

Studies on Synthesis and Physicochemical Properties of New Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide Terpolymers

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ABSTRACT: Synthesis and physicochemical properties of the new glycidyl methacrylate, styrene, and bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide terpolymers of different crosslinking degrees are presented. The terpolymers were obtained in the form of regular microspheres by suspension polymerization. The epoxy group content, thermal properties (DSC, thermogravimetric analysis), and swelling

characteristic of the functional microspheres were examined. In addition, a selected terpolymer was modified in the epoxide ring opening reaction with diethylenetriamine. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 59–65, 2012

Key words: glycidyl methacrylate; terpolymers; microbeads; thermal properties; swelling

INTRODUCTION

Rapid development of technology creates a great demand for new materials. Polymers are among the most pervasive ones. The ubiquity of polymeric materials is not only a consequence of their easy processing but also because of their versatility. By adjusting the chemical structure of monomers and polymerization conditions, it is possible to formulate materials with a huge variety of physical properties from hydrogels to hypercrosslinked adsorbents.^{1–5} Morphology of the microspheres depends on the initial state of polymerization mixture, kinetics of polymerization, and mechanism of particle formation. Incorporation of tetrafunctional monomers into polymerization mixture allows to obtain crosslinked copolymers.^{6,7} These copolymers exhibit different structures and properties depending on the amount of the crosslinker and the diluent present during the reaction and on the salvation power of diluent.^{8–10} Applications of the polymeric materials are strongly connected with their structure and properties. For example, microbeads for cell culture must be soft, transparent to visible light, and relatively large (above 150 μm) with a narrow size distribution. On the contrary, microspheres applied in liquid chromatography are more effective when they are relatively small and rigid. In the medical field, a significant group of func-

tional materials are hydrogels. They resemble natural living tissue more than any other class of synthetic biomaterials. They are soft and have a reasonable mechanical strength. High water content is responsible for high diffusivity of small molecules. They have been widely used in controlled drug release materials, cell encapsulation, contact lenses, burn wounds dressings, artificial cartilages, or membranes.^{11,12}

Recently, macroporous copolymers of bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]sulfide and glycidyl methacrylate were synthesized.¹³ They are characterized by high crosslinking degree and developed porous structure.

In this article, we present new three-component glycidyl methacrylate terpolymers of different crosslinking degrees. Considerable thermal stability, good swelling characteristics, and loading capacities from 0.26 to 1.3 mmol of epoxy groups per gram make these terpolymers interesting for their further chemical modification. The selected terpolymer was modified in the epoxide opening reaction with diethylenetriamine. The structure of the terpolymer before and after modification was confirmed by Fourier transform infrared (FTIR) analysis.

EXPERIMENTAL

Chemicals and eluents

Glycidyl methacrylate (GMA), styrene, decan-1-ol, and tetrahydrofuran (THF) were from Fluka AG (Buchs, Switzerland). α, α' -azoisobutyronitrile (AIBN) and poly(vinyl pyrrolidone) (PVP; K90) were obtained from Merck (Darmstadt, Germany). Reagent grade acetone, methanol, propan-2-ol, chlorobenzene, chloroform,

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TABLE I
Experimental Parameters of the Syntheses of Obtained Terpolymers

Terpolymer	Ratio of monomers (mol %)			Epoxy group content (mmol/g)	
	GMA	BES.M	S	Calculated	Determined
1	20	3	77	1.60	1.30
2	20	5	75	1.52	1.23
3	20	10	70	1.32	0.85
4	20	15	65	1.17	0.44
5	20	20	60	1.05	0.29
6	20	30	50	0.87	0.26

hexane, toluene, THF methyl methylene 1,4-dioxane were from POCh (Gliwice, Poland). Bis[4(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulfide (BES.M) was obtained by procedure described in our previous work.¹⁴

Synthesis of terpolymers

Terpolymers containing glycidyl methacrylate, styrene, and BES.M were obtained as microbeads in a typical suspension copolymerization procedure. Experimental parameters of the syntheses of the GMA terpolymers are presented in Table I.

