TG/DSC/FTIR study of porous copolymeric beads based on the dimethacrylate derivative of *m*-xylene

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Abstract

The present study describes the thermal properties of a series of porous microspheres synthesised from the dimethacrylate derivative of *m*-xylene, i.e. (4,6-dimethyl-1,3-phenylene)dimethylene bis(2-methylprop-2-enoate) and divinylbenzene via an aqueous suspension polymerisation in the presence of toluene and decan-1-ol as porogenic diluents. Various molar ratios of monomers were applied in the syntheses (1:4, 1:1, 4:1). The TG/DSC/FTIR analyses were performed in inert (helium) and oxidative (synthetic air) atmospheres. They revealed that the properties of the copolymeric microspheres were dependent on both their chemical composition and the testing atmosphere. The microspheres were stable up to 229–296 °C (in helium) and 302–308 °C (in synthetic air), as determined on the basis of the temperature of 1% mass loss. However, the most thermally stable were those synthesised at the molar ratio of the dimethacrylate derivative of *m*-xylene to divinylbenzene equal to 1:4. In helium, the copolymeric beads decomposed in one, two or three stages, whereas in synthetic air in two ones. The basic decomposition volatiles were carbon monoxide, carbon dioxide and organic carbonyl products, including esters, carboxylic acids and aldehydes as well as unsaturated and aromatic compounds.

Keywords Polymeric microspheres · Divinylbenzene · DSC · Thermogravimetry

Introduction

Porous polymeric microspheres are used in various medical and biological applications, such as blood flow indicators, adsorbents in extracorporeal therapy, cell culture and peptide synthesis media as well as carriers of biologically active substances [1–3]. Regular microspheres are also applied as column packings in different chromatography techniques [4–9]. In reversed-phase high-performance liquid chromatography (HPLC), the most common are styrene–divinylbenzene porous microspheres [10, 11]. They do not contain any functional groups and are hydrophobic. In order to obtain more polar polymers that generally exhibit higher selectivity, monomers with various functional groups, e.g. methacrylate [12, 13], pyrrolidone [14–16], amine [17, 18] and thio [18], can be applied.

Another drawback of the porous polymeric packings is the fact that they swell in organic solvents [11]. This is particularly inconvenient when solvent gradients are used. Our previous studies indicated that promising packings for chromatography column are those synthesised from two tetrafunctional monomers. They guarantee a high cross-linking degree and thus a smaller degree of swelling. As the tetrafunctional monomers divinylbenzene (DVB) and dimethacrylate derivatives of naphthalene [15, 19–22], diphenyl sulphone [20, 21, 23], benzene [23], diphenylmethane [24] and ethylene glycol [6] as well as bis(maleimido) derivative of diphenylmethane [20, 21] were used.

Additionally, the high cross-linking degree improves thermal stability of the obtained materials [25, 26]. It was also found that an aromatic cross-linker provides better thermal resistance compared with an aliphatic one which is particularly important in the case of gas chromatography as well as catalysis [15, 16].

This paper describes the thermal properties of the highly cross-linked microspheres synthesised from DVB and dimethacrylate derivative of *m*-xylene (DMX), i.e. (4,6-dimethyl-1,3-phenylene)dimethylene bis(2-methylprop-2-enoate), via an aqueous suspension polymerisation in the

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presence of toluene and decan-1-ol as pore-forming agents. The particular attention was paid to the influence of various molar ratios of monomers on these properties. They were evaluated on the basis of thermogravimetry coupled online with FTIR spectroscopy (TG/FTIR) and differential scanning calorimetry (DSC) under inert (helium) and oxidative (synthetic air) conditions.

Experimental

Materials

Poly(vinyl alcohol), α,α′-azobisisobutyronitrile (98%), DVB and decan-1-ol were obtained from Sigma-Aldrich (Germany), whereas toluene, acetone and methanol from POCh (Poland). The DMX monomer was prepared in our laboratory in accordance with the procedure described below. The following compounds (analytical reagent grade) were used for its synthesis: *m*-xylene, paraformaldehyde, hydrochloric acid (36–38%), ice acetic acid, ethanol (POCh, Poland), *N,N*-dimethylformamide (DMF), hydroquinone and potassium methacrylate (Sigma-Aldrich, Germany).

Synthesis of DMX

The synthesis was carried out in a 500-cm^3 round-bottomed flask equipped with a thermometer, a mechanical stirrer and a heater. 27 g of *m*-xylene, 27.5 g of paraformaldehyde, 90.5 cm^3 of hydrochloric acid and 65 cm^3 of ice acetic acid were placed in the flask and heated at 85–90 °C for 6 h. Then, the mixture was cooled to room temperature, and the obtained dichloromethylene derivative of *m*-xylene was washed several times with water and then crystallised from ethanol. Next, 40.6 g of this compound was diluted in DMF and heated with 50.4 g of potassium methacrylate in the presence of hydroquinone as an inhibitor. The process was carried out at the boiling temperature of DMF and with vigorous stirring. The reaction product was poured into cold water. The precipitated DMX was crystallised from ethanol (m.p. = 140–145 °C).

