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Synthesis and thermal properties of parent and modified DMN–*co*-GMA copolymers

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Abstract

The porous copolymers of 2,3-epoxypropyl methacrylate (GMA) cross-linked with 1,4-di(methacryloyloxy methyl)-naphthalene (DMN) were prepared in the form of regular microspheres by suspension–emulsion polymerization. The value of specific surface area varied from 106 to 42 $m^2\ g^{-1}$ depending on the molar ratio of functional monomer to cross-linker. In the next step, the porous methacrylate network was modified by subsequent reaction with pyrrolidone. After the process of modification, a significant drop in the value of specific surface area was observed. The thermal behavior of the parent and modified materials was studied using TG/DSC/FTIR methods. It was found that the process of modification also considerably changed the thermal properties of the polymers. The initial temperature of decomposition increases from 269 °C for parent DMN–GMA1 copolymer to 274 °C for modified DMN–GMA + P. At the same time, the final decomposition temperature increases from 521 to 621 °C.

Keywords Porous polymers · Microstructure · Thermal properties · TG/DSC/FTIR

List of symbols

D_{BJH}	Pore diameter (Å)
FDT	Temperature of final decomposition (°C)
IDT	Initial decomposition temperature (°C)
S_{BET}	Specific surface area ($m^2\ g^{-1}$)
T_{1max}	Temperature of the first maximum rate of mass loss (°C)
T_{2max}	Temperature of the second maximum rate of mass loss (°C)
$T_{20\%}$	Temperature of 20% mass loss (°C)
$T_{50\%}$	Temperature of 50% mass loss (°C)
DMN–*co*-GMA1	The parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:1
DMN–*co*-GMA2	The parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:2
DMN–*co*-GMA3	The parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:3
DMN–*co*-GMA4	The parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:4
DMN–*co*-GMA5	The parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:5
DMN–*co*-GMA1 + P	The copolymer modified with pyrrolidone, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:1
DMN–*co*-GMA2 + P	The copolymer modified with pyrrolidone, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:2
DMN–*co*-GMA3 + P	The copolymer modified with pyrrolidone, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:3
DMN–*co*-GMA4 + P	The copolymer modified with pyrrolidone, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:4

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DMN–*co*-GMA5 + P	The copolymer modified with pyrrolidone, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:5
V	Pore volume (cm^3 g^{-1})

Introduction

Polymeric adsorbents with highly developed internal structure have several strategic advantages over other porous materials like carbons, silica gels, or MOFs. For their synthesis, different reactions can be used, and they are insensitive to ambient air, easier to handle, and mechanically more stable. The broad range of available monomers enables their flexible functionalizations. In consequence, they have been the subject of intensive scientific research [1–10]. The traditional, but still exhaustively explored, polymeric adsorbent is macroporous polystyrene-divinylbenzene (PS-DVB). Due to its hydrophobic nature, PS-DVB interacts with analytes basically through van der Waals forces and the Π–Π interactions of the aromatic rings that make up the sorbent structure. The hydrophobic interactions with the adsorbates can lead to low adsorption capacity. This difficulty could be largely overcome by introducing polar functional groups into the adsorbent matrix. This purpose can be achieved by direct synthesis of polar adsorbents from a balanced ratio of a hydrophilic monomer and a cross-linker and the chemical modification of hydrophobic polymer skeleton with a suitable polar moiety. Polar monomer promotes hydrophilic interactions and favors interactions with water, whereas cross-linking agent increases the specific surface area, thermal and mechanical resistance and promotes hydrophobic interactions. As polar monomers, acrylonitrile [11, 12], methacrylonitrile [13], cyanomethyl styrene [14], N-vinylimidazole [15], 4-vinylimidazole [16], 1-vinyl-2-pyrrolidone [17], 2-hydroxyethyl methacrylate [18], 4-vinylpyridine [19–21] are commonly used. Among cross-linking agents, divinylbenzene holds the prominent position. More polar cross-linkers from methacrylate family are also commercially available, but they are mainly aliphatic ones (e.g., ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate) and do not provide considerable thermal resistance [3, 22].

The aim of this study was to obtain polar copolymers with good thermal characteristics. For this purpose, aromatic 1,4-di(methacryloyloxy methyl)naphthalene was applied as cross-linker. In the next step, the porous methacrylate network was modified by subsequent reaction with pyrrolidone. Pyrrolidone was chosen for modification process, because it contains a highly polar amide group conferring hydrophilic and polar-attracting properties and also apolar methylene groups in the backbone and the ring, conferring hydrophobic properties. Due to its nontoxicity, biocompatibility and good complexing properties for ionic or Π-electron system polymers based on pyrrolidone are widely used in different fields: beauty, textile and chemical industry, pharmacy, medicine. Despite the diverse properties in a single material, direct synthesis of VP-based copolymers is not a simple task. This is caused by the fact that radical copolymerizations involving VP are usually characterized by low value of reactivity ratios r_{VP}. In most cases, they approximately equal zero. Consequently, VP and the most available monomers do not copolymerize well. To overcome this drawback, the modification of polymer matrix containing reactive epoxy ring was carried out.

Experimental

Chemicals

2,3-Epoxypropyl methacrylate (GMA) was washed with 5% aqueous sodium hydroxide in order to remove inhibitors. Bis(2-ethylhexyl) sulfosuccinate sodium salt (DAC,BP), α,α′-azoisobutyronitrile (AIBN), and pyrrolidone were purchased from Fluka AG (Buchs, Switzerland), and were used without purification. Toluene, *n*-dodecane, acetone, and methanol (reagent grade) were from POCh (Gliwice, Poland). Diethylenetriamine was purchased from Sigma-Aldrich. 1,4-Di(methacryloyloxy methyl)naphthalene (DMN) was obtained in our laboratory according to the procedure described elsewhere [23–25].

