



TG/DSC/FTIR/QMS analysis of environmentally friendly poly(citronellyl methacrylate)-co-poly(benzyl methacrylate) copolymers

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Received: 30 August 2022

Accepted: 12 December 2022

Published online:

3 January 2023

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ABSTRACT

Polymer materials, not described in the literature so far, were obtained in the process of UV polymerization between methacrylic monomer obtained on the basis of natural, terpene alcohol: citronellyl methacrylate and benzyl methacrylate with different composition. The structures of the novel, environmentally friendly copolymers were confirmed by the FTIR and ¹³C CPMAS/NMR spectra. The copolymers containing more than 50% mass of citronellyl methacrylate were characterized by a high conversion of the double bonds determined on the basis of the FTIR and NMR spectra (95–96% and 92–94%, respectively). The novel materials were highly resistant to polar and non-polar solvents and the chemical stability. The glass transition temperature was from 15.8 to 19.9 °C which confirms that the obtained materials are elastomers at room temperature. Their thermal stability depended on their composition. It was from 185 to 205 °C (inert conditions) and from 149 to 214 °C (oxidizing conditions). TG/FTIR/QMS studies confirmed that their decomposition took place mainly as a depolymerization process combined with a subsequent breaking of the bonds in the resulting monomer/s at higher temperatures, which led to the formation of the gases with lower molecular masses. The main decomposition products emitted in an inert atmosphere were benzyl methacrylate, citronellyl methacrylate, 2-methylpropenal, citronellal and higher molecular mass compounds formed as a result of radical reactions between intermediate volatile products. In turn, under oxidizing conditions, as volatiles, benzyl methacrylate, citronellyl methacrylate, 2-methylpropenal, citronellal and small amounts of inorganic gases (CO, CO₂, H₂O) as a result of depolymerization and some combustion processes of the residues were indicated.

Handling Editor: Gregory Rutledge.

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Introduction

Poly(methacrylates) are polymers, most often obtained in the photopolymerization processes and radical processes using suitable type initiators. This group of the polymeric materials is widely used in the industry as elements and components of many blends and compositions. The use of poly(methacrylates) is known, inter alia, in the cosmetics, optics, biomedicine, dentistry, nanotechnology, etc., due to their great properties. Among these properties, one should mention their reasonable resistance to chemicals, high impact strength, lightness, high resistance to sunshine and weather exposure, shatter and scratch resistances, good thermal resistance, compatibility with human tissue, wide range of glass transition temperature, etc. [1–8].

However, despite these good and excellent properties, research on the search for novel, more environmentally friendly methacrylic polymers with modified and/or improved properties for applications in the industry is still being carried out. The synthesis of such materials can take place in the processes of the chemical modification of natural polymers such as polysaccharides, proteins, biopolyesters, with the use of commercially available or new acrylic and methacrylic monomers [9–18] or in the processes of the polymerization of acrylic and methacrylic monomers prepared from natural compounds.

So far, it is known to use isosorbide to obtain acetylated acrylic and methacrylic isosorbide monomers by the tandem esterification with acetic anhydride and methacrylic anhydride [19–22] or syringyl methacrylate, creosyl methacrylate [23–25], vanillin methacrylate [24–26] to prepare bio-based polymeric materials for high-temperature applications. The use of new alkyl lactate monomers (methyl, ethyl, *n*-propyl and *n*-butyl lactate acrylates) to the preparation of bio-based acrylates is also known [27–31]. The synthesis of fatty acid-based meth(acrylate) monomers prepared in the esterification process of fatty alcohols with different chain lengths and meth(acrylic) acids or meth(acryloyl chlorides) or in the transesterification process of fatty alcohols with different chain lengths and meth(acrylates), e.g., methyl methacrylate is also described [32]. The possible application of new (meth)acrylates synthesized on the basis of 4-(4-hydroxyphenyl)butan-2-one

extracted from the bark of *Betula Pendula* and treated with sodium hydroxide solution and meth(acryloyl chloride) in order to prepare novel polymeric materials is also reported [33]. In addition, the resin formulations based on natural phenolic acrylates containing a structural diacrylate synthesized by a dimerization of eugenol with a dithiol through the radical thiol-ene “click” reaction, a mono-methacrylate diluent (guaiacol methacrylate) and a methacrylate cross-linker (vanillyl alcohol methacrylate) have been tested for their use as more environmentally friendly materials for stereolithography 3D printing [34]. Also, the studies on the use of the new methacrylate monomer: eugenyl-2-hydroxypropyl methacrylate for the preparation of copolymers with methyl methacrylate are described [35]. Moreover, terpenes and terpenoids are very interesting group of compounds, due to the large variety of their structures which makes them interesting compounds for the synthesis of the new terpene bio-based polymers. The preparation of more environmentally friendly polymers based on pinene acrylate and methacrylate, limonene acrylate and methacrylate, carvone acrylate and methacrylate, menthyl acrylate and methacrylate, sorbrol acrylate and methacrylate or tetrahydrogeraniol acrylate to obtain, among others, more environmentally friendly well-defined polymers and precise di- and multiblock copolymer architectures, novel green hydrophilic and amphiphilic terpene-based polymers or high chemical and solvent-resistant, branched terpene methacrylate homopolymers from acrylate and methacrylate monomers prepared from natural terpene alcohols such as geraniol, nerol and citronellol and meth(acryloyl) chlorides is known, so far [36–44].

Of course, the above examples of meth (acrylate) monomers from natural compounds do not exhaust the list of monomers that can be used to synthesize more environmentally friendly polymeric materials compared to the petroleum-based polymers. The given examples only illustrate the recent trend to searching for polymeric materials with a more positive impact on the environment than traditional polymers.

In this paper, the use of methacrylate monomer synthesized in the amine catalyzed esterification process of natural, terpene alcohol: citronellol and methacryloyl chloride to the preparation of environmentally friendly copolymers with commercially available aromatic methacrylate monomer: benzyl

methacrylate was proposed. The copolymers were obtained by the UV polymerization using different mass% of methacrylate monomers and 2,2-dimethoxy-1,2-diphenylethan-1-one as an initiator. The influence of the mass% of methacrylate monomers on the double bond conversion (DC), glass transition temperature (T_g), solvent resistance, chemical resistance, thermal stability and the decomposition course in an inert and oxidizing atmosphere of the novel poly(citronellyl methacrylate)-*co*-poly(benzyl methacrylate) copolymers was presented and discussed.

Materials and methods

Materials

Citronellyl methacrylate was synthesized and purified according to the method described elsewhere [45–47]. Benzyl methacrylate was from Sigma-Aldrich (96%). Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one), methanol, chloroform, hexane, toluene, butanol and silica gel were from Merck. Sodium carbonate, magnesium sulfate, sodium hydroxide, carbon tetrachloride, hydrochloric acid, magnesium sulfate, buffers solutions (pH 4, 7, 10) were from POCh, Gliwice, Poland.

UV polymerization

The UV polymerization of monomer mixtures containing different mass% of methacrylate monomers was carried out in the presence of Irgacure 651 (3.0 mas%). The prepared mixtures of monomers: citronellyl methacrylate (CitM) and benzyl methacrylate (BM), Table 1, were irradiated using a TL20W/05 SLV low pressure mercury lamps with

340–365 nm. The circle samples with a diameter of 30 mm and thickness of 5 mm were irradiated for 10 min at 25 °C. Then, all prepared films were conditioned at 60 °C for 5 h and at 120 °C for 3 h to complete the polymerization.

Characterization of copolymers

FTIR Spectroscopy

The FTIR spectroscopy was used to check and confirm the structure of the prepared polymeric materials. The FTIR spectra (KBr tablets) were gathered from 600 cm^{-1} to 4000 cm^{-1} with 4 cm^{-1} resolution and 62 scans with the use of the FTIR Tensor 27 instrument (Bruker, Germany).