Preparation of copolymers

Copolymerisation of DMX with DVB was conducted by an aqueous suspension polymerisation. To prepare a reaction medium, 195 cm^3 of distilled water and 6.5 g of poly(vinyl alcohol) as the suspension stabiliser were stirred for 6 h at 80 °C in the three-necked flask equipped with a stirrer, a water condenser and a thermometer. Then, 15 g of mixture containing an appropriate mole fraction of DMX to DVB monomers (1:4, 1:1, 4:1) and 0.075 g of α,α′-azobisisobutyronitrile (0.5 mass% based on monomers) in

the solution of 22.5 cm^3 of pore-forming diluents (toluene and decan-1-ol (80:20 v/v)) were added while stirring in the aqueous medium. Copolymerisation was performed for 16 h at 80 °C. Porous microspheres formed in this process were filtered, washed with hot water and extracted in a Soxhlet apparatus with boiling acetone, toluene and methanol.

Testing methods

The chemical structure of the prepared copolymers was investigated by means of attenuated total reflectance Fourier transform infrared (ATR-FTIR). The infrared spectra were recorded with a Bruker Tensor 27 FTIR spectrometer (Germany) in the absorbance mode. The measurements were taken at room temperature. The main parameters were as follows: a resolution of 4 cm^{-1}, the wavenumber region of 4000–600 cm^{-1} and 32 scans per spectrum.

Thermogravimetry (TG) together with differential scanning calorimetry (DSC) was carried out with a Netzsch STA 449 F1 Jupiter instrument (Germany) within the range of 30–1000 °C in helium or synthetic air atmospheres (flow = 20 cm^3 min^{-1}). The heating rate was held 10 °C min^{-1}. The analyses were conducted in Al$_2$O$_3$ crucibles and copolymer samples weighted about 10 mg. At the same time, the gaseous FTIR spectra were collected by a Bruker Tensor 27 FTIR spectrometer (Germany) connected online with a Netzsch STA apparatus by the Teflon transfer line with a diameter of 2 mm heated to 200 °C. The spectra were gathered in the range of 4000–600 cm^{-1} with 16 scans per spectrum and a resolution of 4 cm^{-1}.

In order to obtain more detailed DSC data, the investigations were additionally performed with a Netzsch 204 calorimeter (Germany) operating in the dynamic mode. The dynamic scans were carried out at the heating rate of 10 °C min^{-1} from 20 to 550 °C under argon atmosphere (flow = 20 cm^3 min^{-1}) in two cycles. The first cycle was done from 20 to 120 °C in order to remove any adsorbed moisture, mainly water, while the second one in the range of 20–550 °C. The samples of the tested materials (~7.5 mg) were placed in aluminium pans with a pierced lid. An empty aluminium pan was applied as a reference.

Results and discussion

The aqueous suspension copolymerisation was applied to obtain the cross-linked porous microspheres of poly(DMX-*co*-DVB) with diameters in the range of 50–250 μm (Fig. 1). Various molar ratios of these tetrafunctional monomers were used in the syntheses. The designations of the obtained products are given in Table 1.

The ATR-FTIR analysis confirmed the assumed chemical structure of the copolymers. Namely, in the obtained

spectra one can see bands typical of the ester group (at 1727–1724 cm^{-1} (ν C$=$O) and at 1134–1110 cm^{-1} (ν C–O–C)), methyl and methylene groups (at 2963–2932 cm^{-1} (ν_{asym} C–H) and at 2875–2874 cm^{-1} (ν_{sym} C–H)) and benzene ring (at 1605–1602 cm^{-1} (ν C–C) and at 833–709 cm^{-1} (δ C–H)). The bands at 1467–1450 cm^{-1} can originate from the vibrations of both methyl and methylene groups as well as benzene ring (Fig. 2).

In order to evaluate the thermal behaviour of the obtained porous copolymeric beads, the TG and DSC methods were applied. The studies were carried out in helium and synthetic air. Figures 3 and 4 show the TG and differential TG (DTG) curves obtained for these copolymers, while Table 1 gives

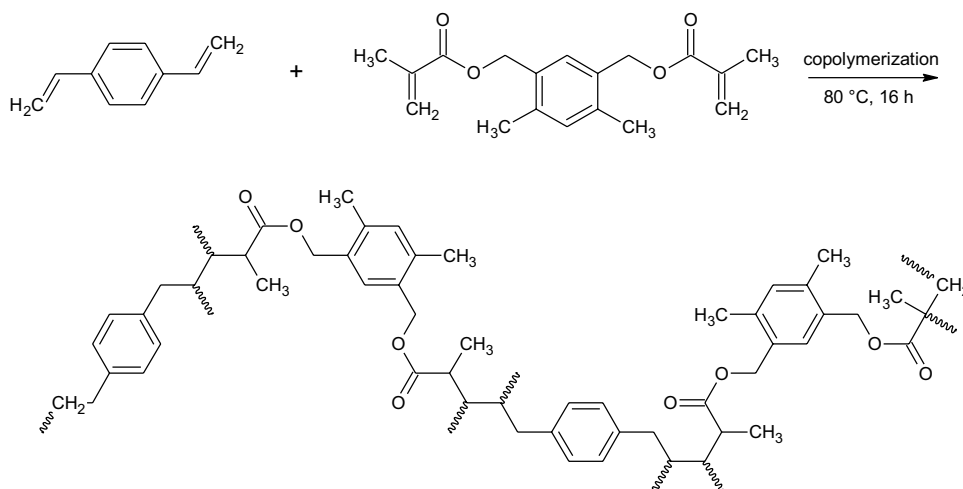**Fig. 1** The general scheme of poly(DMX-*co*-DVB) copolymer syntheses