Preparation of the GMA-*co*-DMN microspheres

Copolymerization was performed in an aqueous suspension medium. In order to dissolve the surfactant, 195 mL of distilled water and 2.2 g of bis(2-ethylhexyl)sulfosuccinate sodium salt were stirred for 2 h at 80 °C. Then, the solution containing 15 g of monomers (GMA and DMN), and 0.2 g of α,α′-azoisobutyronitrile dissolved in 22.5 mL of toluene was prepared and added while stirring to the aqueous medium. Molar ratios of GMA to TRIM were changed from 1:1 to 5:1. Copolymerization was performed for 20 h at 80 °C. Porous beads formed in this process were filtered off, and an extensive cleaning procedure was applied in order to remove the diluent unreacted monomers and physically adsorbed stabilizer. The cleaning process was as follows: The microspheres were separated from the aqueous phase by filtration of the polymerization mixture by 5-μm filter papers. The microspheres were first washed with water, and the polymeric aggregates were removed by sieving. The microspheres were dispersed in water, and the dispersion was sonificated for 0.5 h in an ultrasonic bath. Next, the water phase was removed and the microspheres were resuspended in methyl alcohol. This dispersion was sonificated for 1 h. Methyl alcohol was removed, and the microspheres were transferred into toluene and were kept there by stirring for about 0.5 h. Then, the toluene was removed and microspheres were stirred with methyl alcohol for about 0.5 h. Methyl alcohol was removed, and the microspheres were washed with distilled water, filtered and dried in vacuum oven at 65° for 48 h.

Modification of the epoxy groups

The epoxy groups present in the copolymer were modified during the reaction with pyrrolidone. The procedure was as follows: In a 250-cm^3 round-bottomed two-necked flask equipped with a mechanical stirrer and a thermometer, 10 g of selected beads was placed together with the excess of pyrrolidone and left for 24 h to swell. Then, the whole content was heated at 150 °C for 8 h. The obtained modified beads were washed with distilled water, filtered off, and cleaned as described above.

Methods of analysis

Textural characterization of the copolymers was carried out by the low-temperature nitrogen adsorption–desorption method. Nitrogen adsorption–desorption isotherms were obtained at the liquid nitrogen temperature using a volumetric adsorption analyzer ASAP 2405 (Micromeritics Inc., USA). The measurements of the porous structure of the copolymers were preceded by outgassing of the samples at 140 °C for 2 h. The specific surface area of the investigated samples was calculated by the Brunauer–Emmett–Teller (BET) method for the adsorption data in the range of a relative pressure *p*/*po* 0.05–0.25. The total pore volume was estimated from a single-point adsorption at a relative pressure of 0.985. The pore size was obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) procedure. The surface of the obtained beads was also examined using an atomic force microscope (AFM), AFM Nanoscope III, Digital Instruments, operating in contact mode and scanning microscope Phenom Word, FEI.

The thermal properties of the synthesized composites were evaluated on the basis of measurements taken using the STA449, F1 Jupiter analyzer from Netzsch (Günzbung, Germany). The procedure was as follows: About 10 mg of the sample was placed in the TG pan and heated in helium or in air atmosphere at a rate of 10 K min^{-1} up to 1000 °C with the sample mass of about 10 mg. The initial decomposition temperature (IDT), $T_{20\%}$, $T_{50\%}$ of mass loss, and the final decomposition temperature (FDT) were determined.

The gaseous decomposition products formed under the degradation of functionalized copolymers were analyzed by means of a FTIR spectrometer TGA 585 Bruker (Germany) coupled online to a STA instrument by a Teflon transfer line. Each FTIR spectrum was gathered every 10 °C in the spectral range from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Calorimetric measurements were taken with the Netzsch DSC 204 calorimeter (Germany) operating in the dynamic mode. The dynamic scans were performed at the heating rate of 10 K min^{-1} from room temperature to the maximum of 500 °C under argon (30 mL min^{-1}) atmosphere. The mass of the sample was about 10 mg. As a reference, an empty aluminum crucible was used.

Results and discussion

Porous copolymers of poly(DMN–*co*-GMA) used in this study were synthesized through suspension; modified suspension polymerization was used. In this technique, stabilizers of high molecular weights typical for suspension polymerization were replaced by an anionic surfactant. The surfactant exceeded the critical micelle concentration (cmc). As a result, regular microspheres with diameters in the range of 20–50 μm were formed (Fig. 1).

During the synthesis, DMN served as a cross-linker and is responsible for the mechanical and thermal properties of the resulting polymeric matrix. GMA provides epoxy groups, which are effective for introducing the target groups. The molar ratio of the functional monomer to the cross-linker was increased from 1:1 to 1:5. The resulting poly(DMN–*co*-GMA) microspheres were functionalized by ring-opening reaction of oxirane with the pyrrolidone to produce DMN–GMA + P adsorbent as shown in Fig. 2.

The elemental analysis of the parent and functionalized adsorbents is presented in Table 1. The measured elemental fractions in the copolymer are very close to the values calculated from the initial monomer mixtures. These data suggested that the GMA and DMN copolymerized almost quantitatively. This fact is also confirmed by the values of epoxy group content (Table 2). The determined epoxy group fractions in the copolymers increased with the increase in amount of GMA in the polymerization mixture. This dependence was also confirmed by means of infrared spectroscopy. ATR spectra (Fig. 3) show the increase in the intensity of peaks attributed to the epoxy group (993, 908, and 848 cm^{-1}) along with the increase of GMA in the polymerization mixture.

The method of elemental analysis and infrared spectroscopy was also used to confirm the conversion of the epoxy group with pyrrolidone. The functionalized DMN–GMA + P copolymers show the disappearance of the peak

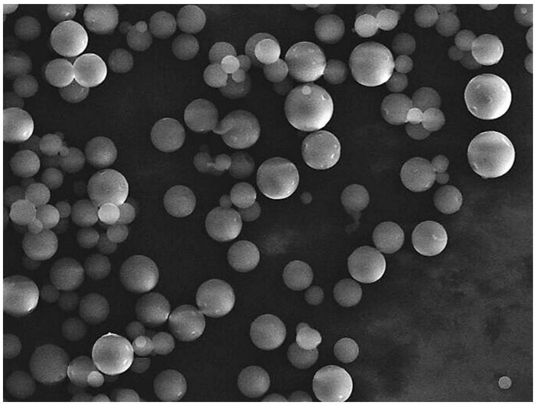


Fig. 1 SEM image of DMN–*co*-GMA copolymer

at 1340 cm^{-1} and a decrease in absorbance of peaks at 993, 908 and 848 cm^{-1} coming from epoxy group, while the new peak at 1650 cm^{-1} appears due to pyrrolidone units suggesting the successful conversion of the epoxy groups with pyrrolidone (Fig. 4). However, the degree of epoxy group conversion (evaluated on the basis of elemental analysis) is not high.