The dispersion medium was prepared through the dissolution of 1 wt % PVP in deionized water, and it was used in a 1/5 (w/w) ratio according to the organic phase. Syntheses were performed 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 1/1 (w/w) proportions. The reaction mixture was stirred at 350 rpm for 12 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. The dry terpolymers were fractionated with sieves. The applied polymerization conditions yielded about 75% beads in the range of 80–170 μm .

Epoxide ring opening reaction

The selected terpolymer (terpolymer 1) was modified in the epoxide ring opening reaction with an excess of diethylenetriamine.

In a 250-cm³ round-bottomed two-necked flask equipped with a mechanical stirrer and a thermometer, 10 g of selected beads (terpolymer 1) was placed together with diethylenetriamine (10 excess for epoxide group) and 200 mL of toluene, and the whole content was heated in 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.

Characterization of the terpolymers

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

The beads were examined using an atomic force microscope (AFM), AFM Nanoscope III (Digital Instruments, USA) 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.

The epoxy group content in the microspheres was determined by the HCl/dioxane method.¹⁵

The calorimetric measurements were performed 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. First scan was performed from 20°C to a maximum of 110°C to remove any adsorb moisture. The second one was conducted between 20 and 500°C under nitrogen atmosphere (30 $\text{mL}\cdot\text{min}^{-1}$). The mass of the sample was ~ 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 performed on a Paulik and Erdey derivatograph (Budapest, Hungary) at a heating rate of 10°C $\cdot\text{min}^{-1}$ in air, in the temperature range of 20 to 1000°C with the sample weight of 100 mg. As a reference, $\alpha\text{-Al}_2\text{O}_3$ was used. The initial decomposition temperature (IDT), $T_{20\%}$, $T_{50\%}$ of weight loss, final decomposition temperature (T_{end}), and the maximum rate of weight loss (T_{max}) were determined.

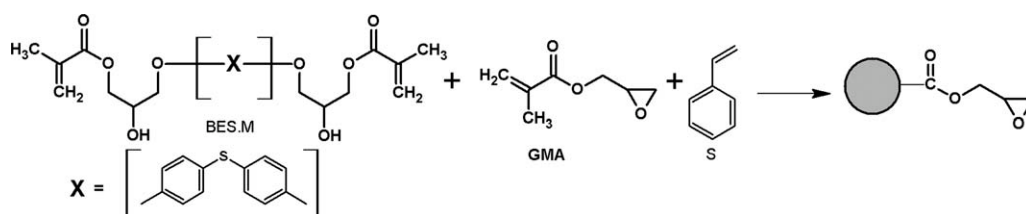


Figure 1 Scheme of synthesis of the studied terpolymers.

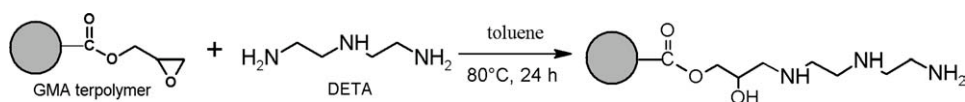


Figure 2 Scheme of the chemical modification of the obtained terpolymers with diethylenetriamine (DETA).

The swellability coefficients, B , are determined by equilibrium swelling in acetone, methanol, propan-2-ol, dichloromethane, acetonitrile, chloroform, toluene, hexane THF, and 1,4-dioxane using the centrifugation method.^{16,17} 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, V_d is the volume of the dry copolymer.

In addition, the swelling process was controlled using an optical microscope Motic (USA). Elementary analysis of the modified copolymers was performed using the Perkin-Elmer CHN 2400 apparatus.