Table 1 Designation and TG and DTG data of copolymers in helium atmosphere

Copolymer	Molar ratio of monomers		T_1^a/°C	T_{20}^a/°C	T_{50}^a/°C	T_{max}^b/°C	Residue/%
Poly(DMX-*co*-DVB)_1:4	1	4	296	393	416	414	8.7
Poly(DMX-*co*-DVB)_1:1	1	1	290	358	395	378, 421	8.7
Poly(DMX-*co*-DVB)_4:1	4	1	229	345	377	351, 373, 415	13.8

[a]The temperature of 1, 20 and 50% mass loss from the TG curve

[b]The temperature of the maximum rate of mass loss from the DTG curve

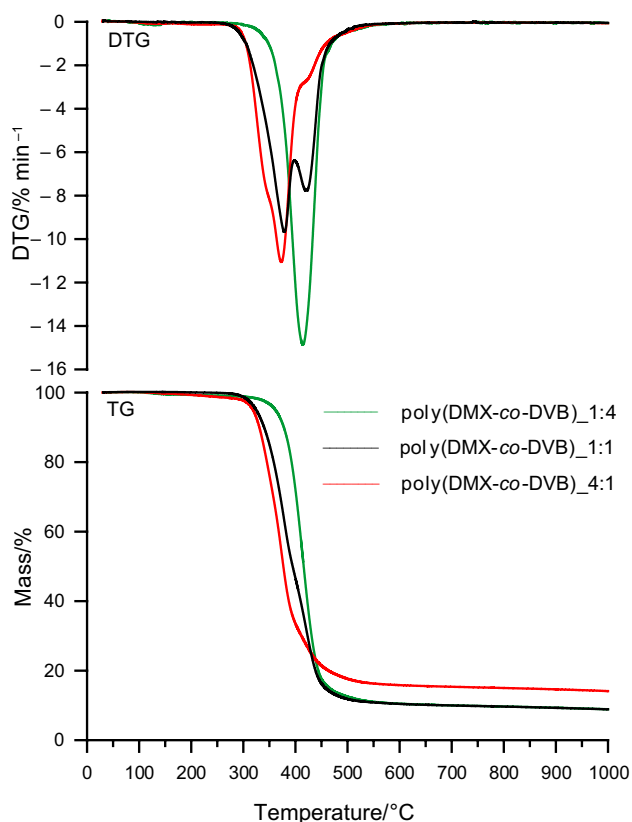**Fig. 2** ATR-FTIR spectra of poly(DMX-*co*-DVB) copolymers

Fig. 3 TG and DTG curves of copolymers obtained in helium
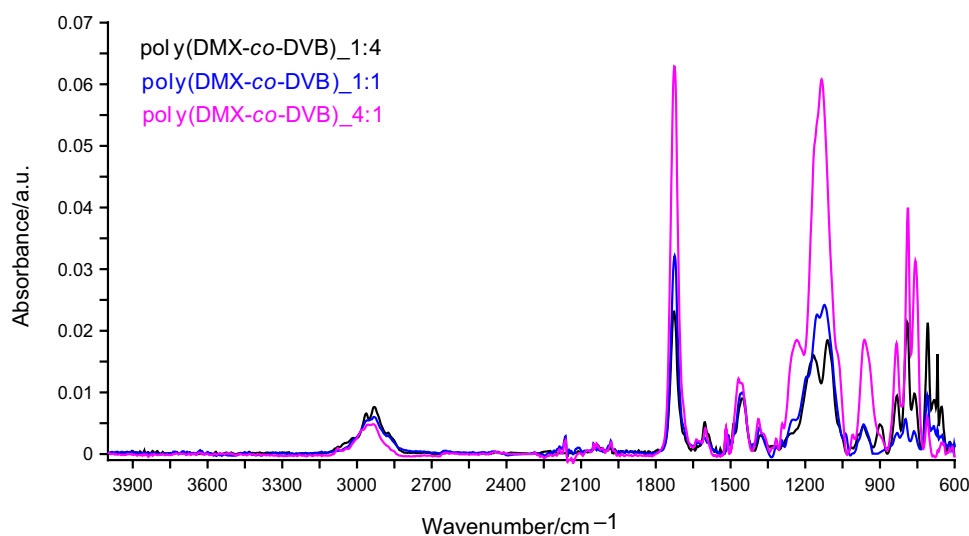
Fig. 4 TG and DTG curves of copolymers obtained in synthetic air

the main parameters assessed on their basis. Furthermore, an analysis of volatiles emitted during the copolymers decomposition was conducted by TG/FTIR. The registered FTIR spectra are displayed in Figs. 5–11. In turn, the received DSC curves are presented in Figs. 12 and 13.