Since the copolymers under study can be applied as adsorbents, it was also of interest to investigate their internal structure. Depending on the molar ratio of the functional monomer to the cross-linker, the value of specific surface area decreases from 106 $m^2\ g^{-1}$ for the DMN–GMA1 (parent copolymer, molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:1) to 42 $m^2\ g^{-1}$ for DMN–GMA5 (molar ratio of di(methacryloyloxy methyl) naphthalene to glycidyl methacrylate equals 1:5). At the same time, pore diameter increases from 40 to 50 nm. What is more, in the case of DMN–GMA1 copolymer, additionally, pores of diameters equal to 25 nm are observed.

The newly obtained modified copolymers considerably differ from the parent ones in terms of porous structure parameters. First of all, the modification process leads to noticeable decrease in the basic parameters of the internal structure (Table 3). The value of specific surface area decreases from 106 $m^2\ g^{-1}$ for DMN–GMA1 to 73 $m^2\ g^{-1}$ for DMN–GMA1 + P copolymer. At the same time, pore

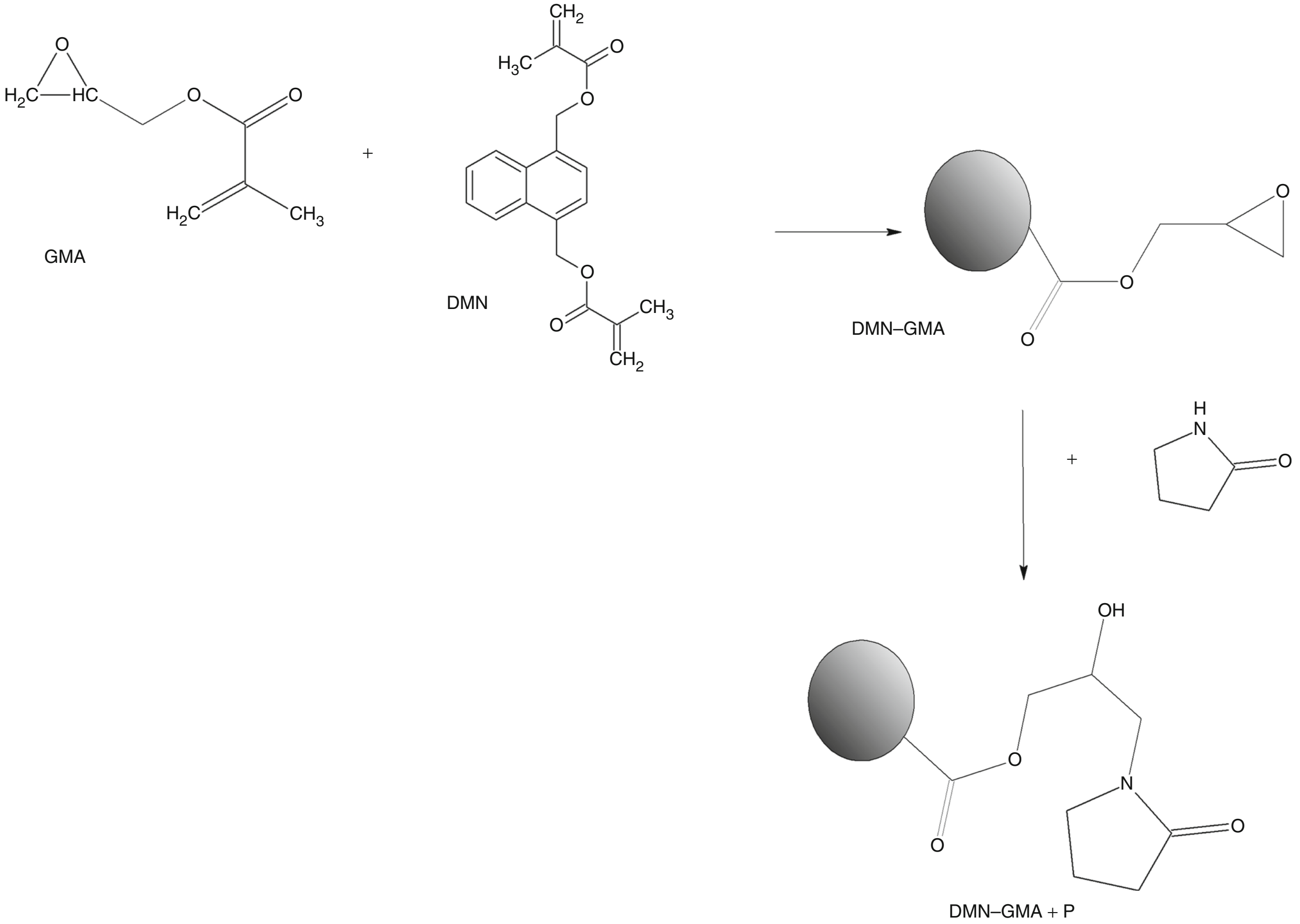


Fig. 2 Scheme of synthesis and modification of poly(glycidyl methacrylate-*co*-di (methacryloyloxy methyl) naphthalene) with pyrrolidone

Table 1 Elemental analysis of the copolymers under study

Copolymer	Element weight fraction/mass%					
	C		H		N	
	Calculated	Determined	Calculated	Determined	Calculated	Determined
DMN–GMA1	69.45	67.68	6.43	6.60	–	–
DMN–GMA2	67.11	64.49	6.57	6.83	–	–
DMN–GMA3	65.53	63.00	6.66	6.97	–	–
DMN–GMA4	64.50	62.33	6.72	7.15	–	–
DMN–GMA5	63.76	61.43	6.76	7.18	–	–
DMN–GMA1 + P	67.50	65.70	6.76	6.78	2.54	0.66
DMN–GMA2 + P	64.77	62.32	6.99	7.09	3.60	1.63
DMN–GMA3 + P	63.27	57.99	7.11	6.96	4.18	2.21
DMN–GMA4 + P	62.32	59.38	7.19	7.26	4.54	2.71
DMN–GMA5 + P	61.67	57.95	7.25	7.21	4.79	2.98

Table 2 Epoxy group content in the copolymers

Copolymer	Molar ratio of monomers		Epoxy group content/mmol g^{-1}	
	DMN	GMA	Calculated	Determined
DMN–GMA1	1	1	2.581	2.405
DMN–GMA2	1	2	3.312	3.229
DMN–GMA3	1	3	3.922	3.668
DMN–GMA4	1	4	4.410	4.201
DMN–GMA5	1	5	4.766	4.601

