80	0.44	220
3	53	0.31	233
4	44	0.23	184
5	43	0.20	214
6	5	0.01	–
Copolymer No. 2 modified DETA	121	0.45	147

differentiate these spectra from that of the parent copolymer (Fig. 3). The results of FTIR analysis are also presented in Table II.

THERMOGRAVIMETRIC ANALYSIS

The results of thermal resistance of the selected copolymers are presented in Table III. The IDT for the starting (parent) copolymer is recorded at 220°C. Its final decomposition temperature (T_{end}) is 700°C. The differential thermogravimetric analysis (DTG) curves contain three separate degradation steps. The first decomposition peak is observed at 220–280°C with the maximum of weight loss (T_{max1}) at 240°C. The second decomposition stage takes place between 300 and 420°C with T_{max2} at 360°C, and the third at 460–680°C with T_{max3} at 560°C. The first decomposition peak is a consequence of poly(GMA) breaking into fragments, the second decomposition peak is associated with the ester bonds breakdown in copolymers, while the third one could be attributed to the total degradation of copolymers.³³ The results of thermal resistance of the modified copolymers are also presented in Table III. The IDTs are the same, only for T_{max50} and T_{End} and is observed rather average increase of temperature and disappearance of T_{max1} .

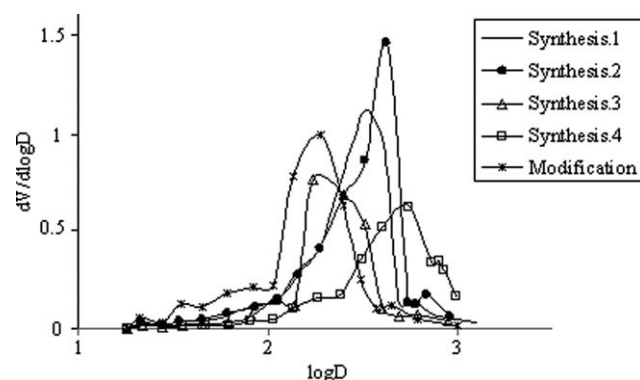


Figure 4 Differential pore size distributions as a function of the logarithm of the pore diameter, D , for the studied copolymers.

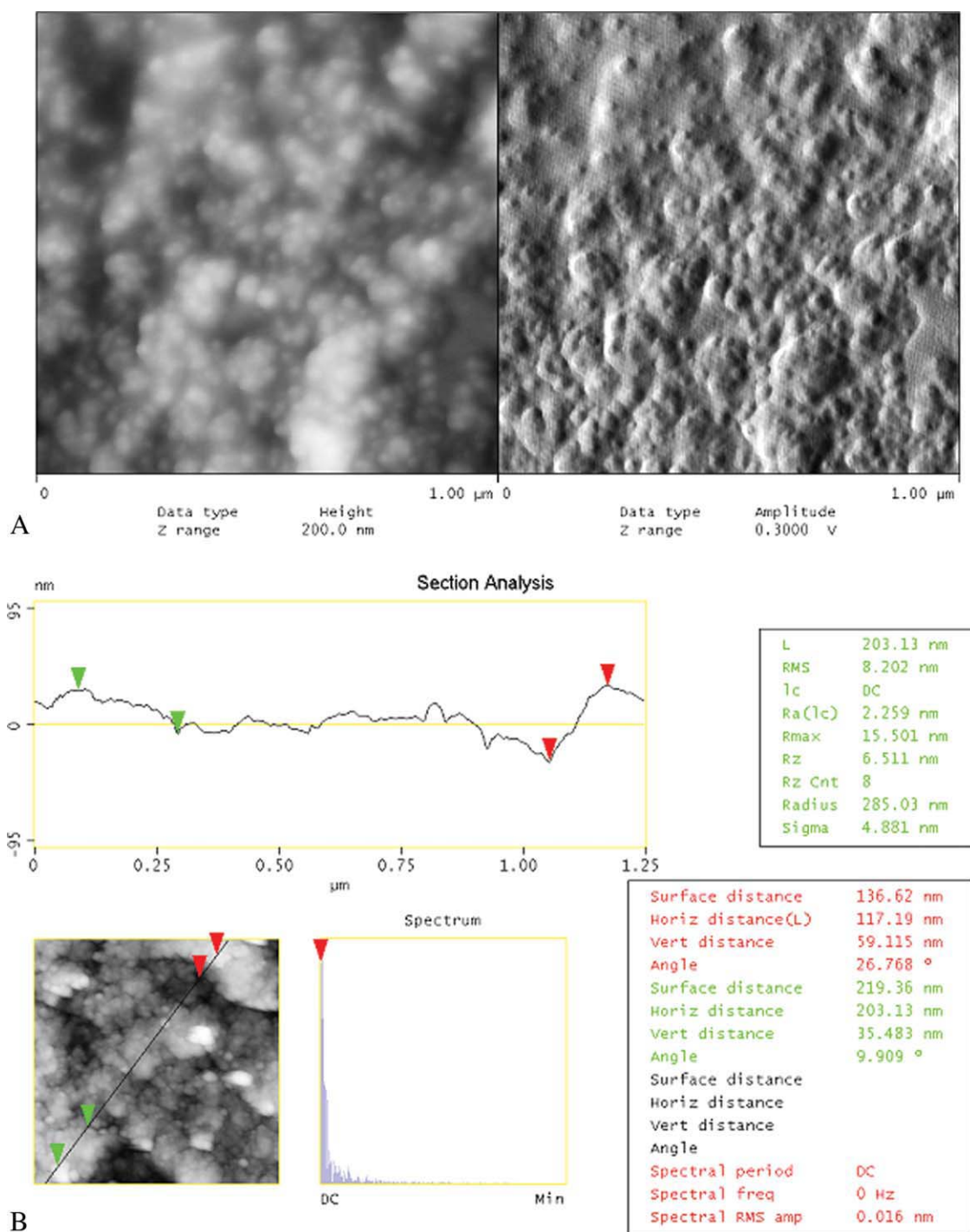


Figure 5 Contact-mode AFM images for the parent copolymer. (A) The fragment surface. (B) The section analysis. Magnification $\times 135,000$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SWELLING STUDIES