RESULTS AND DISCUSSION

Preparation of polymeric microspheres

Polymeric microspheres are mainly produced by heterogeneous free radical polymerization. There are four main types of heterogeneous polymerization: emulsion, suspension, dispersion, and precipitation polymerization. Among them, suspension polymerization is particularly suited to formation of both crosslinked microspheres and as three-component terpolymers. In our work, six types of GMA resin were obtained by suspension polymerization. The process was performed at constant concentration of functional monomer and increasing amount (from 3 to 30 mol %) of the crosslinker. BES.M was used as a crosslinking agent. Styrene was applied to dilute epoxy groups in the resin. Chemical structures of the studied monomers and copolymer are presented in Figure 1. The epoxy group content in the microspheres was determined by the HCl/dioxane method described in literature.¹⁵ The loading capacities of the terpolymers were 30–81% of the values calculated from the monomer composition.

They strongly depended on the amount of the crosslinker (Table I). The difference increased with the increasing of BES.M in the monomer mixture. In the case of highly crosslinked polymers, some internal epoxy groups are not available for HCl molecules.

Modification

In addition, chemical modification with diethylenetriamine was performed. The scheme of the modification is shown in Figure 2. During the elementary analysis of the modified copolymer, the content of nitrogen was found to be equal to 5.29% (Table II). High percentage of nitrogen in the obtained product indicates the high yield of epoxide ring opening reaction (97%).

AFM studies

The surface texture of the studied terpolymer (3% mol. BES.M, 77% mol. S, and 20% mol. GMA) is shown in Figure 3. It presents the contact-mode AFM images of the obtained material in the two photos: A, shows a fragment of the surface of the studied terpolymer; B, section analysis of the fragment of the surface. Magnification of both photos is 135,000 \times . From these photos, one can see that the obtained terpolymer is characterized by a developed structure.

FTIR spectroscopy

FTIR of terpolymers

The FTIR data of the new terpolymers are listed in Table III. In the spectra of the studied terpolymers, 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 906 cm^{-1} . The aromatic skeletal absorption

TABLE II
The Results of the Modification of Terpolymer in the Reaction with Amine

Crosslinker % mol	Epoxy group content in parent terpolymer (mmol/g)	Terpolymer modified with diethylenetriamine		
		N		Degree of modification (%)
		(mmol N/g)	(%)	
3	1.30	3.80	5.29	97