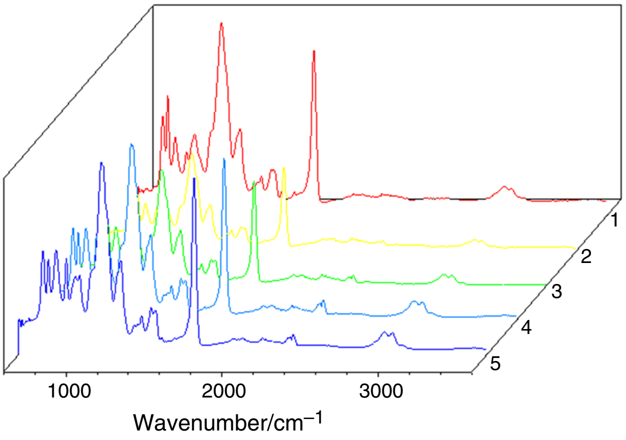


Fig. 3 ATR spectra of the copolymers under study: 1 DMN–*co*-GMA1; 2 DMN–*co*-GMA2; 3 DMN–*co*-GMA3, 4 TRIM-*co*-GMA4; 5 TRIM-*co*-GMA5

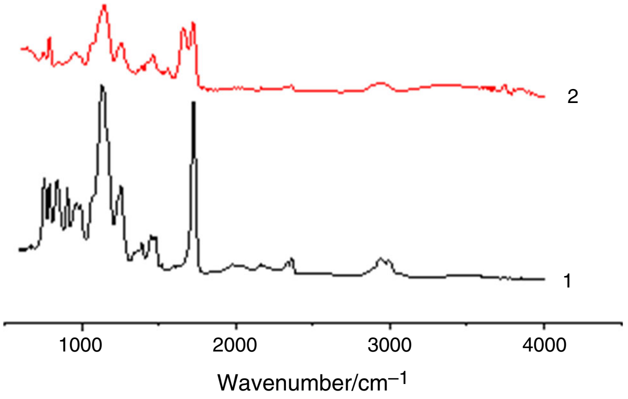


Fig. 4 ATR spectra parent (1) and modified with pyrrolidone (2) DMN–*co*-GMA copolymer

volume declines from 0.380 to 0.254 cm^3 g^{-1}. Pore size distribution maintains its bimodal character, but the maxima are shifted toward smaller values (19 and 22 nm). After the process of modification of the DMN–GMA5 copolymer, a significant drop in the specific surface area from 42 to 26 m^2 g^{-1} was observed.

Figure 5 presents the AFM image of the parent DMN–GMA1 copolymer. It was found out that there is a strong relationship between the porosity and roughness parameters [26]. Calculated on the basis of AFM measurements, the root-mean-square (RMS) roughness is equal to 10.5 nm. The value is in good correlation with the mesoporous structure of the copolymer.

The process of modification of the DMN–*co*-GMA copolymers with pyrrolidone also changes the thermal properties of the newly obtained materials. The main parameters evaluated on the basis of these curves determined in helium atmosphere for the whole series of copolymers are presented in Table 4. From these data, one can see that increasing the molar ratio of GMA to DMN

Table 3 Basic parameters of porous structure of the parent and modified copolymers

Copolymer	Specific surface area $S_{BET}/m^2\ g^{-1}$	Pore volume $V/cm^3\ g^{-1}$	D_{BJH}/Å
DMN–GMA1	106	0.380	250/40
DMN–GMA2	81	0.500	400
DMN–GMA3	64	0.453	450
DMN–GMA4	53	0.386	490
DMN–GMA5	42	0.305	500
DMN–GMA1 + P	73	0.254	190/22
DMN–GMA2 + P	57	0.243	160
DMN–GMA3 + P	51	0.354	400
DMN–GMA4 + P	32	0.228	350
DMN–GMA5 + P	26	0.218	470

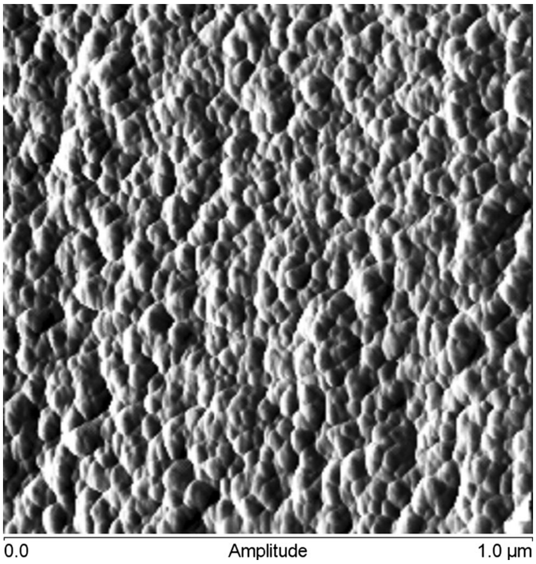


Fig. 5 AFM micrographs of the surface of the obtained DMN–*co*-GMA1 copolymer

from 1:1 to 5:1 slightly changes the thermal resistance of the copolymers. The enlargement of the quantity of GMA in the copolymers causes changes in the curse of TG and DTG curves. Along with the increasing of GMA amount, additional peak on the DTG curve at temperature of about 290 °C appears (Fig. 6). It can be connected with the degradation of epoxy group. This process is also confirmed by the lack of such a peak in the case of copolymers modified with pyrrolidone (Fig. 7).

It was also of interest to compare the impact of different cross-linkers on the thermal resistance of the obtained copolymers. It was found out that the type of cross-linker has a significant impact on the thermal behavior of the synthesized materials. GMA-*co*-DMN copolymers start to decompose at temperature 50 °C higher comparing with copolymers cross-linked with trimethylene trimethacrylate (Fig. 8) [27]. This fact clearly shows the desirability of the usage of aromatic cross-linkers like di(methacryloyloxy methyl)naphthalene.

In the case of analysis conducted in air, the pyrrolidone groups introduced on the surface of the copolymers contribute to the changes in thermal behavior of the materials under study. The IDT of modified copolymers is higher in comparison with the values of their unmodified counterparts (Table 5).