The conversion degree (DC) of the C = C bonds in methacrylate monomers after the UV polymerization and after post-polymerization was estimated based on the FTIR spectra. The DC was evaluated by the comparison of the area of the C = C stretching vibrations bands at 1635–1637 cm^{-1} (methacrylate bonds) and at 1674 cm^{-1} (ethylenic bonds) with the area of the C=O stretching vibration band at 1724 cm^{-1} . The DC values for the obtained polymeric materials were calculated from the equation:

$$\text{DC}/\% = 100 \times [1 - (R_{\text{polymer}}/R_{\text{monomer}})]$$

where R is the surface area of C=C absorption band/surface area of C=O absorption band [48, 49].

¹³C CPMAS/NMR The cross-polarization magic angle spinning (¹³C CPMAS/NMR) measurements were computed on a Bruker Avance 300 MSL instrument (Bruker, Germany) at resonance frequency of 75.5 MHz with the number of scans 2048 and the spin rate 7300 Hz.

Table 1 The prepared compositions

Polymeric material	Citronellyl methacrylate (CitM)/g	Benzyl methacrylate (BM)/g	Irgacure 651/g	Mass ratio of monomers (CitM or BM)/%
Copolymer 1	0.6	2.4	0.09	20:80
Copolymer 2	1.5	1.5	0.09	50:50
Copolymer 3	2.4	0.6	0.09	80:20
PCitM	3.0	–	0.09	100:0
PBM	–	3.0	0.09	0:100

where: *PCitM*–poly(citronellyl methacrylate), *PBM*–poly(benzyl methacrylate).

Solubility Tests

The solubility of the obtained polymeric materials was determined by the gravimetric method at 25 °C. The solvents of different polarity such as water, methanol, butanol, toluene, hexane, carbon tetrachloride, chloroform, cyclohexane, dioxane, acetone, acetic acid, ethyl acetate, tetrahydrofuran, diethyl ether were chosen. The sample of ca. 0.2 g was immersed in the suitable solvent and kept over 6 months. Then, the samples were removed from the solvents, dried and weighed. The percentage change in the mass (ΔmS) is determined from the following equation:

$$\Delta mS = (m_1 - m_2)/m_1 \times 100\%$$

where m_1 —the initial mass of the polymeric sample, m_2 —the final mass of the polymeric sample, ΔmS —the percentage change in mass (the solubility of the materials).

Chemical resistance

The chemical resistance of the obtained polymeric materials was evaluated in alkaline, buffers and acidic environments at 25 °C. As environments 1 M NaOH, buffer solutions with pH 4, 7 and 10 and 1 M HCl were used. The sample of ca. 0.2 g was placed in a suitable chemical environment and kept over 6 months. Then, the samples were removed from these solutions, carefully washed with distilled water, dried and weighed. The percentage change in the mass (ΔmR) was evaluated from equation [50]:

$$\Delta mR = (m_1 - m_2)/m_1 \times 100\%$$

where m_1 —the initial mass of the polymeric sample, m_2 —the final mass of the polymeric sample, ΔmR —the percentage change in the mass (the chemical resistance of the polymeric material to a specific environment).

Glass transition temperature (T_g)

The glass transition temperature (T_g) of the obtained polymeric materials was evaluated using a DSC method. The sample of ca. 10 mg was placed in an aluminum crucible with a pierced lid and heated from minus 120 °C to 150 °C in an argon atmosphere (a flow rate 40 mL/min). The heating rate was 10 K/min. Two DSC scans from minus 120 °C to 150 °C

were performed. The T_g was evaluated from the second DSC scan.

Thermal properties (TG/DTG)

The thermal properties (TG/DTG) of the materials were determined with a use of a TG/DTG method. The STA 449 Jupiter F1 instrument (Netzsch, Germany) was used. The sample of ca. 10 mg was heated from 40 °C to 550 °C in an open Al_2O_3 crucible and with a heating rate 10 K/min. The TG/DTG analyses were performed in an inert atmosphere (a helium with a flow rate 40 mL/min) and in an oxidizing atmosphere (a synthetic air atmosphere with a flow rate 100 mL/min). The initial decomposition temperatures marked as temperatures where there is a mass loss of 5% ($T_{5\%}$), maximum decomposition temperatures (T_{max}), mass loss in each decomposition stage (Δm) and residual masses (rm) were evaluated.

Simultaneous TG-FTIR-QMS analysis

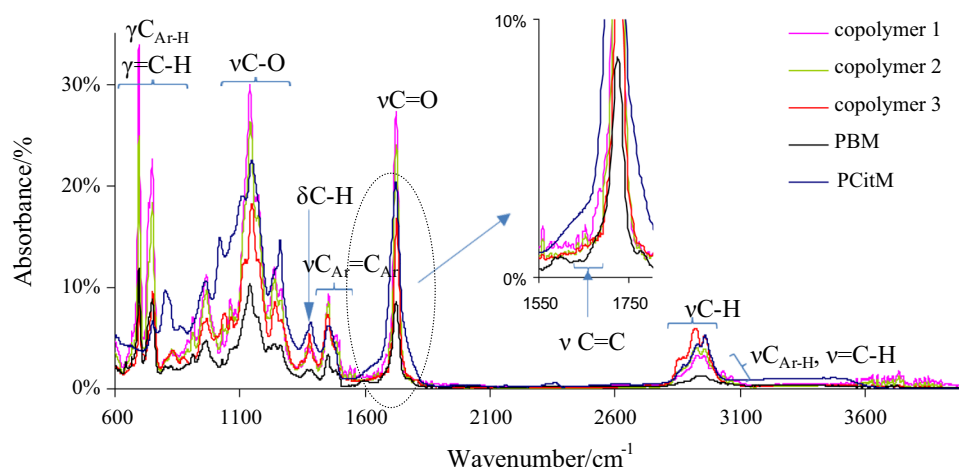
The volatiles emitted during the heating of the polymeric materials were analyzed by a simultaneous TG-FTIR-QMS analysis. A STA 449 Jupiter F1 instrument (Netzsch, Germany) was connected on-line to the FTIR analyzer (FTIR TGA 585, Bruker, Germany) and the QMS analyzer (QMS 403 C Aëolos, Germany). The emitted volatiles were collected in both atmospheres: inert and oxidizing. The FTIR analyzer was connected on-line to a STA instrument through a Teflon tube 2 mm with a diameter and heated to 200 °C to avoid the condensation process of volatiles. The gaseous FTIR spectra were collected from 600 to 4000 cm^{-1} and 4 cm^{-1} resolution. The QMS analyzer was linked on-line to a STA instrument by a quartz capillary heated to 300 °C. The QMS was operated under electron ionization 70 eV. The QMS spectra were gathered from 10 to 170 m/z.

Results and discussion

FTIR Spectroscopy

The FTIR spectra for the tested polymeric materials are presented in Fig. 1. The FTIR spectra show all the absorption signals for the characteristic groups present in the structure of the copolymers. The following vibrations are observed from the FTIR spectra of the

Figure 1 The FTIR spectra for the obtained polymeric materials.



copolymers: the stretching vibrations of the C_{Ar-H} and $=C-H$ ($3014-3070\text{ cm}^{-1}$), the stretching vibrations of the $C-H$ ($2877-2966\text{ cm}^{-1}$), the stretching vibrations of the $C=O$ (1724 cm^{-1}), the stretching vibrations of $C=C$ ($1635-1637\text{ cm}^{-1}$ and 1674 cm^{-1} with a very low intensity for copolymers 2 and 3), the stretching vibrations of the $C_{Ar}=C_{Ar}$ ($1456-1496\text{ cm}^{-1}$), the deformation vibrations of the $C-H$ ($1353-1456\text{ cm}^{-1}$), the stretching vibrations of the $C-O$ ($1099-1272\text{ cm}^{-1}$) and the out of plane deformation vibrations of the C_{Ar-H} and $=C-H$ ($663-970\text{ cm}^{-1}$) as it is marked in Fig. 1. The FTIR results confirm that the two types of double bonds present in citronellyl methacrylate are involved in the UV polymerization process. The absorption bands responsible for the stretching vibrations for methacrylate $C=C$ bonds are localized at $1635-1637\text{ cm}^{-1}$. In turn, the absorption bands for ethylenic $C=C$ double bonds appeared at 1674 cm^{-1} [38]. If we look at the FTIR spectra for the copolymers, it can be seen that the absorption bands characteristics for two types of the $C=C$ stretching vibrations have residual intensities, Fig. 1.