In Table IV, swelling properties of the studied copolymers are presented. The results of swellability coefficients for copolymer beads vary from 0 to 42%. For the copolymer obtained in synthesis No. 1 (33.3 mol % GMA and 66.7 BES.DM), the largest value is observed in THF (42%). In 1,4-dioxane, chloroform, acetonitrile, and acetone, its swellabilities vary from

18 to 31%. In alcohols, it swells significantly less while in nonpolar hexane and toluene, the lack of swelling is observed. Copolymer obtained in synthesis No. 6 generally swell less. It is especially visible for 1,4-dioxane and THF. In alcohols, its swelling is similar to that of copolymer obtained in synthesis No. 1. Only in acetonitrile, its swellability coefficient is higher.

TABLE VI
Results of Elemental Analysis Parent (BES.DM–GMA)
and Modified Copolymers with DETA and TETA

Copolymer	Epoxy group concentration (mmol/g)	Yield of modification (%)			Yield of modification (%)
		C	H	N	
1. BES.DM–GMA	1.40	62.21	6.39	–	97
2. BES.DM–GMA with DETA	–	60.33	7.29	5.08	99
3. BES.DM–GMA with TETA	–	58.99	7.01	6.45	99

From these data, one can see that with the decrease of BES.DM concentration in the copolymer swellability, coefficients generally decrease. It is known that decrease of polymer crosslinking degree causes increase of its swelling. In the case of BES-GMA copolymers, not only degree of crosslinking but also complicated chemical structure should be taken into consideration. In their chemical structures hydroxyl, ester, epoxide, and sulfide, functional groups are presented. The hydroxyl groups from BES.DM can interact with proton acceptors while sulfide atoms with proton donors. Epoxide groups coming from GMA are of proton acceptor character and these groups are the most readily accessible for solvent molecules. Additionally, both monomers deliver ester groups which should be treated as proton acceptors. It means that with the decrease of BES.DM concentration in copolymers chemical structure, their proton donor properties diminish. In consequence, in alcohols (solvent of proton donor properties), the copolymer with the lowest concentration of BES.DM swells the least.

Swelling coefficients for the modified copolymers are generally lower in all organic solvents. The maximum is achieved in THF (12%). A low value of swelling coefficient is needed when frequent changes of mobile phase during chromatographic analysis takes place.

POROUS STRUCTURE

In Table V, characterization of the porous structure of the BES.DM–GMA copolymers obtained by the nitrogen adsorption–desorption method is presented. From these data, one can see that copolymers with the highest concentration of BES.DM have the most developed porous structures.³⁴ The decrease of BES.DM concentration in the monomers mixture causes decrease of their specific surface areas and pore volumes. The largest specific areas and pore volumes are observed for the copolymers obtained in syntheses No. 1 and No. 2 (33.3 : 66.7 mol % GMA/BES.DM and 50 : 50 mol % GMA/BES.DM) while the copolymer obtained in synthesis No. 6 (85.8 : 14.2 mol % GMA/BES.DM) is rather non-

porous. Figure 4 presents pore size distributions for the porous samples of copolymers determined by nitrogen adsorption–desorption method. In their pore size distributions, single peaks are observed with the maximum resembling the most probable pore diameters. Among them, copolymers (synthesis 1 and synthesis 2) have the most narrow pore size distribution with the most probable pore diameters 360 and 350 Å, respectively. Pore size distribution of the copolymer after chemical modification is also monodisperse but it is the most probable pore diameters become larger.

AFM

The surface texture of the parent copolymer obtained in synthesis No. 2 is shown in Figure 5. It presents the contact-mode AFM images of the obtained materials in the two photos: Figure 5(A) shows a fragment of the surface of the studied copolymer whereas Figure 5(B) shows the section analysis of the surface fragment. The magnification of both photos is 135,000 \times . These photos confirm that the obtained copolymer has a developed structure. To obtain a measure of surface roughness on the nanometer scale, the AFM is used. Root mean square (RMS) [Fig. 5(B)] roughness of the obtained copolymer is about 8.202 nm. In our earlier studies, RMS was in the range from 0.200 to 22.031 nm. The value obtained for BES.DM–GMA is of the average level.

Modification

The samples of copolymers with the most developed porous structures were modified by amines: DETA or TETA in the epoxide ring-opening reaction. Modification efficiency was confirmed by elemental analysis (Table VI). For comparison, Table VI also contains the results for the starting copolymer. For both samples, high percentage concentration of nitrogen after modification was obtained. It means that these reactions run with high yields close to 100%. The high reactivity of epoxy groups makes these microspheres very engaging, e.g., biochemical modifications.

CONCLUSIONS

Synthesis, copolymerization, and properties of the new copolymers of BES.DM and GMA of different crosslinking degree in the form of microspheres are presented. The results show that the increase of BESDM—the crosslinking agent concentration affects their chemical and porous structures. Thermal resistance of the studied copolymers increased with increase of BESDM concentration. Swelling characteristics and

the epoxide content around 0.73–2.79 mmol of epoxy groups per gram make these copolymers very interesting for their further chemical modification.

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