Volatile decomposition products

Figure 9 presents FTIR 3D spectrum of the volatile decomposition products. As it is clearly visible at temperatures ranging from 40 to 235 °C, only the moisture vaporization from the studied materials is observed. As the temperature increased, the formation of additional gaseous products was observed what suggested the beginning of decomposition processes of the copolymers. The analysis of the chemical structure of GMA and DMN molecules suggests that the ester bonds present in matrices' networks will decompose at the first stage. Both α-hydrogen bond scission (formation and emission of aldehydes) and β-hydrogen bond scission (formation and emission of carboxylic and vinyl compounds) are possible in the case of GMA-derived units [22]. In DMN-derived units present in networks, only β-hydrogen bond scission is likely. At the emission spectrum of DMN–*co*-GMA at the first maximum of decomposition (Fig. 10), bands confirming the α- and β-hydrogen bonds scission are visible, leading to the formation of alkenes [bands at 814 and 936 cm^{-1} (δ =C–H), at 1650 cm^{-1} (ν C=C) and at 3105 cm^{-1} (ν =C–H)], aldehydes, especially acetaldehyde [bands at 1741 cm^{-1} (ν C=O) and at 1162 cm^{-1} (ν C=O)] and carboxylic spices [bands at 1790 cm^{-1} (ν C=O) and 3238 cm^{-1} (ν O–H)]. What is more, on the FTIR spectrum, vibrations representative of CO_2 (2354 cm^{-1}) and CO (2171 and 2120 cm^{-1}) are present. Moreover, the evolution of water was confirmed by absorption bands in the spectrum region of 3800–3600 and

Table 4 Thermal stability of the copolymers under study determined in helium

Copolymer	IDT/°C	$T_{20\%}$/°C	$T_{50\%}$/°C	FDT/°C	$T_{1\max}$/°C	$T_{2\max}$/°C
DMN–GMA1	269	352	391	521	–	393
DMN–GMA2	261	357	394	500	293	394.5
DMN–GMA3	260	341	382	493	275	384.4
DMN–GMA4	268	356	393	520	280	398
DMN–GMA5	258	350	392	500	287	396.8
DMN–GMA1 + P	274	318	359	621	–	399.5
DMN–GMA2 + P	266	319	361	609	–	355
DMN–GMA3 + P	255	336	382	538	–	388.5
DMN–GMA4 + P	256	328	380	531	–	388
DMN–GMA5 + P	252	325	370	527	–	381

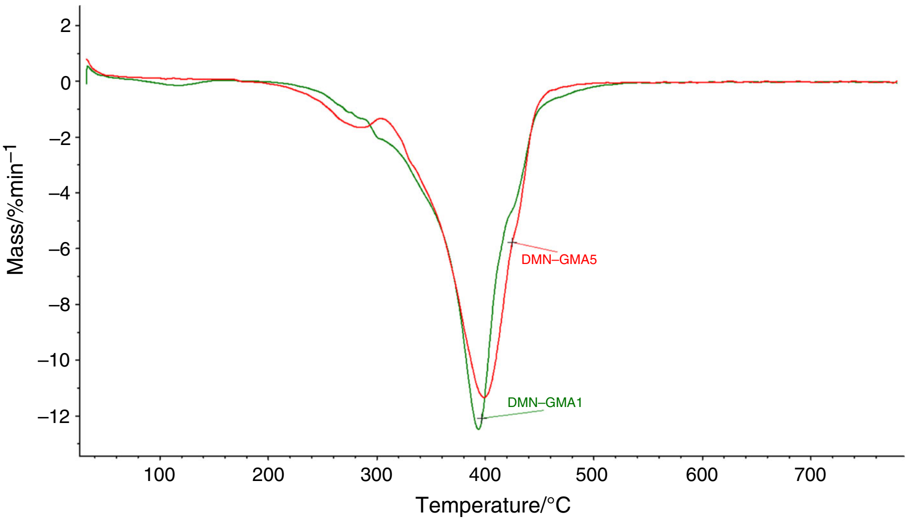


Fig. 6 DTG curves of parent DMN–*co*-GMA1 and DMN–*co*-GMA5 copolymers

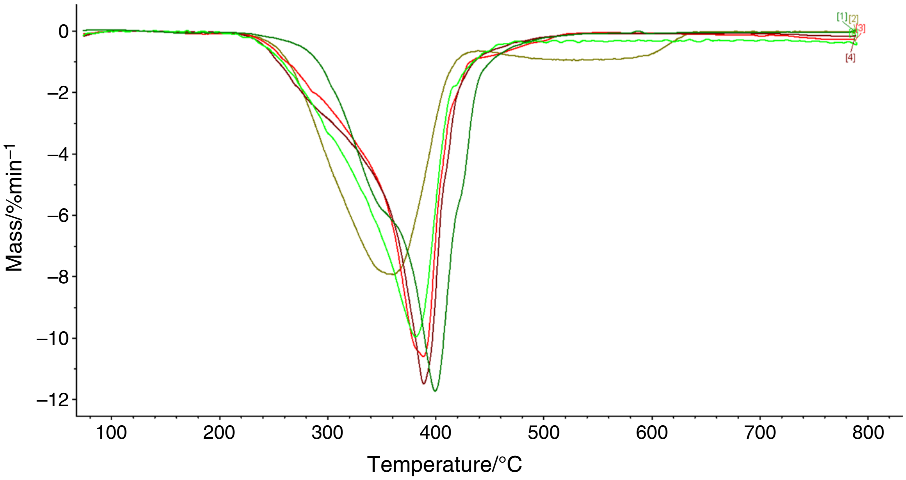


Fig. 7 DTG curves of the DMN–*co*-GMA copolymers modified with pyrrolidone [1] DMN–*co*-GMA1+P, [2] DMN–*co*-GMA2+P, [3] DMN–*co*-GMA3+P, [4] DMN–*co*-GMA4+p, [5] DMN–*co*-GMA5+P

1600–1400 cm^{-1}. The next maximum of emission of gases produced during the sample decomposition was observed at about 400 °C. At this temperature the cross-linked parts of the sample decomposed, and in consequence, significant evolution of carbon dioxide (peaks at 2357, 2311 and 670 cm^{-1}) and carbon monoxide (peaks at 2174, 2120 cm^{-1}) connected with decarboxylation processes was observed. In the case of DMN–*co*-GMA copolymers modified with pyrrolidone, only one maximum of emission gases at temperature of about 400 °C is observed (Fig. 11).