On the basis of the conversion degree (DC) calculations, it can be seen that the polymerization process and subsequent cross-linking process take place with high efficiency, especially for the copolymers with a certain composition. The DC values are in the range 95–96% for the copolymers containing from 50 to 80 mass% of citronellyl methacrylate (copolymers 2 and 3). In addition, after post-polymerization DC value increases by an average of 5–11%, Table 2. It confirms that the polymeric materials with a high degree of polymerization are obtained. This also indicates that both methacrylic and ethylenic $C=C$ bonds

participate in the polymerization process. This leads to the formation of branched, cross-linked materials [38, 51, 52]. However, for copolymer containing 20 mass% of citronellyl methacrylate (copolymer 1), the lower value of DC may be caused by a steric hindrance (benzyl rings), Table 2.

¹³C CP/MAS NMR

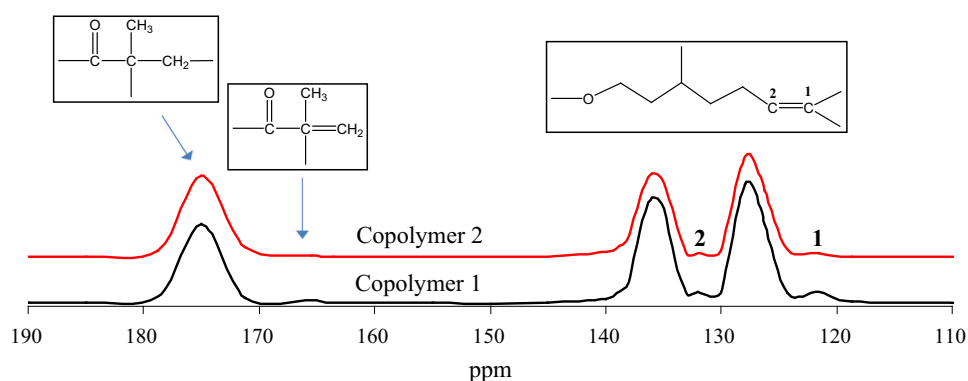
The assignments for the chemical shifts in the ¹³C CP/MAS NMR for the studied polymeric materials are presented in Table 3. The presented results indicate that the peaks associated with the carbonyl in unreacted methacrylate groups for the tested copolymers are visible at 166 ppm. Their intensity is low, in particular for the copolymers 2 and 3, Fig. 2. However, the carbonyl in reacted methacrylate groups is present at 175–176 ppm. This confirms the results obtained from the FTIR analysis and proves high conversions of methacrylate double bonds during the UV polymerization and stabilization of these materials. In addition, low-intensity NMR signals for the carbons with unreacted ethylene bonds at 132 and 122 ppm are observed for the copolymers 2 and 3. The intensity of the carbons with unreacted ethylene bonds for copolymer 1 is higher as compared to this intensity for the copolymers 2 and 3. It confirms the lower reactivity of ethylenic double bonds compared to the reactivity of methacrylate bonds in the polymerization process. The % of the unreacted $C=C$ double bonds is in agreement with the FTIR data. The % of unreacted $C=C$ double bonds calculated from the ¹³C CP/MAS NMR spectra was 22% (copolymer 1), 6% (copolymer 2) and 8% (copolymer 3).

Table 2 The conversion degree (DC) of the double bonds

Polymeric material	DC/% (after UV polymerization)	DC/% (after post-polymerization)
Copolymer 1	75	80
Copolymer 2	85	96
Copolymer 3	86	95
PCitM	81	90
PBM	80	90

Table 3 The assignments for chemical shifts in the solid-state ^{13}C NMR spectra

Copolymer1	Copolymer 2	Copolymer 3	PCitM	PBM	Group/carbon
<i>Chemical shift/ppm</i>					
<i>Polymer</i>					
175	175	176	175	176	C=O (carbonyl)
166	166	166	166	166	C = O (carbonyl)
132	132	132	132	–	= C (quaternary carbons)
135	136	136	–	135	C (quaternary ring)
122	122	122	122	–	= CH
128	127	128	–	128	protonated ring
66	65	66	–	66	–O–CH ₂ –ring
62	62	62	62	–	–CH ₂ –O–
55	56	56	–	55	–CH ₂ –
45	45	46	–	45	quaternary carbon
30–38	30–38	30–38	30–38	–	–CH ₂ –
16–27	16–27	17–27	18–27	16	–CH ₃
24, 30	24, 30	24, 30	24, 30	–	CH

Figure 2 The fragment of the ^{13}C CP/MAS NMR of tested copolymers.

Based on the results of the FTIR spectroscopy and the cross-polarization magic angle spinning (^{13}C CPMAS/NMR) measurements, the simplified structure of the copolymers is presented in Scheme 1.

Solubility Tests

The results from the solubility tests are placed in Tables 4 and 5. As it can be seen, the solubility of the copolymers and PCitM in both types of solvents (polar and non-polar) is very low. The solubility is

below 1.8% for the samples kept in the solvents for 6 months. This is connected with its branched structure containing additional cross-links as it was confirmed based on the FTIR and ^{13}C CP/MAS NMR analyses.

Chemical resistance

Table 6 contains the chemical resistance results. The tested polymeric materials are highly resistant to alkaline, buffer and acidic environments. The

Scheme 1 The simplified structure of the obtained copolymers.