As it follows from DTG curves obtained in helium atmosphere, the decomposition of the copolymer with the lowest DMX-derived units content (poly(DMX-co-DVB)_1:4) proceeded in one step (with T_{max} at 414 °C), whereas the decomposition of two remaining ones occurred in two or three steps. On the curve of poly(DMX-co-DVB)_1:1 copolymer peaks with T_{max} at 378 °C (corresponding to 53% mass loss) and at 421 °C (corresponding to 37% mass loss) can be observed. On the other hand, the curve of poly(DMX-co-DVB)_4:1 copolymer exhibits peaks with T_{max} at 351, 373 and 415 °C. These peaks are poorly resolved, but it is possible to approximate the mass losses corresponding to the decomposition steps. Thus, for the first and second steps the total mass loss equals ~70% and for the third one ~14%. From the comparison of all DTG data, it appears that the number of decomposition steps increased with the increase in DMX content. It can be assumed that the step with T_{max} at 414–421 °C is associated with the decomposition of DVB-derived units, while the steps with T_{max} at 351–378 °C can be ascribed to the decomposition of DMX-derived ones.
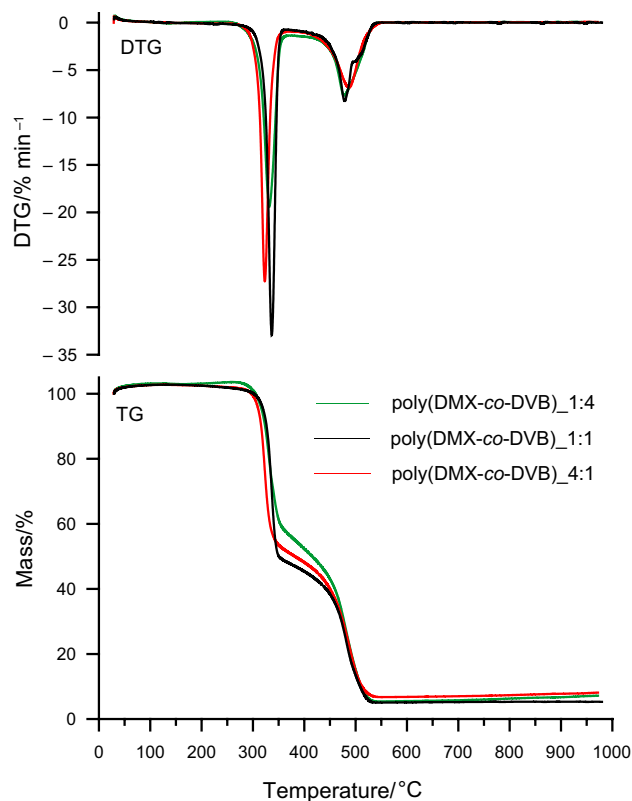
Moreover, it was observed that the newly obtained materials are decomposed in around 90%. The highest residual mass (13.8%) was detected in the case of the copolymer containing the largest amount of DMX-based units.

Taking into account the T_1, T_{20} and T_{50} values, one can say that the incorporation of a larger amount of DMX-based units in the material structure deteriorates the thermal stability of the synthesised copolymers. A particularly significant drop is observed in the case of T_1 values (from 296 °C for poly(DMX-co-DVB)_1:4 to 229 °C for poly(DMX-co-DVB)_4:1) and T_{20} values (from 393 °C for poly(DMX-co-DVB)_1:4 to 345 °C for poly(DMX-co-DVB)_4:1). This is caused by the presence of a significant content of less thermally stable ester groups. Generally, it can be stated that the decomposition of methacrylate-derivative materials begins with the degradation of the ester groups [27]. As a result, CO_2, CO, aldehydes and alcohols can be formed. The cross-linked network of the copolymers which contain aromatic rings decomposes at higher temperatures. To confirm these assumptions, the analysis of decomposition volatiles was conducted.

The FTIR spectrum registered during the decomposition of poly(DMX-co-DVB)_1:4 (T_{max} at 414 °C) presented in Fig. 6 shows the absorption peak (at 1765 cm^{-1}—ν C=O) which can be attributed to the carbonyl products. The other