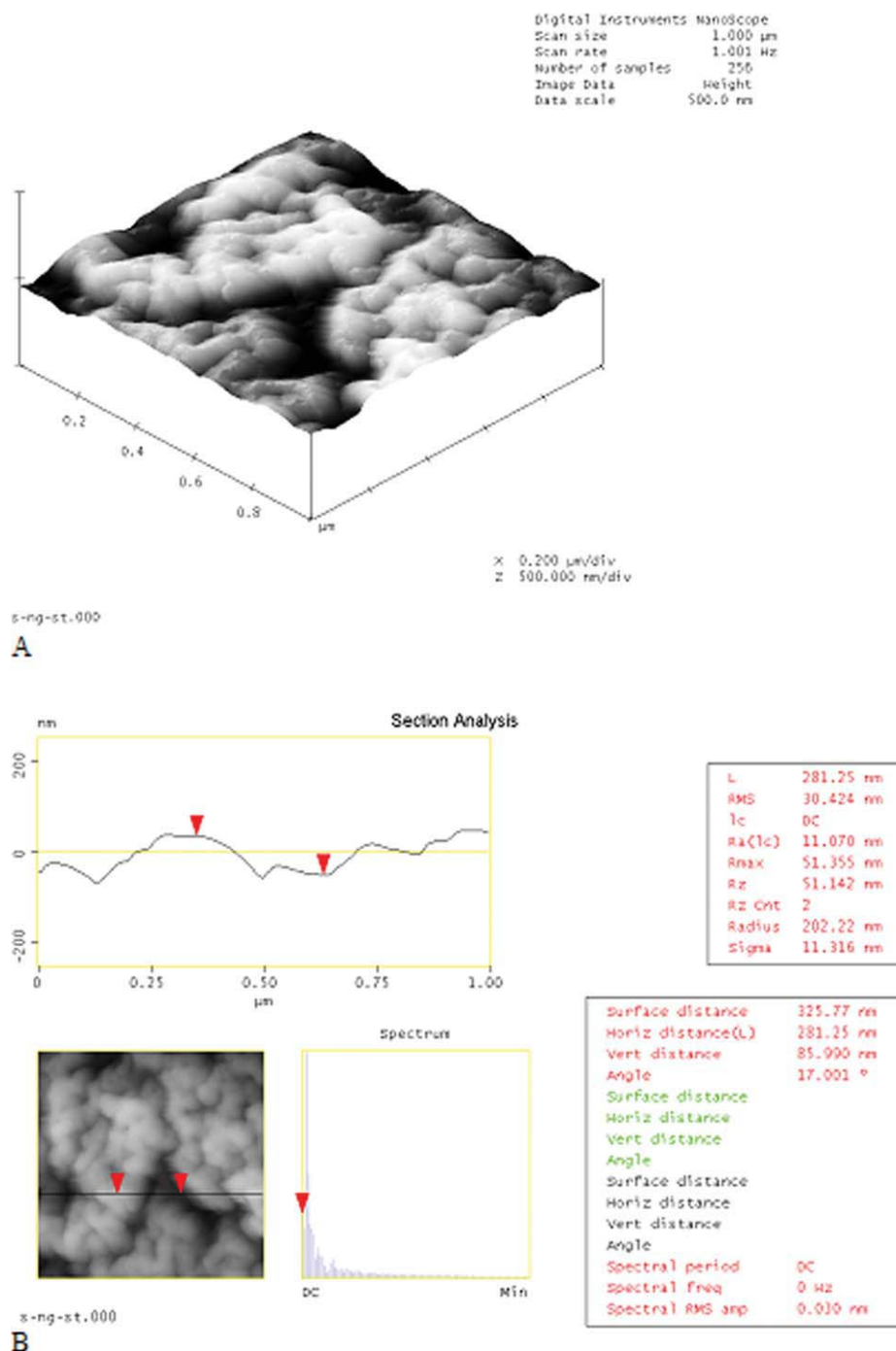


Figure 3 Contact-mode AFM images. (A) A fragment of surface. (B) Section analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is observed at about 1600 cm^{-1} . In the spectra vibrations of $-\text{OH}$ group are visible at about 3500 cm^{-1} . The signal of $\text{C}=\text{O}$ group occurs at approximately 1730 cm^{-1} .

FTIR of the modified terpolymer






FTIR spectra of the parent and modified terpolymer are presented in Figure 4. Generally, similar signals are present in both spectra. However, for the modi-

fied terpolymer, the disappearance of the bands characteristic of epoxy groups (906 cm^{-1}) was observed. It confirms the planned course of reaction.

Swelling studies

In rigid, glassy polymers, the process of diffusion of even small particles is difficult. Polymer chains are in close contact with each other. The interaction of polymers with solvents changes their internal

TABLE III
FTIR Spectra of Obtained Terpolymers

Terpolymer	/cm ⁻¹ /					
						
1	1600	3502	907	1728	3059; 2923	
2	1592	3480	906	1728	3059; 2924	
3	1592	3481	906	1728	3082; 2925	
4	1591	3462	905	1730	3082; 2922	
5	1591	3462	906	1729	3059; 2927	
6	1592	3447	906	1724	3059; 2926	
1 after modification with amine	1601	3480	—	1725	3059; 2922	

structure. Swellability is the main factor that determines access to the internal functional group.¹⁸ The ability to swell causes increase in the volume of polymer beads (Fig. 5) and network flexibility. These processes allow molecules to penetrate and chemically explore the whole polymer network. In Table IV, swelling properties of the studied terpolymers are presented. The swellability coefficient is a function of the solvent nature and composition of the terpolymers. The values of swellability coefficients for

terpolymers beads vary from 2 to 221%. Their largest values are observed for the product of lowest crosslinking degree (terpolymer 1) in THF (220%), chloroform (221%), and dichloromethane (131%). Along with the increase of the degree of crosslinking (up to 30% of crosslinker), the swellability coefficients decrease to 105, 30, and 64% for the THF, chloroform, and dichloromethane, respectively. In nonpolar hexane, terpolymers swell to a small extent. These results show that larger swelling occurs when polymeric network can interact with the solvents containing suitable polar groups. Solvents of proton-donor and proton-acceptor character interact specifically with ester and secondary hydroxyl functional groups present in the chemical structure of the terpolymers. These results indicate that larger swelling is observed for nonpolar solvents for terpolymer crosslinked in lower degree.