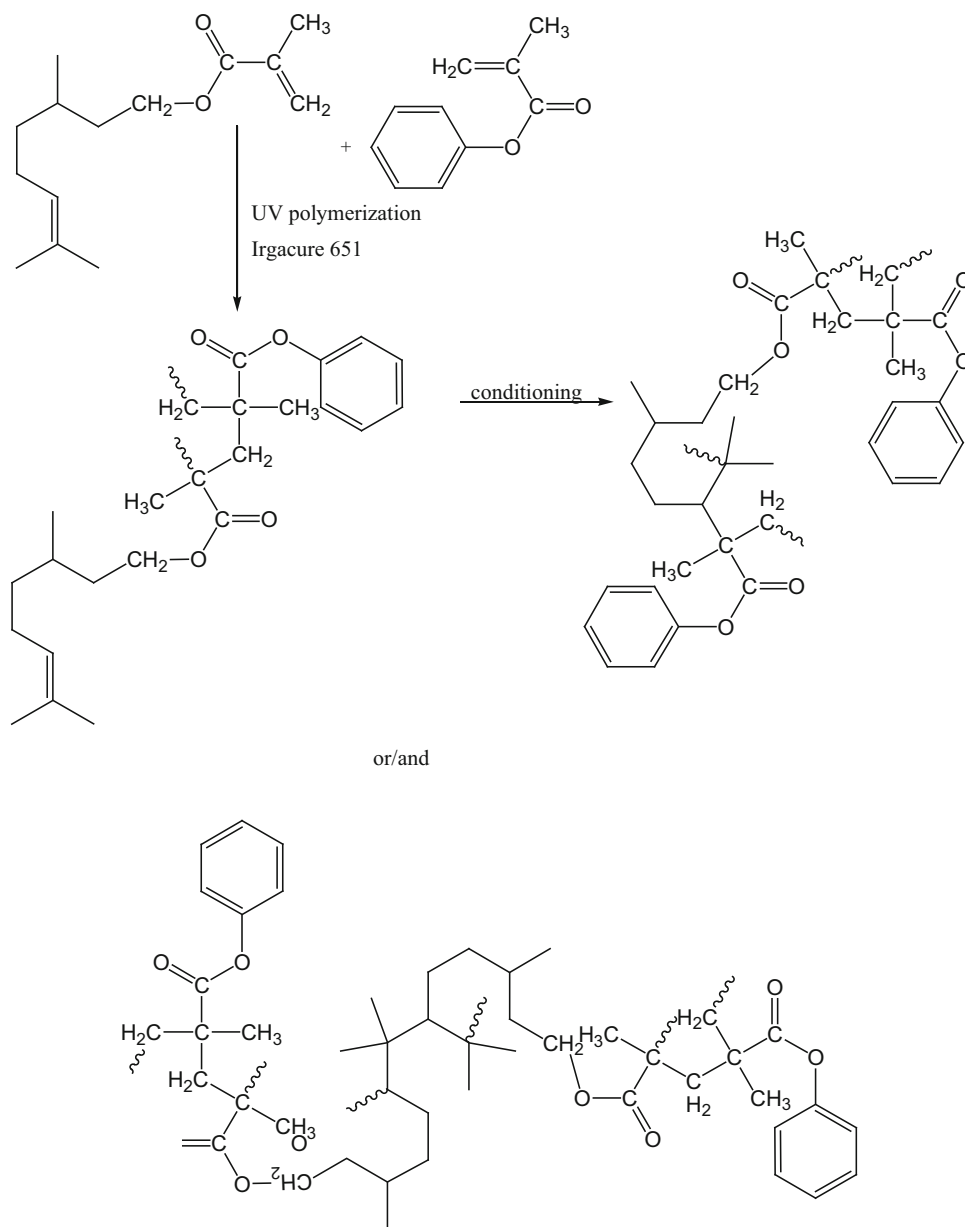


Table 4 The percentage change in the mass (ΔmS) in polar solvents

Polymer name	$\Delta mS/\%$						
	water	methanol	butanol	acetone	acetic acid	ethyl acetate	tetrahydrofuran
Copolymer 1	1.0	1.2	1.5	1.1	1.3	0.8	0.6
Copolymer 2	0.5	0.6	0.7	0.9	1.1	0.8	0.6
Copolymer 3	0.5	0.6	0.8	0.9	1.1	0.7	0.5
PCitM	0.4	0.3	0.3	0.5	0.9	0.7	0.6
PBM	0	0	0	18	20	15	soluble

percentage change in the mass is below 1.6%. In addition, it was noticed that the samples have not changed their color or shape after chemical resistance

tests. Before the tests, the samples were colorless or slightly yellowish.

Table 5 The percentage change in the mass (ΔmS) in non-polar solvents

Polymer name	$\Delta mS/\%$						
	diethyl ether	dioxane	chloroform	CCl_4	hexane	cyclohexane	toluene
Copolymer 1	0.5	0.8	1.2	1.1	1.0	0.9	1.8
Copolymer 2	0.4	0.8	0.9	0.7	0.8	0.8	0.9
Copolymer 3	0.4	0.9	0.8	0.6	0.9	0.8	0.9
PCitM	0.3	0.9	0.6	0.6	0.8	0.6	0.7
PBM	2.0	soluble	soluble	7.0	13	10	soluble

Table 6 The percentage change in the mass (ΔmR) in different environments

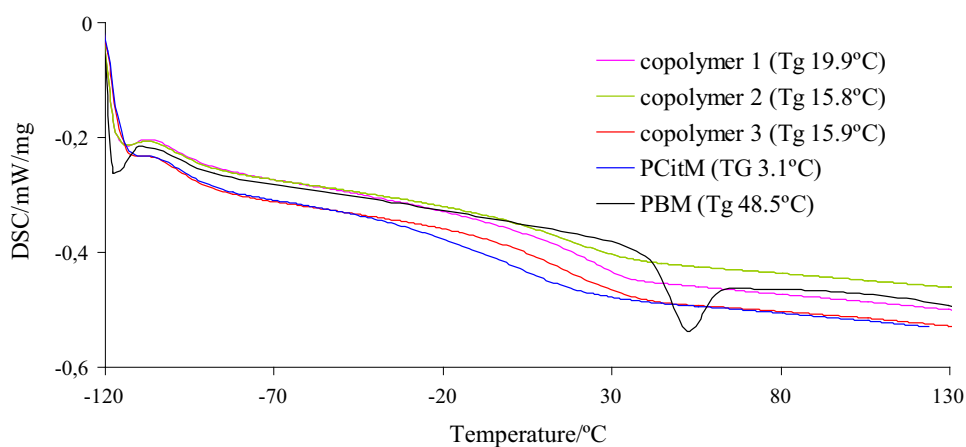
Polymer name	$\Delta mR/\%$				
	1 M NaOH	1 M HCl	Buffer pH = 4	Buffer pH = 7	Buffer pH = 10
Copolymer 1	1.5	1.2	1.2	1.4	1.6
Copolymer 2	0.6	0.4	0.3	0.4	0.5
Copolymer 3	0.4	0.3	0.2	0.4	0.4
PCitM	0.4	0.0	0.0	0.1	0.1
PBM	swell	swell	swell	swell	swell

The results confirm that the prepared copolymers can be applied as high chemical and solvent-resistant polymeric materials for the preparation of different parts and elements work in aggressive environments or as potential protective coatings.

Glass transition temperature (T_g)

As tested using a DSC method, the glass transition temperature of the copolymers is slightly depended on the percentage of monomers used to obtain them. PCitM homopolymer is characterized by T_g of ca. 3.1 °C. In turn, PBM homopolymer has T_g of ca. 48.5 °C, while the copolymers show T_g of 15.8–19.9 °C, Fig. 3. The same T_g values for

copolymers containing from 50 mass% to 80 mass% of citronellyl methacrylate also indicate the similar degree of polymerization and cross-linking, as it is confirmed based on the FTIR and ^{13}C CP/MAS NMR analyses. However, a slightly higher T_g for the copolymer 1 (19.9 °C) with a lower DC value may be due to the higher content of aromatic rings in its structure. However, as can be seen from the results, the addition of citronellyl methacrylate to the copolymers causes a significant reduction in T_g compared to PBM and thus an increase in the flexibility of the materials at room temperature. Moreover, the copolymers show only one T_g indicating that random copolymers are obtained.

Figure 3 The DSC curves for the tested materials.

Thermal properties (TG/DTG) in inert atmosphere

The thermal stability of the tested copolymers is in the range of 185–205 °C, Fig. 4, Table 7. As it is visible, the thermal resistance of the novel polymeric materials is lower than the thermal stability of PCitM

and PBM homopolymers. In addition, the values of $T_{5\%}$ decrease with increasing citronellyl methacrylate monomer in the composition. The lower thermal stability of the copolymers compared to that of homopolymers may be due to the initiation of depolymerization at the ends of the chain for the copolymers at lower temperatures. Most likely, the

Figure 4 The TG-DTG-DSC curves for the tested copolymers (an inert atmosphere).

