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The highly crosslinked dimethacrylic/divinylbenzene copolymers

Characterization and thermal studies

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Abstract The series of highly crosslinked, hydrophilic stable spherical microspheres based on the new aromatic tetrafunctional methacrylate monomers and divinylbenzene (DVB) were prepared by emulsion–suspension polymerization in the presence of pore-forming diluents (toluene/decan-1-ol). The new monomers were generated by treatment of epoxides derived from various diphenols: naphthalene-2,7-diol (NAF-2,7) naphthalene-2,3-diol (NAF-2,3), bis(4-hydroxyphenyl)methanone (BEP) or 4,4′-thiodiphenol (BES), and epichlorohydrin with methacrylic acid. The copolymerization process of new methacrylate monomers with DVB was carried out at constant mole ratio of methacrylate monomers: DVB (1:1) and constant volume ratio of pore-forming diluents to monomers (1:1) using α,α′-azoisobisbutyronitrile (AIBN) as initiator. The effect of the structure of new methacrylate monomers on the surface appearance, porous structure, swelling behavior in polar, and non-polar diluents as well as thermal properties of obtained copolymer beads was evaluated. The obtained results confirmed that the monomer's structure considerably influenced on the microspheres characteristic. In general, higher swelling properties of dimethacrylic/divinylbenzene copolymers were observed in polar diluents due to the presence of polar groups: hydroxyl and ester groups in copolymer's structure. Moreover, both the swelling properties of dimethacrylic/divinylbenzene copolymers as well as thermal properties studied by DSC and TG analysis confirmed that diacrylic/divinylbenzene copolymers described in previous article were more crosslinked compared to those actually studied. It was attributed to the presence of additional groups (methyl groups) in dimethacrylic/divinylbenzene copolymer's structure and thus producing of more flexible polymeric networks due to the steric hindrance.

Keywords Copolymerization · Methacrylate monomers · Microspheres · Porous structure · Thermal properties

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Introduction

Among widely available polymer-based packing materials, the most popular are non-polar styrene–divinylbenzene (ST-DVB) copolymers. As these materials are highly hydrophobic, they possess rather restriction and specific applications. It seems to be decisive to incorporate more polar groups into polymer skeleton. It can be done by polymerization of monomers containing epoxy group with suitable crosslinker. Epoxy rings can be opened by attack of nucleophiles, so obtained copolymers are appropriate for further chemical modification.

The free-radical copolymerization of (meth)acrylate derivatives provides polymers with special chemical/physical properties, e.g., copolymers described by high thermal stability, porous structure, mechanical strength, and resistance to solvent absorption due to the presence of hydrophilic groups in the structure of obtained materials [1–10]. Such hydrophilic (wetting) copolymers are important materials of both fundamental and technological interest. Hydrophilic copolymers in spherical bead shape have attracted attention as carrier matrices in a wide variety of medical and biological applications, such as affinity chromatography, immobilization technologies, and drug delivery systems [11–13].

Due to the fact that the derivatives of aromatic diols and epoxides have been used in several applications and have a good physico-chemical properties, we used them for the synthesis of porous microspheres [14–18].

Therefore, the development of new techniques to synthesize highly crosslinked polymer particles as well as the searching of new, more hydrophilic monomers has been a subject of intensive research in porous polymer fields.

In this article, characterization and thermal properties of highly crosslinked, hydrophilic stable spherical microspheres based on the new aromatic tetrafunctional methacrylate monomers and divinylbenzene (DVB) prepared by emulsion–suspension polymerization in the presence of pore-forming diluents (toluene/decan-1-ol) were presented. The new monomers were generated by treatment of epoxides derived from various diphenols: naphthalene-2,7-diol (NAF-2,7) naphthalene-2,3-diol (NAF-2,3), bis(4-hydroxyphenyl) methanone (BEP) or 4,4′-thiodiphenol (BES), and epichlorohydrin with methacrylic acid. The influence of monomer's structure on surface appearance, porous structure, and swelling behavior in polar and non-polar diluents as well as thermal properties of obtained copolymer beads was evaluated. The results were compared to those obtained for diacrylic/divinylbenzene copolymer beads prepared in the same way and described in previous article [19].

Experimental

Materials

The new tetrafunctional methacrylate monomers were prepared according to [9, 10, 20, 21].