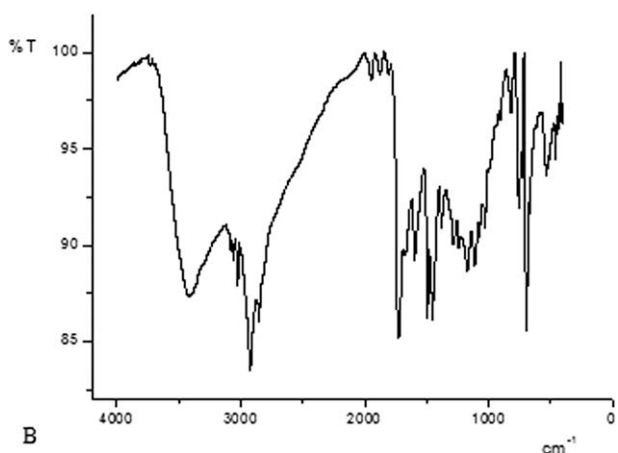
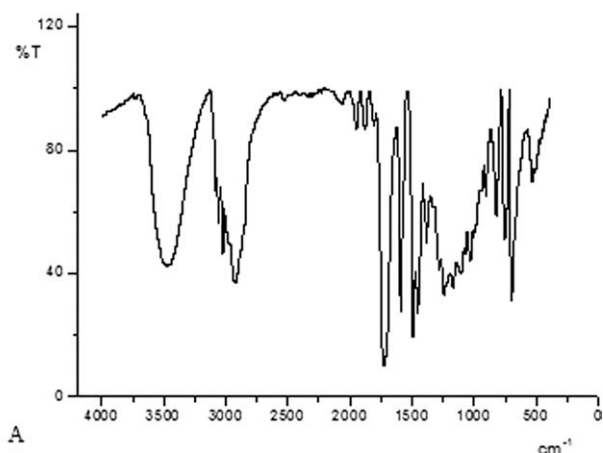


Figure 4 FTIR spectra of the parent (A) and modified (B) terpolymer.

Thermal properties

DSC analysis

Thermal properties of the obtained copolymers were studied by means of DSC and TG analyses. The DSC was performed in a nitrogen atmosphere from 20 to 500°C. TG was conducted in air from 20 to 1000°C. The DSC curves of acrylate copolymers are presented in Figure 6. In addition, the characteristic temperatures: T_g , T_d , and the enthalpy of decomposition (ΔH_d) are given in Table V. DSC analysis showed similarity in thermal behavior of all prepared copolymers. They had a characteristic, well-shaped calorimetric profile, revealing two nondistributed asymmetrical peaks. The first, exothermic peak (T_1), which started at about 320°C, can be attributed to the additional double bonds copolymerization. The endothermic peaks at 410–421°C can be connected with the thermal degradation of microspheres.¹⁹ The enthalpy of decomposition (ΔH_d) values range from 159 to 441 J·g⁻¹ depending on the amount of the crosslinker used during synthesis. The higher the degree of crosslinking, the higher the thermal stability, and consequently a lower value of