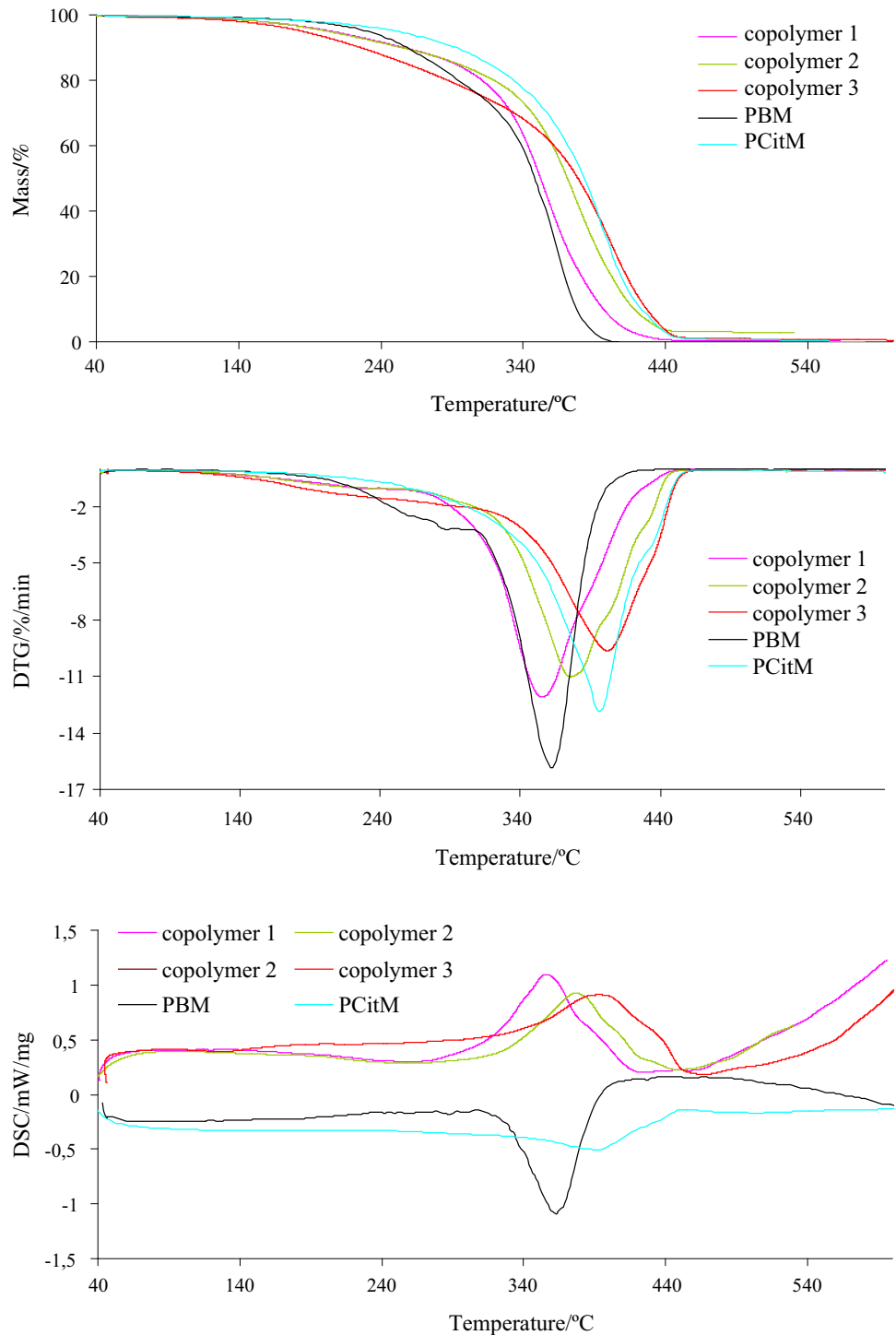


Table 7 The TG-DTG data of the copolymers (an inert atmosphere)

Polymer name	$T_{5\%}/^{\circ}\text{C}$	$T_{\text{max}1}/^{\circ}\text{C}$	$\Delta m_1/\%$	$T_{\text{max}2}/^{\circ}\text{C}$	$\Delta m_2/\%$	rm/%
Copolymer 1	205	223	10.5	355	89.5	0
Copolymer 2	203	202	11.4	376	85.8	2.8
Copolymer 3	185	209	22.9	401	77.1	0
PCitM*	251	396	99.2	577	0.8	0
PBM	233	290/360	100	–	–	0

*As cited in Ref [38]