Figure 12 presents the Gram–Schmidt plots obtained during the thermal decomposition of the parent

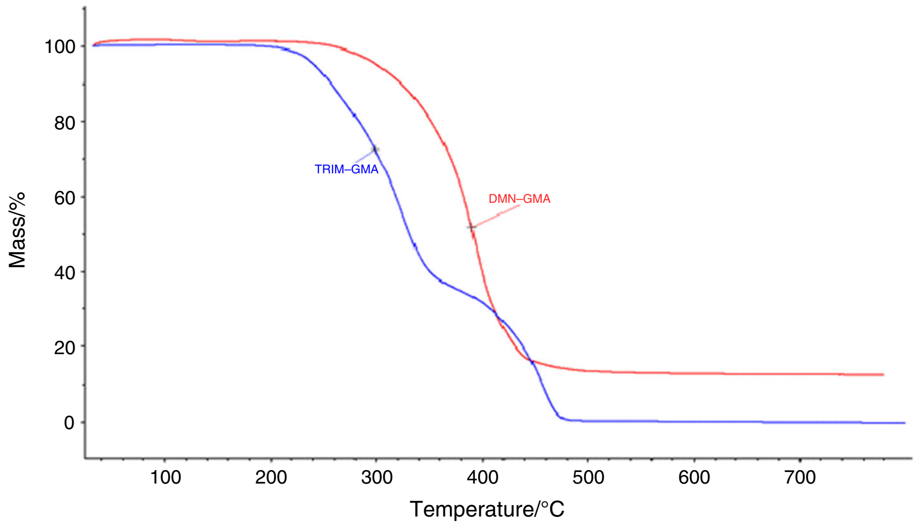


Fig. 8 TG curves of TRIM-*co*-GMA and DMN–*co*-GMA copolymers determined in helium

Table 5 Thermal stability of the copolymers under study determined in air

Copolymer	IDT/°C	$T_{20\%}$/°C	$T_{50\%}$/°C	FDT/°C	$T_{1\max}$/°C	$T_{2\max}$/°C
DMN–GMA1	269	315	357	597	325	528
DMN–GMA2	253	306	346	603	327	522
DMN–GMA3	253	309	343	617	334	518
DMN–GMA4	249	298	335	594	328	513
DMN–GMA5	250	292	333	517	331	505
DMN–GMA1 + P	281	316	352	573	320	507
DMN–GMA2 + P	271	301	334	534	307	466
DMN–GMA3 + P	261	296	322	585	303	467
DMN–GMA4 + P	259	291	321	539	299	453
DMN–GMA5 + P	255	287	312	521	293	402

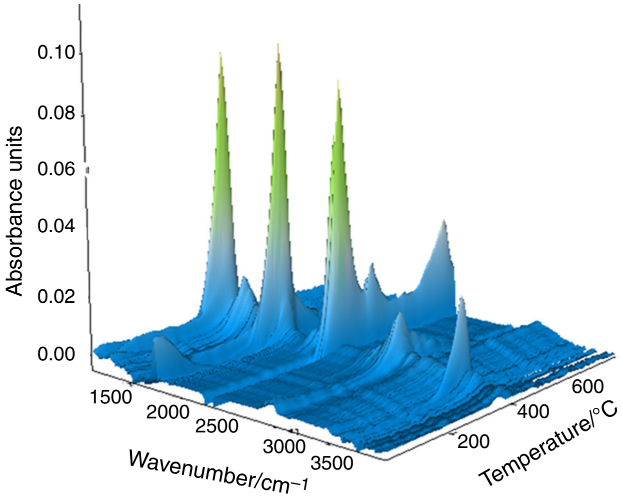


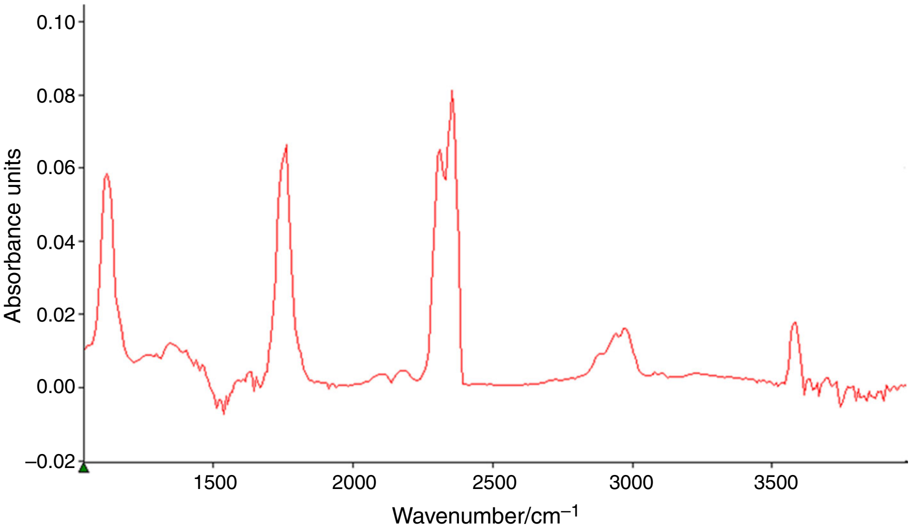
Fig. 9 3D diagram of FTIR spectrum of gases evolved during thermal decomposition of DMN–*co*-GMA1 copolymer

copolymers. Two separated peaks are visible on the curves. Their maxima remain in accordance with $T_{1\max}$ and $T_{2\max}$ on the DTG curves (Fig. 10). After the process of modification with pyrrolidone, only one peak on the Gram–Schmidt plot is visible (Fig. 13). The FTIR spectrum that corresponds to the maximum of the Gram–Schmidt plots is presented in Fig. 14.