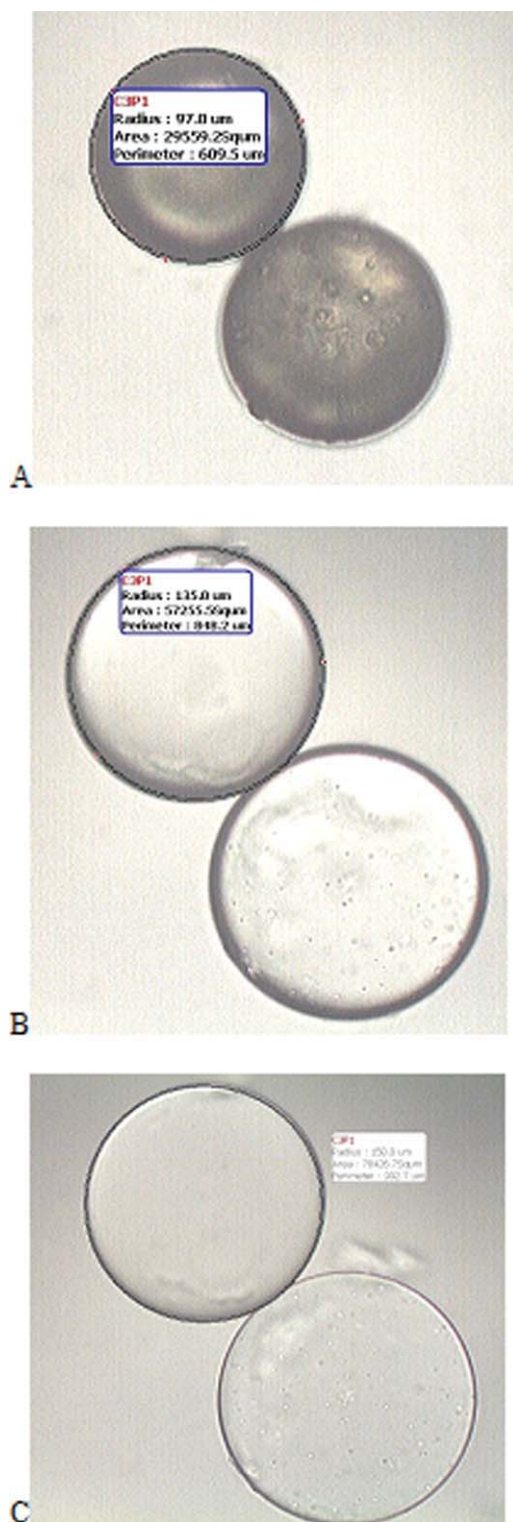


Figure 5 Swelling process. (A) Dry terpolymer 3. (B) Terpolymer 3 in acetone. (C) Terpolymer 3 in 1,4-dioxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ΔH_d . Although all of the obtained copolymers possess thermal stability, no endothermic decomposition peak until 320°C was observed. The attempts to determine glass transition (T_g) for the terpolymers

TABLE IV
Swelling Studies

Solvent	Swellability coefficient, B (%)					
	Terpolymer					
	1	2	3	4	5	6
Acetone	50	53	60	68	72	84
Methanol	20	13	17	21	30	64
Dichloromethane	131	89	57	55	60	62
Acetonitrile	4	6	14	27	61	64
Chloroform	221	105	90	65	38	30
Toluene	18	10	9	8	5	4
Hexane	2	3	4	6	8	11
THF	220	181	156	138	122	105
1,4-Dioxane	182	170	86	36	29	20

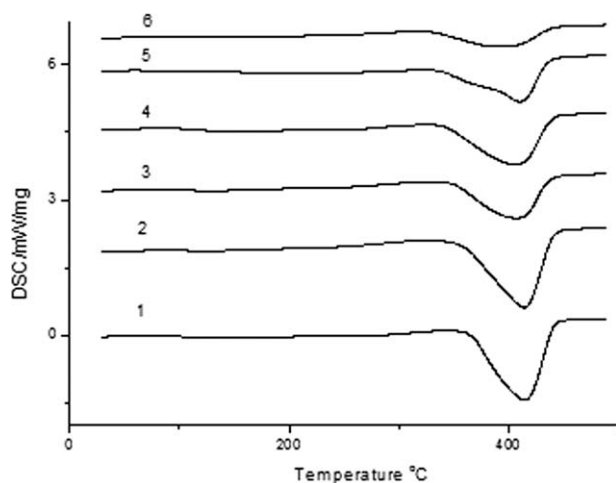


Figure 6 DSC curves of the obtained terpolymers (numbering according to Table I).