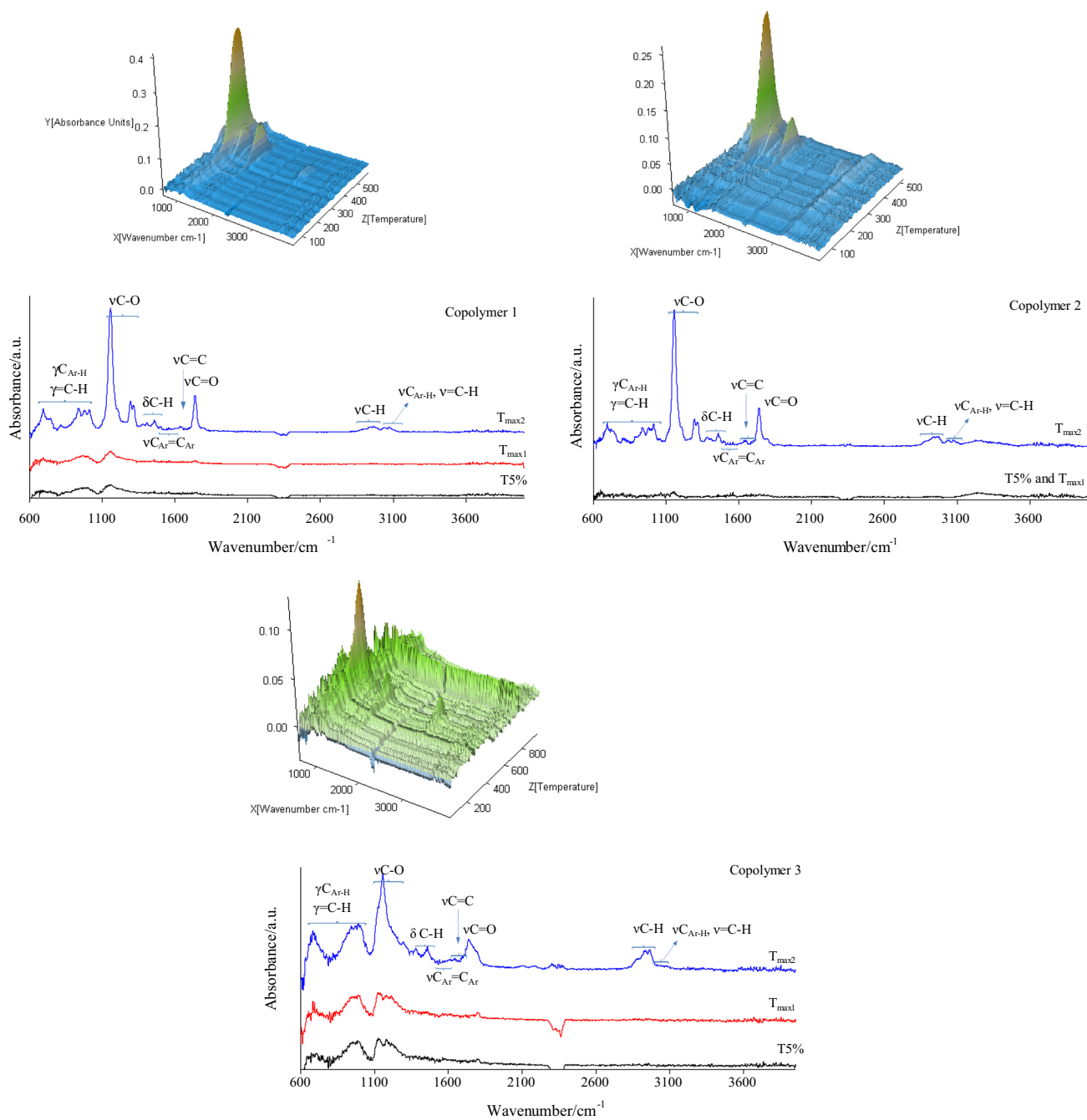
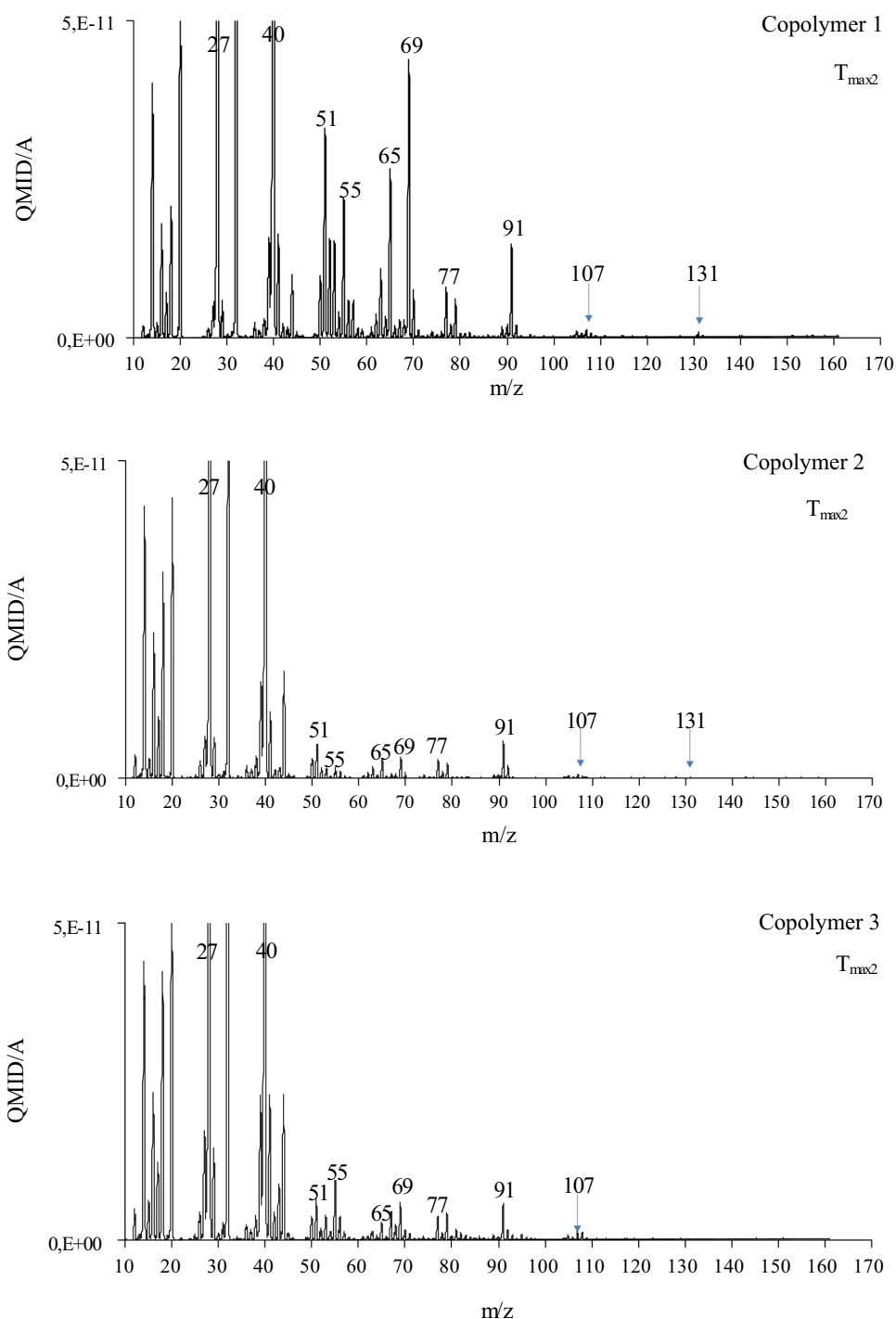


Figure 5 The 3D FTIR spectra and the extracted FTIR spectra for the copolymers (an inert atmosphere).

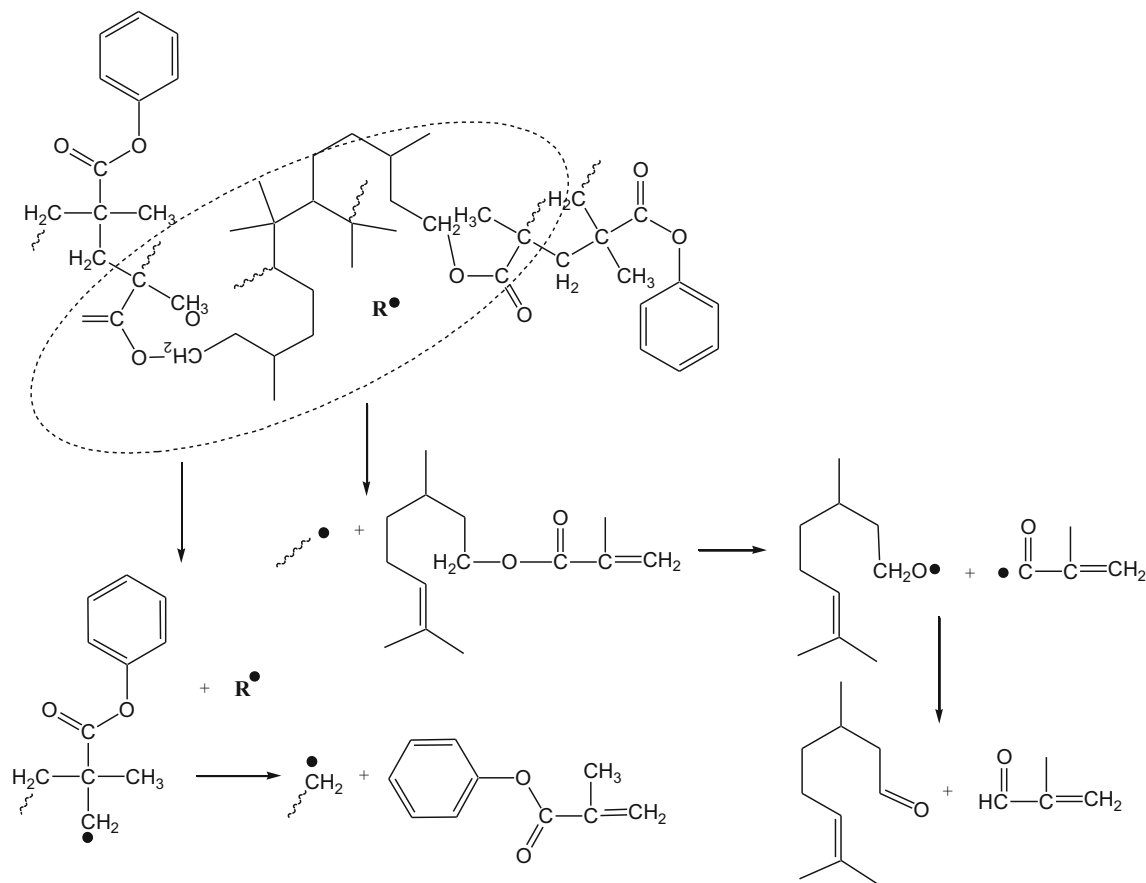
Figure 6 The m/z ions characteristic for the gaseous decomposition products for copolymers at $T_{\max 2}$ (an inert atmosphere).



addition of citronellyl methacrylate to the composition with benzyl methacrylate in this system reduces the activation energy and breaks the bonds at a lower temperature.