poly(DMX-*co*-DVB)_1:4

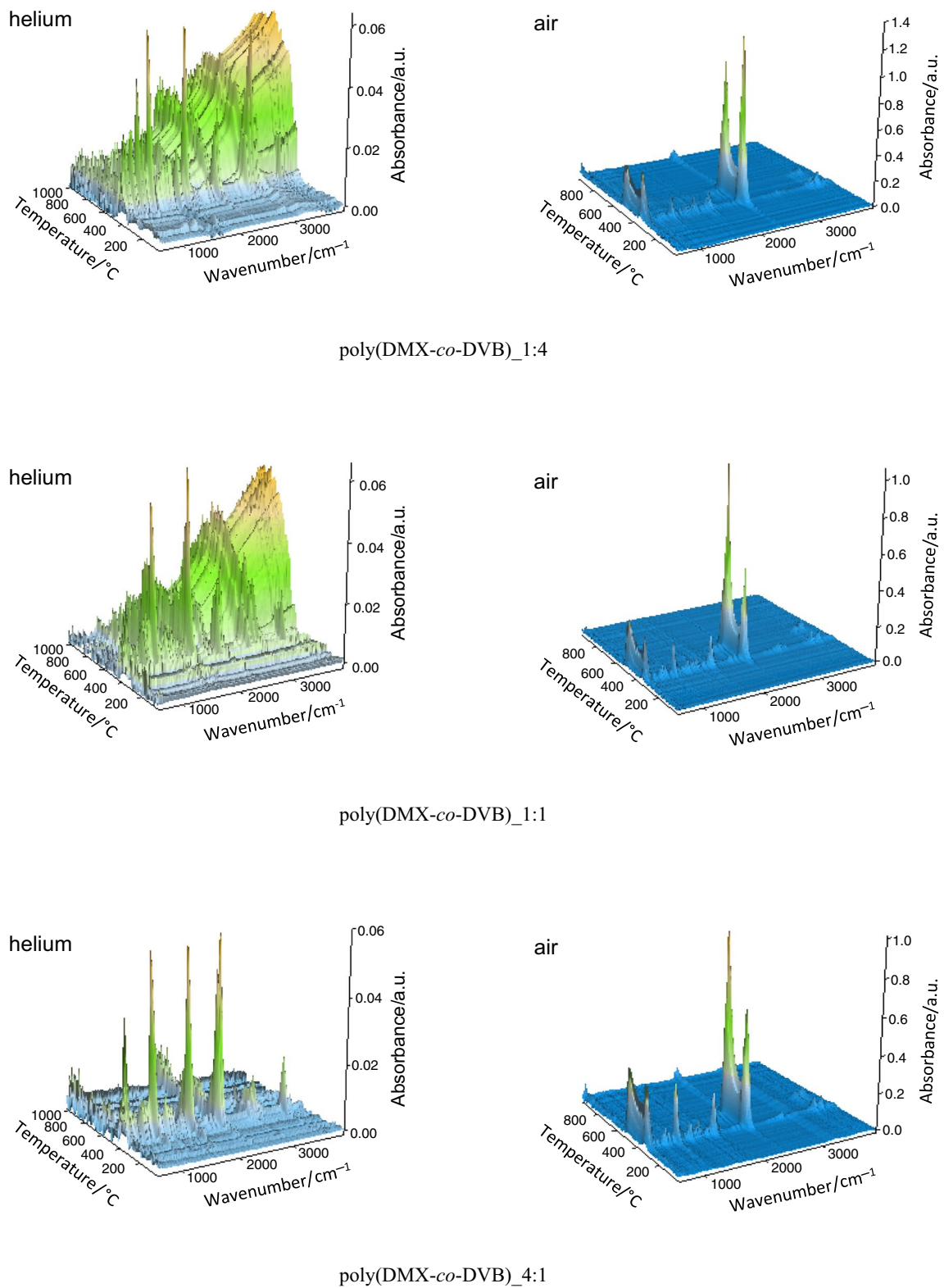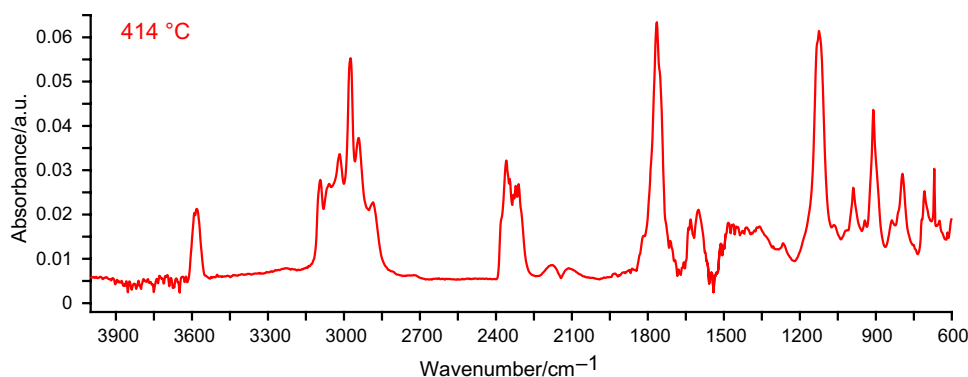poly(DMX-*co*-DVB)_1:1

poly(DMX-*co*-DVB)_4:1

Fig. 5 3D diagrams of FTIR spectra of volatiles obtained during the thermal decomposition of copolymers in helium and synthetic air

Fig. 6 FTIR spectrum of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_1:4 copolymer in helium

peaks indicate the presence of aldehydes (at 2725 cm^{-1}—ν C–H of the aldehyde group), esters (at 1124 cm^{-1}—ν C–O of the ester group) and carboxylic acids (at 3240 cm^{-1}—ν O–H of the carboxylic group). Bands at 2974–2885 cm^{-1} assigned to the C–H stretching vibrations of the methyl and methylene groups are also visible. Moreover, one can see the peaks at 3093 and 3058 cm^{-1} which can come from aromatic and unsaturated products (ν C–H). The creation of unsaturated compounds is also manifested by the peaks at 1631 cm^{-1} (ν C=C), 3017 cm^{-1} (ν=CH–) and 989 and 910 cm^{-1} (δ_{oop} C–H of the vinyl group). In turn, the bands at 1600 cm^{-1} (ν C–C of the benzene ring) and 836 and 795 cm^{-1} (δ_{oop} C–H of the disubstituted benzenes) confirm the existence of aromatic compounds. In turn, the absorption peak at 3591 cm^{-1} is due to the O–H stretching vibrations, while that at 1060 cm^{-1} is characteristic of the C–OH stretching vibrations. Both these peaks point to the presence of alcohols. Also, in the spectrum there appear bands typical of H$_2$O (at ~4000–3600 cm^{-1}), CO$_2$ (at 2359–2310 cm^{-1} and 669 cm^{-1}) and CO (at 2176 and 2113 cm^{-1}).

The FTIR spectra from the first (T_{max} at 378 °C) and second (T_{max} at 421 °C) decomposition steps of poly(DMX-*co*-DVB)_1:1 are shown in Fig. 7. Similarly to the spectrum of poly(DMX-*co*-DVB)_1:4 they display the adsorption peaks originating from CO$_2$, CO, H$_2$O, carbonyl and aromatic compounds, alkenes and alcohols. The incorporation of a larger amount of DMX units resulted in the appearance

of additional peaks, at 1508 and 1458 cm^{-1}. The former is due to the C–C stretching vibrations of the benzene ring, whereas the latter can be attributed to both the C–H deformation vibrations of the methyl group and the C–C stretching vibrations of the benzene ring. Comparing the intensity of the absorption bands at 1772 and 1125 cm^{-1}, one can state that in the second decomposition step there is a significantly smaller amount of carbonyl compounds, including esters. Moreover, in this step slighter amounts of unsaturated products are detected.