DSC measurements

The differences in thermal behavior between parent and functionalized copolymers were also noticed during DSC measurements (Table 6). By looking at the DSC curves of parent copolymers obtained at helium, few thermal events can be seen, both exothermic and endothermic ones (Figs. 15, 16). The first endothermic peak (T_1) on the DSC curve can be attributed to the process of moisture vaporization from the studied materials. Along with increasing of the amount of epoxy group in parent copolymers and pyrrolidone units in modified ones, the amount of adsorbed water and consequently the enthalpy of vaporization process (ΔH_1) significantly increase. The second endothermic peak with the maximum at the temperature of about 350 °C (T_3) can be attributed to the decomposition of epoxy ring in the case of parent copolymers and the pyrrolidone

Fig. 10 FTIR spectrum of gases evolved from DMN–co-GMA copolymer at the maximum of decomposition



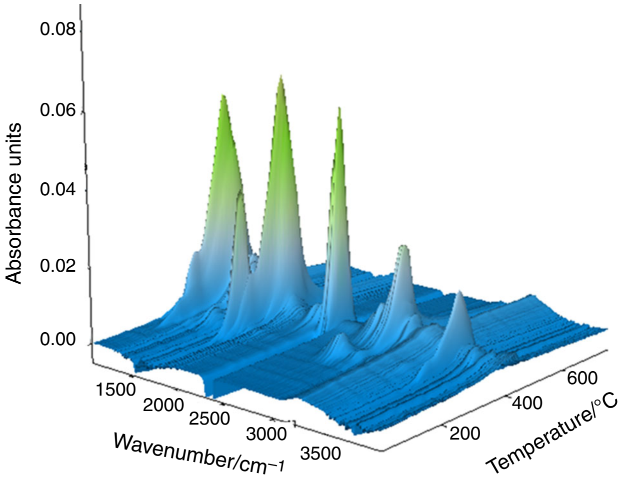


Fig. 11 3D diagram of FTIR spectrum of gases evolved during thermal decomposition of DMN–*co*-GMA1+P copolymer

functionalities in the case of modified ones. The third endothermic peak with the maximum from 400 to 427 °C indicates the thermal degradation of the cross-linked parts of the copolymers.

The exothermic reactions in the thermal treatment of DMN–*co*-GMA copolymers could be caused by pendant double bonds. It has been reported that highly cross-linked porous copolymers can contain considerable amount of unreacted double bonds [27]. They can undergo reaction of thermal polymerization. As a result, exothermic peak at about 260 °C (T_2) can be observed. After the process of modification with pyrrolidone, the course of DSC curves has been changed. Due to high temperature of modification (150 °C), the exothermic peek connected with thermal polymerization of double bounds does not appear.

Fig. 12 Gram–Schmidt plots of parent copolymers [1] DMN–*co*-GMA1, [2] DMN–*co*-GMA2, [3] DMN–*co*-GMA3, [4] DMN–*co*-GMA4, [5] DMN–*co*-GMA5. DTG curve [1] and Gram–Schmidt plot [2] for DMN–*co*-GMA5 copolymer

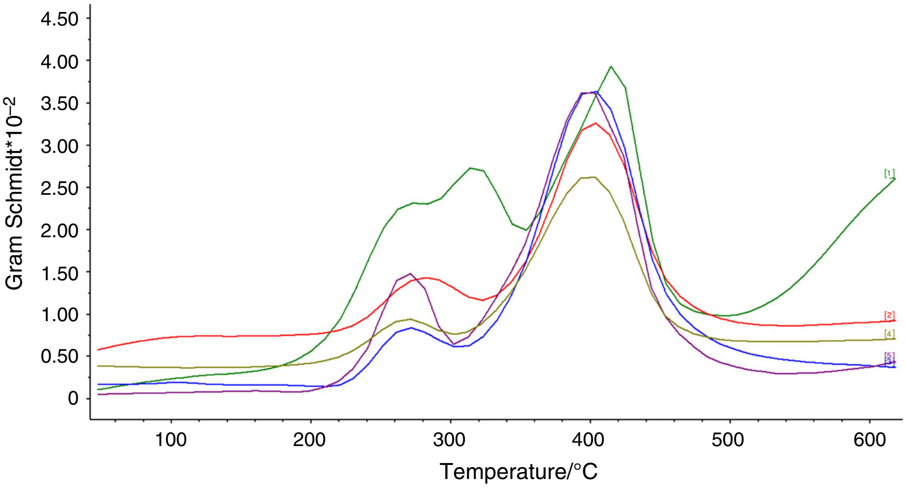


Fig. 13 Gram–Schmidt plots of copolymers modified with pyrrolidone [1] DMN–*co*-GMA1+P, [2] DMN–*co*-GMA2 +P, [3] DMN–*co*-GMA3 +P