As can be seen from the presented graphs, the degradation of the copolymers in an inert atmosphere is at least two-stage process. The first decomposition stage is visible as a low intensity, “stretch” DTG peak

from $T_{5\%}$ to 265 °C with $T_{\max 1}$ at 202–223 °C and the mass loss (Δm_1) ranges from 10.5% (copolymer 1) to 22.9% (copolymer 3). The second decomposition stage is observed as a DTG peak of significant intensity from 265 °C to 470 °C with $T_{\max 2}$ at 355–401 °C and the mass loss (Δm_2) 89.5% (copolymer 1), 85.8% (copolymer 2) and 77.1% (copolymer 3) and with the rate of $-11.94\%/min$ (copolymer 1), $-$



Scheme 2 The pyrolysis path of the studied polymeric materials.

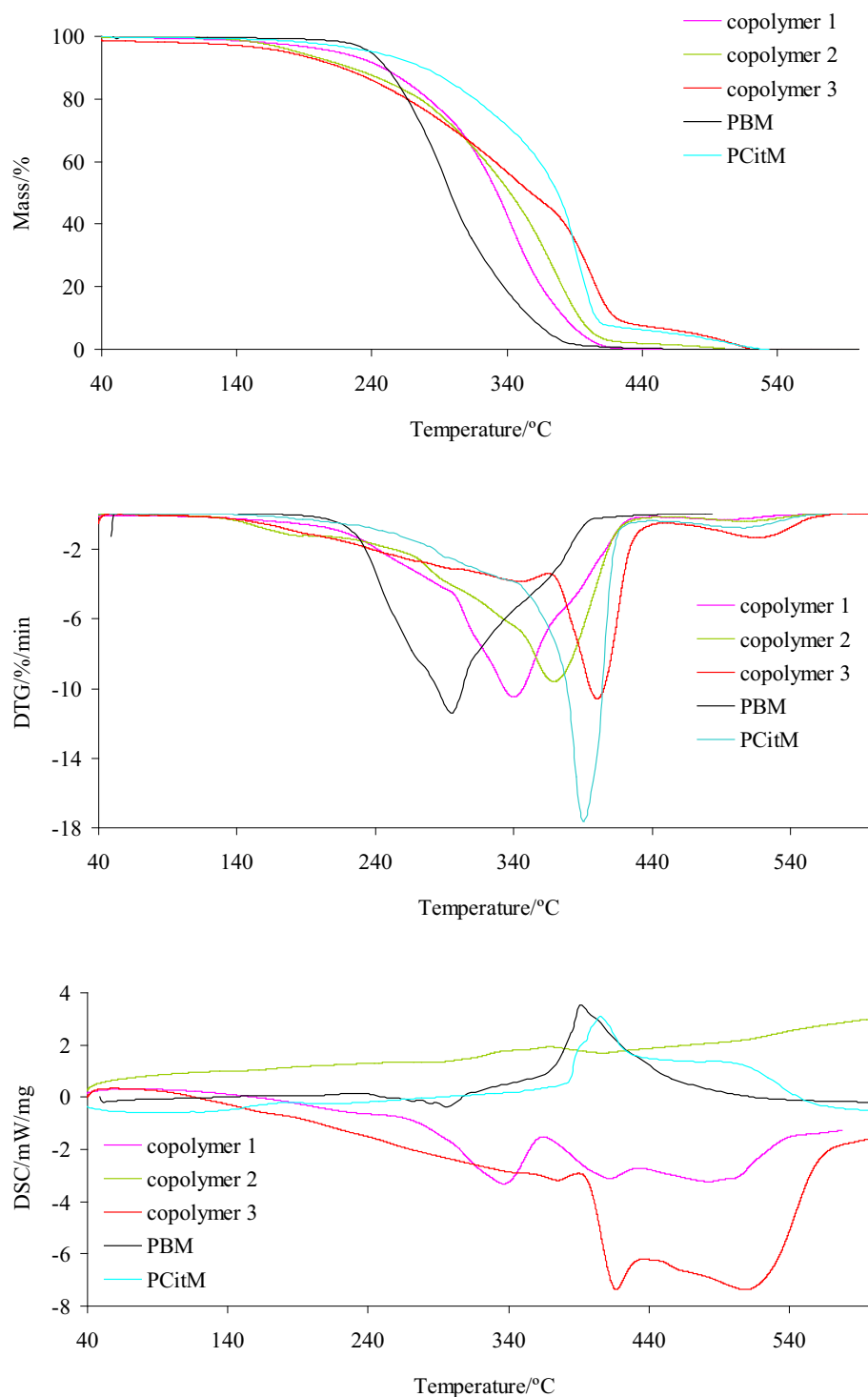
10.83%/min (copolymer 2) and $-9.46\%/min$ (copolymer 3). Also, the decomposition of homopolymers (PCitM and PBM) runs also in at least two stages connecting with the breaking of the bonds in their structures, Fig. 4 and Table 7. The full decomposition of homopolymers is observed at 470 °C.

What's interesting is that the PCitM and PBM homopolymers decomposition in an inert atmosphere is described as an endothermic DSC peak. The presence of only the endothermic peak indicates the pyrolysis processes of the bonds present in the structure of homopolymers. While if we look at the DSC curves for the copolymers, we can observe the presence of an asymmetric, exothermic peak in an inert atmosphere. Its presence suggests the simultaneous pyrolysis reactions of the bonds present in the copolymer structure and the chemical reactions that may take place between gaseous decomposition products and/or residues formed during the decomposition of the tested materials.

Simultaneous TG-FTIR-QMS analysis in inert atmosphere

The gaseous 3D FTIR spectra and the gaseous FTIR spectra extracted at $T_{5\%}$, $T_{\text{max}1}$ and $T_{\text{max}2}$ are presented in Fig. 5. On the basis of the presented FTIR spectra, it can be seen that the emission of the mixture of volatiles is observed. In addition, the intensity of a gas emission decreases with increasing citronellyl methacrylate content in the copolymers. In principle, no gas emissions are observed at $T_{5\%}$, which may be due to their low concentration undetectable by the FTIR analyzer. The gradual increase in the temperature to $T_{\text{max}1}$ causes that the FTIR spectra begin to show a signal characteristic for the stretching vibration of carbonyl group (at $1735\text{--}1776\text{ cm}^{-1}$) but still of very low intensity. However, increasing the heating temperature to $T_{\text{max}2}$ causes a high intensity of the emitted gases. Among them, we can notice the presence of the absorption signals characteristic for unsaturated and aromatic fragments: the stretching

Figure 7 The TG-DTG-DSC curves for the copolymers (a synthetic air atmosphere).



vibrations of the $=C-H$ and $C_{Ar} = C_{Ar}$ at 3018 cm^{-1} and 3052 cm^{-1} , the stretching vibrations of the $C = C$ at $1621\text{--}1625\text{ cm}^{-1}$ and the out of plane deformation vibrations of the $=C-H$ and $C_{Ar} = C_{Ar}$ at $930\text{--}990\text{ cm}^{-1}$ and $692\text{--}798\text{ cm}^{-1}$, respectively. Additionally, the presence of the absorption bands is

noticeable for compounds with the $C = O$ and $C-O$ groups in their structure: the stretching vibrations of the $C = O$ at 1735 cm^{-1} and at $1780\text{--}1785\text{ cm}^{-1}$ and the stretching vibrations of the $C-O$ at $1153\text{--}1297\text{ cm}^{-1}$ [53–57].