Bis(2-ethylhexyl)sulfosuccinate sodium salt (DAC,BP), decan-1-ol, tetrahydrofuran (THF), and methacrylic acid (M) were from Fluka AG (Buchs Switzerland). Bis(4-hydroxyphenyl)sulfide, α,α′-azoisobisbutyronitrile (AIBN), and divinylbenzene (DVB) were obtained from Merck (Darmstadt, Germany). DVB was washed with 3% aqueous sodium hydroxide before use. Reagent grade acetone, methanol, chloroform, toluene, sodium hydroxide, potassium hydroxide, and hydroquinone were from POCh (Gliwice, Poland).

Preparation of dimethacrylic/divinylbenzene copolymers

Two-component copolymers containing DVB and NAF-2,7.M (or NAF-2,3.M, or BEP.M or BES.M) were obtained in a suspension–emulsion copolymerization procedure. Copolymerization was carried out in a three-necked flask equipped with a stirrer, a water condenser, and a thermometer. The initiator AIBN (1.5 wt%) was dissolved in monomers, and then the mixture was diluted with a mixed solvent (toluene/decan-1-ol) taken in different proportions. The dispersion medium was prepared through the dissolution of 1 wt% bis(2-ethylhexyl)sulfosuccinate sodium salt (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 washing procedure was applied to remove the diluents and unreacted monomers from the products. The obtained microspheres (NAF-2,7.M-DVB, NAF-2,3.M-DVB, BEP.M-DVB, or BES.M-DVB) were thoroughly filtered out, dried, and extracted in a Soxhlet apparatus with boiling acetone and methanol.

Characterization

Porous structure of copolymers was investigated by nitrogen adsorption at 77 K using adsorption analyzer ASAP 2405 (Micrometrics Inc., USA). Before measurements, the copolymers were outgassed at 150 °C for 2 h. Specific surface areas were calculated by the BET method, assuming that the area of a single nitrogen molecule in the adsorbed state is 16.2 Å^2. Pore volumes and pore size distributions were determined by the BJH method.

The beads were also examined using an atomic force microscope, AFM Nanoscope III (Digital Instruments, USA) 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 swellability coefficients, B, were determined by equilibrium swelling in acetone, methanol, 1,4-dioxane, dichloromethane, isopropanol, and n-heptane using the centrifugation method [22, 23]. B is expressed as:

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

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

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Selb, Germany) operating in a dynamic mode. The dynamic scans were performed at a heating rate of 10 K min^{-1} at two temperature scans. The first scan was performed from 20 °C to a maximum of 110 °C to remove any adsorbed moisture. The second one was conducted between 20 and 500 °C under nitrogen atmosphere (30 mL min^{-1}). The mass of the sample was $\sim$10 mg. As a reference, an empty aluminum crucible was used. The glass transition temperature (T_g), decomposition temperature (T_d), and enthalpy of decomposition (ΔH_d) were evaluated.

Thermogravimetric analysis (TG) was carried out using a Paulik and Erdey derivatograph (Budapest, Hungary) at a heating rate of 10 °C min^{-1} in air, in the temperature range of 20–1,000 °C with the sample weight of 100 mg. As a reference α-Al_2O_3 was used. The initial decomposition temperature (IDT), $T_{20\%}$, $T_{50\%}$ of weight loss, the final decomposition temperature (T_{end}), and the temperature of the maximum rate of weight loss (T_{max}) were determined.

Results and discussion

Characterization of dimethacrylic/divinylbenzene copolymers

Scheme 1 presents the chemical structure of the aromatic dimethacrylate monomers and its copolymerization with divinylbenzene. The dimethacrylate monomers were generated by treatment of epoxides derived from various diphenols: naphthalene-2,7-diol (NAF-2,7) naphthalene-2,3-diol (NAF-2,3), bis(4-hydroxyphenyl)methanone (BEP), or 4,4′-thiodiphenol (BES) with epichlorohydrin. Next, the epoxide derivatives were reacted with methacrylic acid to obtain the dimethacrylic monomers: NAF-2,7.M, NAF-2,3.M, BEP.M, and BES.M, respectively. The highly crosslinked, hydrophilic copolymers beads were prepared during the emulsion–suspension polymerization of dimethacrylate monomers with DVB in the presence of pore-forming diluents. This process was performed at constant mole ratio of dimethacrylate monomers: DVB (1:1) and constant volume ratio of pore-forming diluents to monomers (1:1). The different concentrations of toluene in the mixture with decan-1-ol were used, but for further studies, the microspheres which were characterized by largest porous structure (obtained using 8 cm^3 of toluene and 8 cm^3 of decan-1-ol) were selected. The effect of the structure of methacrylate monomers on the surface appearance, porous structure, and swelling behavior in polar and non-polar diluents as well as thermal properties of obtained copolymer beads was evaluated.