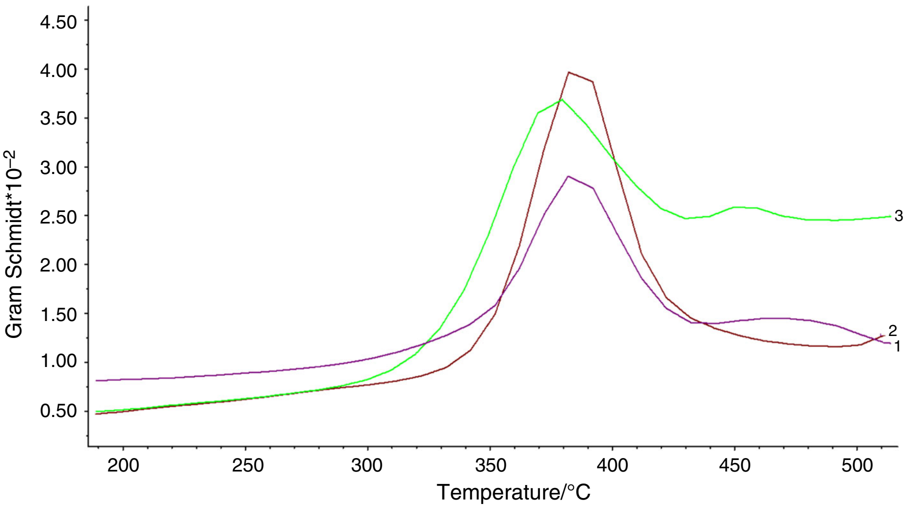


Fig. 14 DTG curve [1] and Gram–Schmidt plot [2] for DMN–*co*-GMA1+P

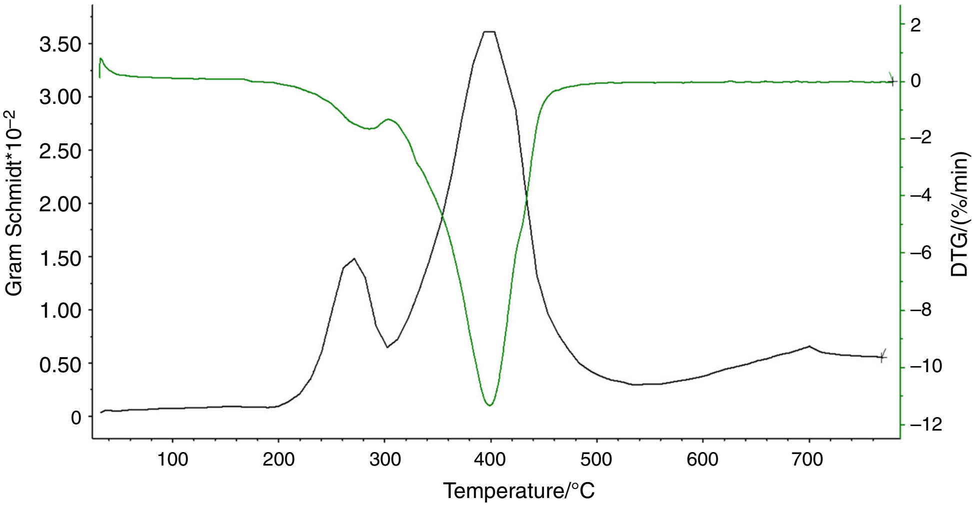


Table 6 DSC data

Copolymer	T_1/°C	ΔH_1/μV s mg^{-1}	T_2/°C	ΔH_2 Δ/μV s mg^{-1}	T_3/°C	ΔH_3/μV s mg^{-1}	T_4/°C	ΔH_4/μV s mg^{-1}
DMN–GMA1	88	60	273	275	343	209	420	151
DMN–GMA2	69	174	264	136	343	275	418	46
DMN–GMA3	89	179	256	241	358	183	425	19
DMN–GMA4	86	184	263	257	353	256	427	18
DMN–GMA5	81	149	263	279	343	283	421	24
DMN–GMA1 + P	87	50	–	–	358	169	417	123
DMN–GMA2 + P	97	112	–	–	357	276	413	27
DMN–GMA3 + P	108	236	–	–	348	251	405	16
DMN–GMA4 + P	92	284	–	–	344	317	402	7
DMN–GMA5 + P	90	294	–	–	349	398	400	3

Fig. 15 DSC curves of the parent copolymers determined in helium [1] DMN–*co*-GMA1, [2] DMN–*co*-GMA2, [3] DMN–*co*-GMA3, [4] DMN–*co*-GMA4, [5] DMN–*co*-GMA5

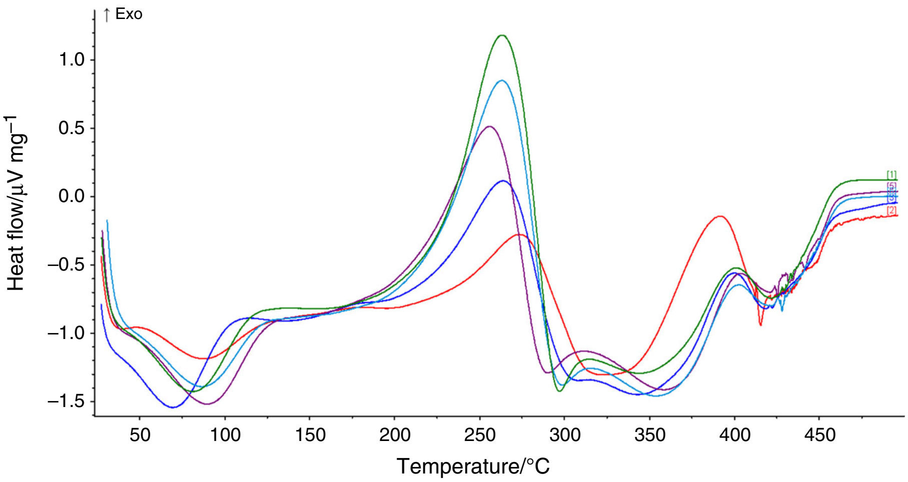
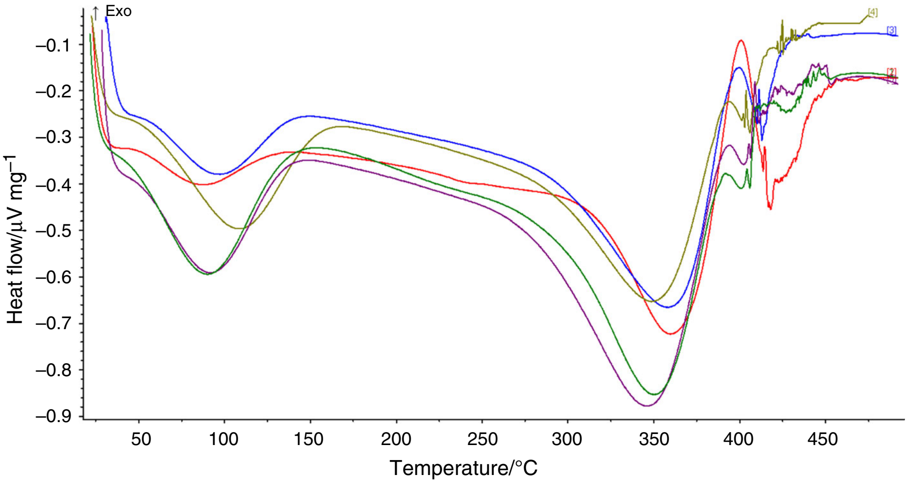


Fig. 16 DSC curves of the modified copolymers determined in helium [1] DMN–*co*-GMA1+P, [2] DMN–*co*-GMA2+P, [3] DMN–*co*-GMA3+P, [4] DMN–*co*-GMA4+P, [5] DMN–*co*-GMA5+P



Conclusions

Porous copolymers of glycidyl methacrylate cross-linked with di(methacryloyloxy methyl) naphthalene were synthesized in the form of microspheres. The application of the aromatic cross-linker allowed to obtain material with better thermal resistance comparing with copolymers on the basis of aliphatic ones. In the next step, the reactive epoxy groups present in the copolymers were modified by subsequent reaction with pyrrolidone. The process of modification led to significant changes in the textural and thermal properties of the functionalized materials. Considerable decreasing of the value of specific surface area, pore volume and pore diameter were observed in the case of modified copolymers. What is interesting is that the thermal stability of the polymer increases with the introduction of the functional groups. What is more, the course of TG, DTG and DSC curves of parent copolymer is at variance with the functionalized ones.

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