In the FTIR spectra received for poly(DMX-*co*-DVB)_4:1 copolymer (Fig. 8), one can see almost the same bands as for poly(DMX-*co*-DVB)_1:1 one. This indicates that as a rule, the decomposition of these materials was connected with the evolution of the same compounds. The differences occur only in the amounts of the generated products (different peak intensities). The differences in the peak intensities are also present in the particular steps of poly(DMX-*co*-DVB)_1:4 copolymer decomposition. In the second step, one can notice smaller amounts of CO$_2$, alcohols and carbonyl compounds, among others esters in comparison with the first one. In turn, in the third step one can observe a further decrease in the amounts of the above mentioned substances as well as unsaturated compounds, while the amount of aromatic ones increases (the increase of peaks at 821–750 cm^{-1}).

In the synthetic air atmosphere, all the investigated copolymeric beads are decomposed in two steps. The DTG curves

Fig. 7 FTIR spectra of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_1:1 copolymer in helium
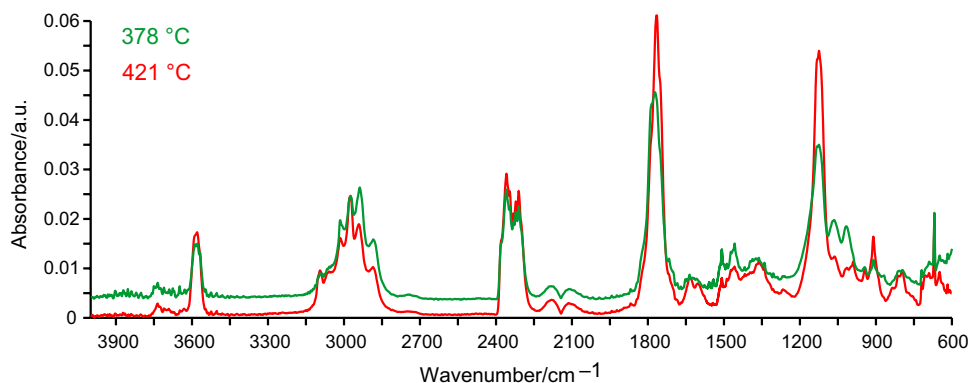
Fig. 8 FTIR spectra of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_4:1 copolymer in helium
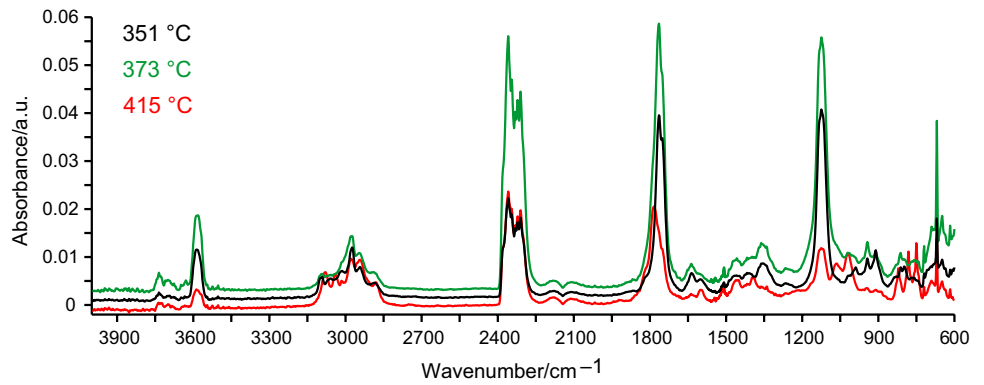

Fig. 9 FTIR spectra of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_1:4 copolymer in synthetic air

Fig. 10 FTIR spectra of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_1:1 copolymer in synthetic air
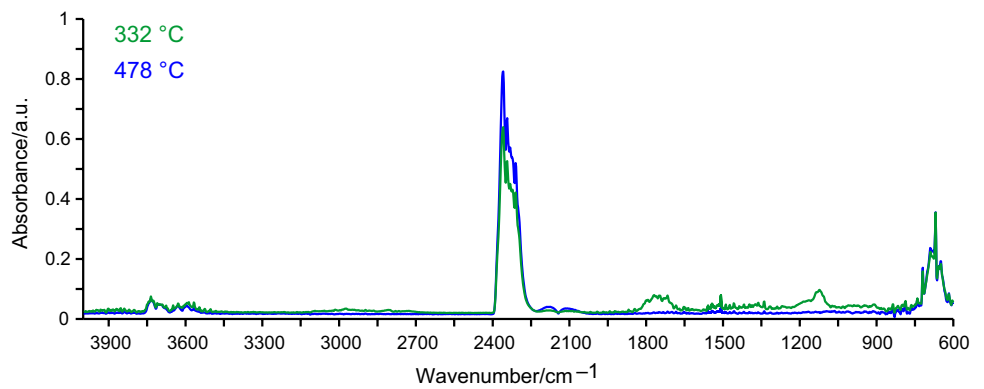