The results shown in Tables 1 and 2 suggest that the surface characteristic and the porous structure of dimethacrylic/divinylbenzene copolymers have varied considerably depending

Scheme 1 Structure of dimethacrylate monomers and their copolymerization with DVB

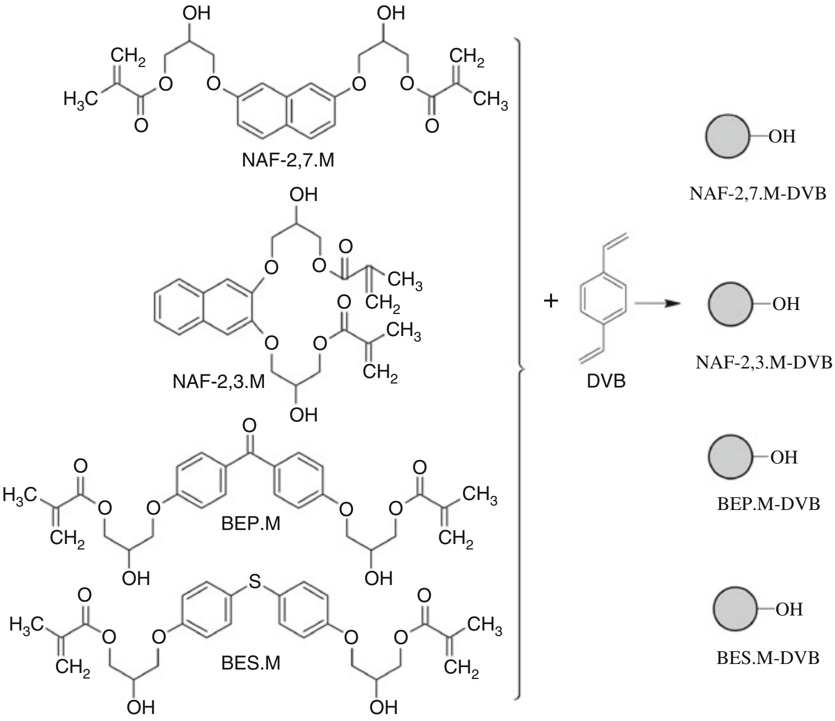

Table 1 Swelling studies for dimethacrylic/divinylbenzene copolymers

Copolymer	Swellability coefficient, *B* %				
	Acetone	Methanol	THF	Dichloromethane	Hexane
NAF-2,7.M-DVB	15	8	16	10	5
NAF-2,3.M-DVB	21	12	25	18	10
BEP.M-DVB	10	6	15	8	5
BES.M-DVB	25	27	28	20	12

Table 2 Parameters of the porous structure of the dimethacrylic/divinylbenzene copolymers obtained from BET methods

Copolymer	Specific surface area/m^2 g^{-1}	Pore volume/mL g^{-1}	Most probable pore diameter/Å
NAF-2,7.M-DVB	138	0.655	200
NAF-2,3.M-DVB	70	0.240	110
BEP.M-DVB	108	0.380	140
BES.M-DVB	163	0.530	130

on the employed diluent and the chemical structure of dimethacrylate monomers used. The significantly higher values of swellability coefficients (*B*) of the copolymers in polar diluents compared to those values obtained in non-polar hexane were achieved. It was directly connected with the presence of polar pendant functional groups (hydroxyl groups) as well as ester groups in copolymers structure. Moreover, the dimetacrylic/divinylbenzene copolymers were generally characterized by higher values of *B* in all solvents compared to diacrylic/divinylbenzene copolymers presented in previous article [19]. The presence of additional methyl groups (–CH_3) in dimetacrylic/divinylbenzene copolymer's structure probably caused the production of less rigid structure of those copolymers due to steric hindrance which resulted in increasing the swellability coefficient values (*B*). Moreover, the highest swelling in all solvents for NAF-2,3.M-DVB and BES.M-DVB copolymers indicated, that more developed porous structure comparing to NAF-2,7.M-DVB and BEP.M-DVB copolymers. The BET studies confirmed this supposition. The NAF-2,3.M-DVB and BES.M-DVB were characterized by higher specific surface area but lower average pore diameter compared to others (Table 2). It was probably connected with the presence of macro- and micropores in the structure of NAF-2,3.M-DVB and BES.M-DVB copolymers. The surface texture studies additionally performed by AFM confirmed that all dimethacrylic/divinylbenzene copolymers were porous materials (Fig. 1), but NAF-2,3.M-DVB and BES.M-DVB had more developed surface area compared to NAF-2,7.M-DVB and BEP.M-DVB which was clearly observed from AFM images.