TABLE V
DSC Data of Thermal Behaviour of Obtained Terpolymers

Terpolymer	T_g (°C)	T_1 (°C)	T_d (°C)	ΔH_d / (J·g ⁻¹)
1	104	350	421	441.4
2	—	324	416	414.4
3	—	330	412	286.9
4	—	331	411	357
5	—	328	415	284
6	—	320	410	159

TABLE VI
TG and DTG Data of the Thermal Degradation

Terpolymer	IDT (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_{end} (°C)	T_{max1} (°C)	T_{max2} (°C)
1	270	310	360	605	380	550
2	280	340	365	610	370	560
3	300	340	370	620	380	570
4	300	360	380	640	380	570
5	300	350	380	660	390	580
6	305	360	385	680	390	595

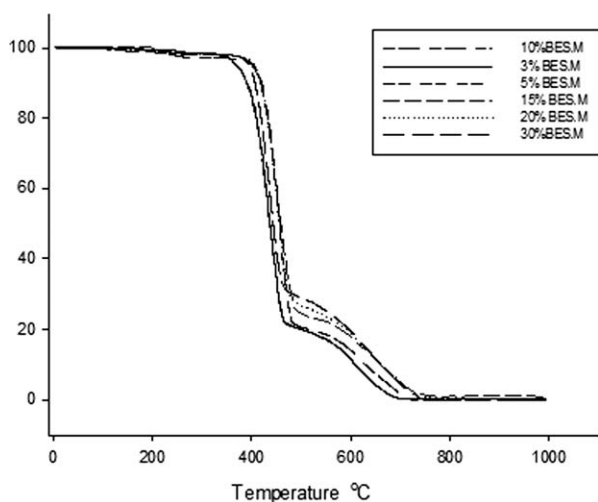


Figure 7 TG curves of the terpolymers.

were also undertaken. T_g is defined as the temperature at which a polymer changes from a hard rigid glass to a rubber-like state. The transition is accompanied by a large increase in diffusivity of small molecules and by a possibility of motion of polymer segments of 20–30 C-atoms. For the crosslinked polymers, the movement of chains is limited. They are bond together in a three-dimensional network. In the case of our three-component terpolymers, the T_g was found only for the product obtained in the presence of 3% of crosslinker, and its value (104°C) is close to the T_g of polystyrene (100°C).

Thermogravimetric analysis

The IDT for all copolymers were from 270 to 305°C. The final decomposition temperatures (T_{end}) were in the range of 605–680°C. The DTG curves contained two separated degradation steps. The first decomposition peak was observed in the range of 280–420°C with the maximum of weight loss (T_{max1}) at 380–390°C. The second decomposition stage took place between 460 and 660°C with T_{max2} at 550–595°C (Table VI). The first decomposition peak could be associated with the ester bonds breakdown in copolymers, and the second one could be attributed to the total degradation of copolymers.¹⁹ TG curves of the studied terpolymers are presented in Figure 7.

CONCLUSIONS

The new glycidyl methacrylate, styrene, and BES.M terpolymers were synthesized using suspension polymerization. They were obtained in the form of regular microspheres of different crosslinking degrees. The obtained results indicate that the increase of BES.M—the crosslinking agent—concentration affects their physicochemical properties. Thermal resistance of the studied terpolymers increased with the increasing BES.M concentration. The dependence of crosslinking degree on the epoxy group content in the terpolymers followed a different pattern. Along with the increasing concentration of crosslinker in the monomers mixture, the amount of epoxy group decreased significantly from 1.30 to 0.23 mmol/g. The terpolymer with the highest value of epoxy group was functionalized with diethylenetriamine. The high yield of the epoxide ring opening reaction (97%) makes it interesting for further use in biochemical applications.

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