Fig. 11 FTIR spectra of volatile products obtained at the maximum rate of mass loss of the thermal decomposition of poly(DMX-*co*-DVB)_4:1 copolymer in synthetic air
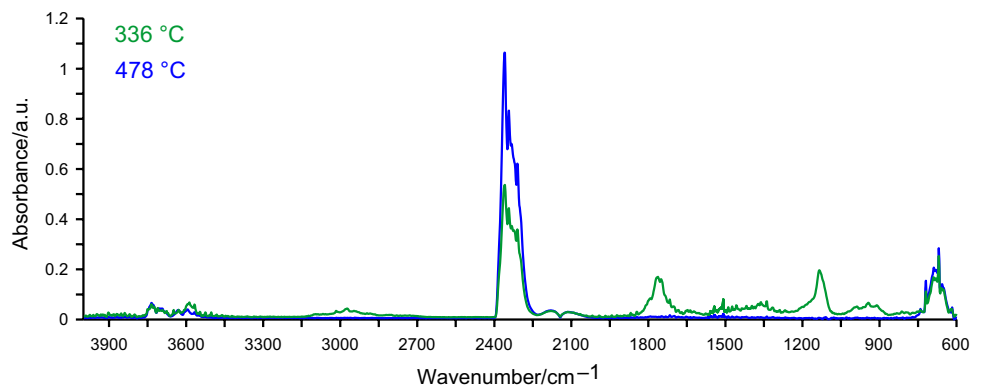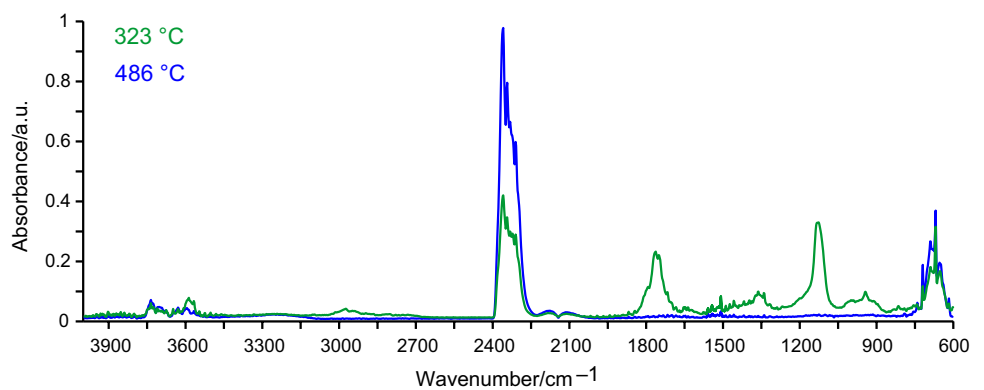
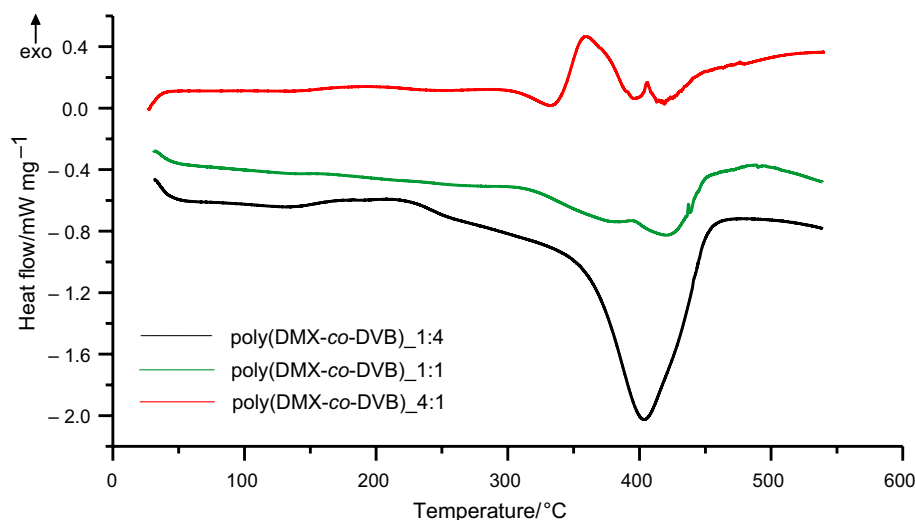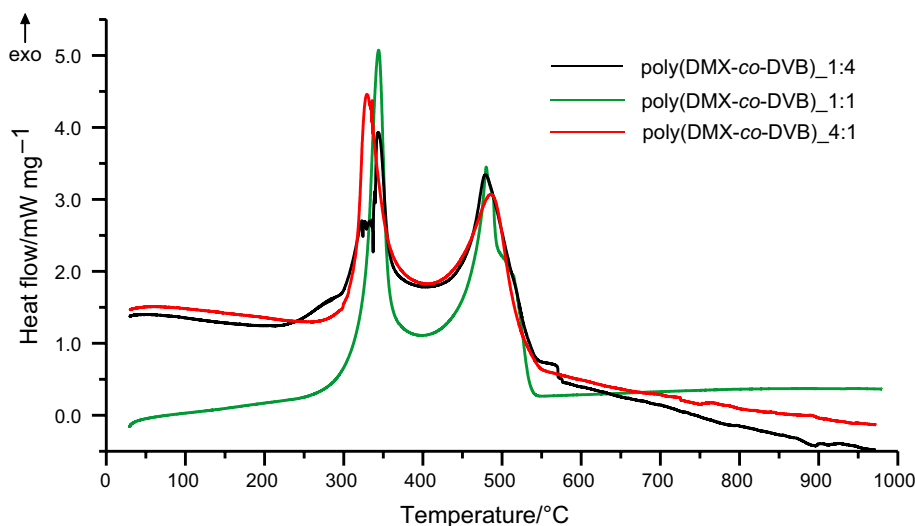**Fig. 12** DSC curves of copolymers obtained in helium