Thermal properties of NAF-2,7.M-DVB, NAF-2,3.M-DVB, BEP.M-DVB, and BES.M-DVB copolymers were studied by means of DSC and TG analyses. The DSC was performed in a nitrogen atmosphere from 20 to 500 °C. The thermogravimetric analysis was conducted in air from 20–1,000 °C. The DSC curves of dimethacrylic/divinylbenzene copolymers were presented in Fig. 2. Additionally, the characteristic temperatures: T_g, T_d and the enthalpy of decomposition (ΔH_d) were given in Table 3. The DSC analysis showed similarity in thermal behavior for all prepared copolymers. The endothermic peaks at 418.0–431.7 °C with ΔH_d values from 36.1 to 161.3 J g^{-1} were connected with the thermal degradation of cross-linked microspheres. Moreover, the copolymers were characterized by rather high thermal stability, no endothermic decomposition peak until 250–300 °C was observed. The TG analysis confirmed those observations. The initial decomposition temperatures (IDT) for all copolymers were

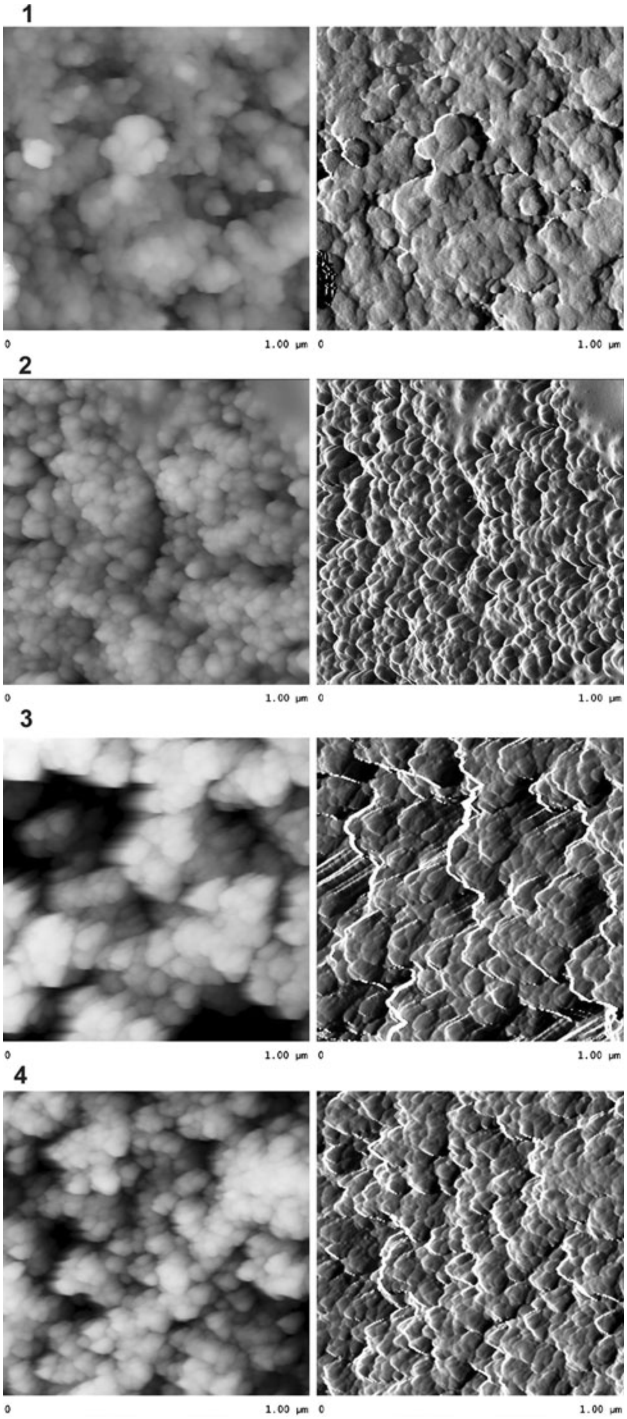

Fig. 1 Contact-mode AFM images of dimethacrylic/divinylbenzene copolymers: *1* NAF-2,7.M-DVB, *2* NAF-2,3.M-DVB, *3* BEP.M-DVB, and BES.M-DVB