Fig. 13 DSC curves of copolymers obtained in synthetic air

(Fig. 4) exhibit two partially overlapped peaks with T_{max} at 323–336 and 478–486 °C, with a higher intensity of the lower-temperature one. These peaks correspond to ~47–53 and 43–48% mass losses. The first decomposition step can be connected with the thermal degradation of methacrylate bonds and immediate oxidation of newly created products, while the second one is probably associated with the oxidation process of the remaining cross-linked part which can be confirmed by the detailed analysis of FTIR spectra (Figs. 9–11). On the basis of this analysis, it can be stated that all copolymers in the first step are decomposed with the emission of CO_2, CO, H_2O, organic carbonyl products (mainly esters and aldehydes) as well as unsaturated and aromatic ones. In turn, in the second step their degradation was associated with the evolution of only CO_2 and CO, but their amounts were higher.

Similarly to the situation in helium atmosphere, the larger amount of DMX-based units, the worse thermal stability of

Table 2 TG and DTG data of copolymers in synthetic air atmosphere

Copolymer	T_1^a/°C	T_{20}^a/°C	T_{50}^a/°C	T_{max}^b/°C	Residue/%
Poly(DMX-co-DVB)_1:4	308	332	416	332, 478	7.2
Poly(DMX-co-DVB)_1:1	307	332	351	336, 478	5.3
Poly(DMX-co-DVB)_4:1	302	322	323	323, 486	8.1

[a]The temperature of 1, 20 and 50% mass loss from the TG curve

[b]The temperature of the maximum rate of mass loss from the DTG curve

the synthesised copolymers (lower T_1, T_{20} and T_{50}). However, in the case of T_1 and T_{20} values the differences were relatively small (Table 2). When it comes to the residual masses, it can be said that the studied materials were more degraded in synthetic air than in helium (~5–8 vs. ~9–14%).

As it was mentioned earlier, the thermal behaviour of the copolymers was also monitored by the means of the DSC analysis. The DSC curves of the copolymers under study measured in helium are shown in Fig. 12. In the case of poly(DMX-*co*-DVB)_4:1 copolymer, the first endothermic peak with the maximum at 332 °C can be attributed to the decomposition of mainly ester bonds originating from the functional monomer (DMX). Unsaturated compounds produced in this reaction can undergo the cross-linking process. As a result, an exothermic peak with the maximum at 360 °C appears. After that, the decomposition of the cross-linked part of the copolymeric matrix based mainly on DVB takes place which is represented by endothermic peaks with the maxima at 400 and 421 °C [19]. On the DSC curve of poly(DMX-*co*-DVB)_1:1 copolymer, only two superimposed endothermic peaks are observed. The first one with the maximum at 384 °C is associated with the thermal degradation of functional groups originated from DMX, whereas the second one with the maximum at 420 °C can be a result of the decomposition process of the cross-linked part of the copolymer. During the examination of poly(DMX-*co*-DVB)_1:4, two peaks of opposite energetic effects occur. As it was reported [25], copolymers based mainly on DVB contain a significant amount of unreacted bonds; so the exothermic peak with the maximum at 219 °C can be ascribed to the cross-linking reaction of double bonds located inside microspheres. In turn, an endothermic peak with the maximum at 404 °C is connected with the thermal degradation of entire polymer matrix. Due to the fact that this copolymer is considerably enriched in DVB-derived units, only one peak is visible on the DSC curve.

In the oxidative atmosphere for all the copolymers under study, the DSC curves possess a similar course (Fig. 13). Two exothermic peaks can be observed. Their maxima are in accordance with the decomposition maxima determined on the basis of DTG curves. The first one with the maximum at 329–344 °C can be associated with oxidative degradation of mostly ester bonds. The second one (maximum at 480–486 °C) can be ascribed to oxidative processes that take place in the cross-linked part of the copolymers.

Conclusions

Porous copolymers poly(DMX-*co*-DVB) were synthesised via the radical suspension polymerisation in the presence of the toluene and decan-1-ol mixture as porogenic diluents. To introduce a significant amount of methacrylate groups, the molar ratios of DMX to DVB (1:4, 1:1, 4:1) were increased in the syntheses. The utilisation of dimethacrylate derivative of *m*-xylene (DMX) is advantageous because it allows to obtain copolymers of more polar character compared with hydrophobic styrene–divinylbenzene

commonly used in various chromatographic techniques. What is more, the copolymers derived from DMX are generally also more thermally stable in relation to the earlier described materials based on DMN [15, 17, 19]. This is especially beneficial because it broadens the range of their applications of techniques requiring a high thermal resistance. The temperatures of 1% mass loss of the copolymers under study were contained in the range of 229–296 °C (in helium) and 302–308 °C (in synthetic air). Unfortunately, the significant increase in the DMX amount in the polymerisation mixture caused the deterioration of the thermal stability of the synthesised copolymers. The degradation patterns showed two degradation steps in synthetic air. On the other hand, in helium atmosphere the number of degradation steps increased from 1 to 3 along with the increasing DMX-derived units. The analysis of decomposition volatiles pointed out that the formation of CO_2, CO, organic carbonyl compounds (esters, carboxylic acids and aldehydes) and aromatic and unsaturated products took place. These types of substances were also detected for the familiar copolymeric beads [14, 15, 17, 19]. The thermal behaviour of the copolymers under study determined by the DSC method is generally in accordance with the decomposition patterns determined on the basis of DTG curves.

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