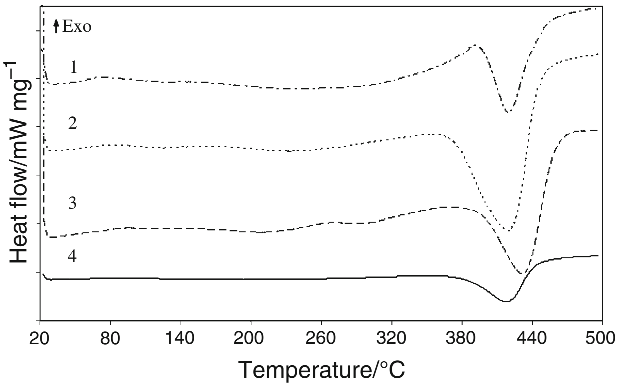

Fig. 2 DSC curves of dimethacrylic/divinylbenzene copolymers: *1* NAF-2,7.M-DVB, *2* NAF-2,3.M-DVB, *3* BEP.M-DVB, and BES.M-DVB

Table 3 DSC data for dimethacrylic/divinylbenzene copolymers

Copolymer	T_g/°C	T_d/°C	ΔH_d/J g^{-1}
NAF-2,7.M-DVB	97.5	419.7	57.9
NAF-2,3.M-DVB	98.0	419.2	161.3
BEP.M-DVB	118.1	431.7	116.4
BES.M-DVB	109.0	418.0	36.1

Table 4 TG and DTG data for dimethacrylic/divinylbenzene copolymers

Copolymer	IDT/ °C	$T_{20\%}$/ °C	$T_{50\%}$/ °C	T_{end}/ °C	T_{max1}/ °C	T_{max2}/ °C
NAF-2,7.M-DVB	280	360	430	780	360	575
NAF-2,3.M-DVB	260	380	420	860	380	595
BEP.M-DVB	240	380	480	900	400	580
BES.M-DVB	260	320	460	800	345	600

from 240 to 280 °C. The final decomposition temperatures (T_{end}) were in the range of 780–900 °C. The DTG curves contained two separated degradation steps. The maximum of the first decomposition peak (T_{max1}) was observed at 345–400 °C. The second decomposition stage (T_{max2}) took place at 575–600 °C (Table 4). The first decomposition peak could be associated with the ester bonds breakdown in copolymers, the second one could be attributed to the total degradation of copolymers. The IDT and T_{end} temperatures were generally lower for studied dimethacrylic/divinylbenzene copolymers compared to those values observed for diacrylic/divinylbenzene copolymers [19], which was connected with higher elasticity and thus lower crosslinked density of obtained polymer networks due to the steric hindrance of the presence of additional groups (methyl groups) in copolymer's structure.

Conclusions

- The characterization and thermal properties of highly crosslinked, hydrophilic stable, and spherical microspheres based on the new aromatic tetrafunctional methacrylate monomers and divinylbenzene (DVB) were presented.
- The emulsion–suspension copolymerization process of dimethacrylate monomers with DVB in the presence of pore-forming diluents (toluene + decan-1-ol) allowed to obtain more hydrophilic microspheres due to the presence of ester and hydroxyl groups in their structure.
- Based on the performed analyses, it was confirmed that the structure of used methacrylate monomers had a significant influence on the surface appearance, porous structure, and swelling behavior in polar and non-polar diluents as well as thermal properties of obtained copolymer beads.
- Higher swelling properties of dimethacrylic/divinylbenzene copolymers were observed in polar diluents due to the presence of polar groups: hydroxyl and ester groups in copolymer's structure. Moreover, more developed porous structure and thus higher swelling properties were observed for copolymers obtained in the presence of BES.M-DVB and NAF-2,3.M-DVB which was connected with their chemical structure.
- Both the swelling properties of dimethacrylic/divinylbenzene copolymers as well as thermal properties studied by DSC and TG analysis, confirmed that diacrylic/divinylbenzene copolymers described in previous article [19] were more crosslinked compared to those actually studied. It was attributed to the presence of additional groups (methyl groups) in dimethacrylic/divinylbenzene copolymer's structure and thus producing more flexible polymeric networks due to the steric hindrance.

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