Table 8 The TG-DTG data for the copolymers (a synthetic air atmosphere)

Polymer name	$T_{5\%}/^{\circ}\text{C}$	$T_{\text{max1}}/T_{\text{max1a}}/T_{\text{max1b}}/^{\circ}\text{C}$	$\Delta m_1/\%$	$T_{\text{max2}}/^{\circ}\text{C}$	$\Delta m_2/\%$
Copolymer 1	214	271/340	98.1	486	1.9
Copolymer 2	185	184/369	90.3	510	9.7
Copolymer 3	149	158/333/392	77.8	503	22.2
PCitM	241	292/392	93.7	505	6.3
PBM	238	296/358	100	–	–

To more accurately confirm the structure of gases released during the decomposition of the copolymers, the QMS analysis was also performed, and the results are shown in Fig. 6. The QMS analysis indicates that one of the decomposition products is aromatic monomer: benzyl methacrylate. Its presence, among volatiles, is confirmed based on the following m/z ions in the QMS spectrum: 39, 41, 65, 69, 79, 90, 91, 107, 131 [58]. In addition, it should be noted that as the content of benzyl methacrylate in the copolymers decreases, the intensity of the aforementioned m/z ions decreases, which is correct and understandable. Apart from the emission of benzyl methacrylate, the emission of volatiles formed from citronellyl fragments is expected. Our previous research showed that the poly(citronellyl methacrylate) homopolymer decomposed to a monomer in inert conditions. It was confirmed by the presence in the FTIR spectrum of, inter alia, the stretching vibrations for the C = O group at 1736 cm^{-1} [38]. The FTIR spectra collected during the decomposition of the tested copolymers also show this absorption signal but this signal is asymmetrical with two maxima, one at $1733\text{--}1735\text{ cm}^{-1}$, and the other at 1776 cm^{-1} . The presence of the absorption signals for the carbonyl group with two maxima and the presence of the exothermic DSC peak may indicate the formation of ester and the decomposition products with lower masses. Analyzing the QMS spectra, the presence of m/z ions characteristic for citronellyl methacrylate such as 50, 51, 52, 53, 54, 55, 56, 57, 58, 65, 68, 69, 70, 77, 79, 91, 92 [38, 58] and for the decomposition products of citronellyl methacrylate such as 2-methylpropenal (m/z 41, 70, 39, 42, 29, 38, 40, 27, 37, 69) and citronellal (m/z 41, 69, 55, 95, 43, 56, 67, 29, 39, 27) is noticed, Scheme 2. However, due to the presence of an exothermic peak on the DSC, it is highly probable that the formed unsaturated aldehydes can undergo polymerization under the test conditions to form compounds with higher molecular masses. The pyrolysis path of the tested copolymers evaluated

based on the simultaneous TG-FTIR-QMS analysis is shown in Scheme 2.

Thermal properties (TG/DTG) in a synthetic air atmosphere

Figure 7 presents the TG/DTG/DSC curves obtained for the tested copolymers heated in synthetic air conditions. Generally, the tested copolymers show lower thermal resistance than homopolymers and copolymers tested in an inert atmosphere, except for the copolymer 1. Their thermal resistance ranges from 214 to 149 °C and depends on the mass% of monomers used to obtain them. The highest thermal stability is observed for the copolymer 1, which is obtained with the composition of the monomers: 80 mass% of benzyl methacrylate and 20 mass% of citronellyl methacrylate. As citronellyl methacrylate content of the compositions increases, the thermal resistance of the copolymers decreases, Table 8.

The oxidative decomposition of the copolymers run at least in two main stages, wherein the first decomposition stage is composed of at least two or three steps. The first decomposition stage is described as an asymmetric DTG signal from $T_{5\%}$ to 450 °C with two or three maxima marked as T_{max1} , T_{max1a} and T_{max1b} . The mass loss (Δm_1) at this stage of the decomposition is significant. The mass loss is 98.1% with a rate of $-10.42\%/min$ (copolymer 1), 90.3% with a rate of $-9.53\%/min$ (copolymer 2) and 77.8% with a rate of $-10.45\%/min$ (copolymer 3) and depends on the nature of the copolymers. In turn, the second decomposition stage of the copolymers is described by a symmetric DTG peak visible from 450 to 580 °C and with T_{max2} from 486 to 510 °C. The mass loss (Δm_2) is from 1.9 to 22.2% and depends on the composition of the copolymers. Moreover, in the case of homopolymers, mainly exothermic signals are observed in the DSC curves. It proves the chemical reactions taking place between the decomposition products of homopolymers and oxygen. What is

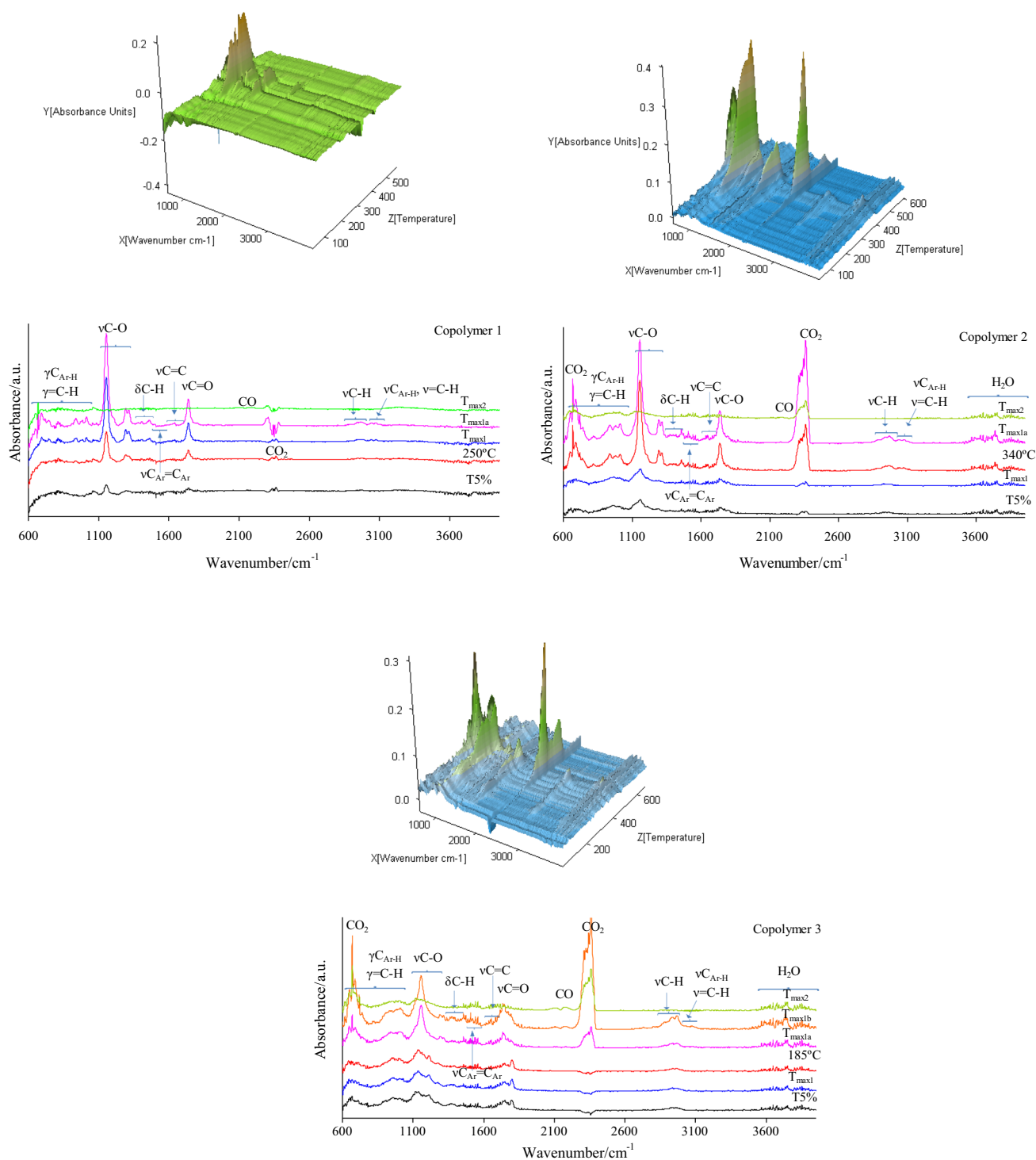
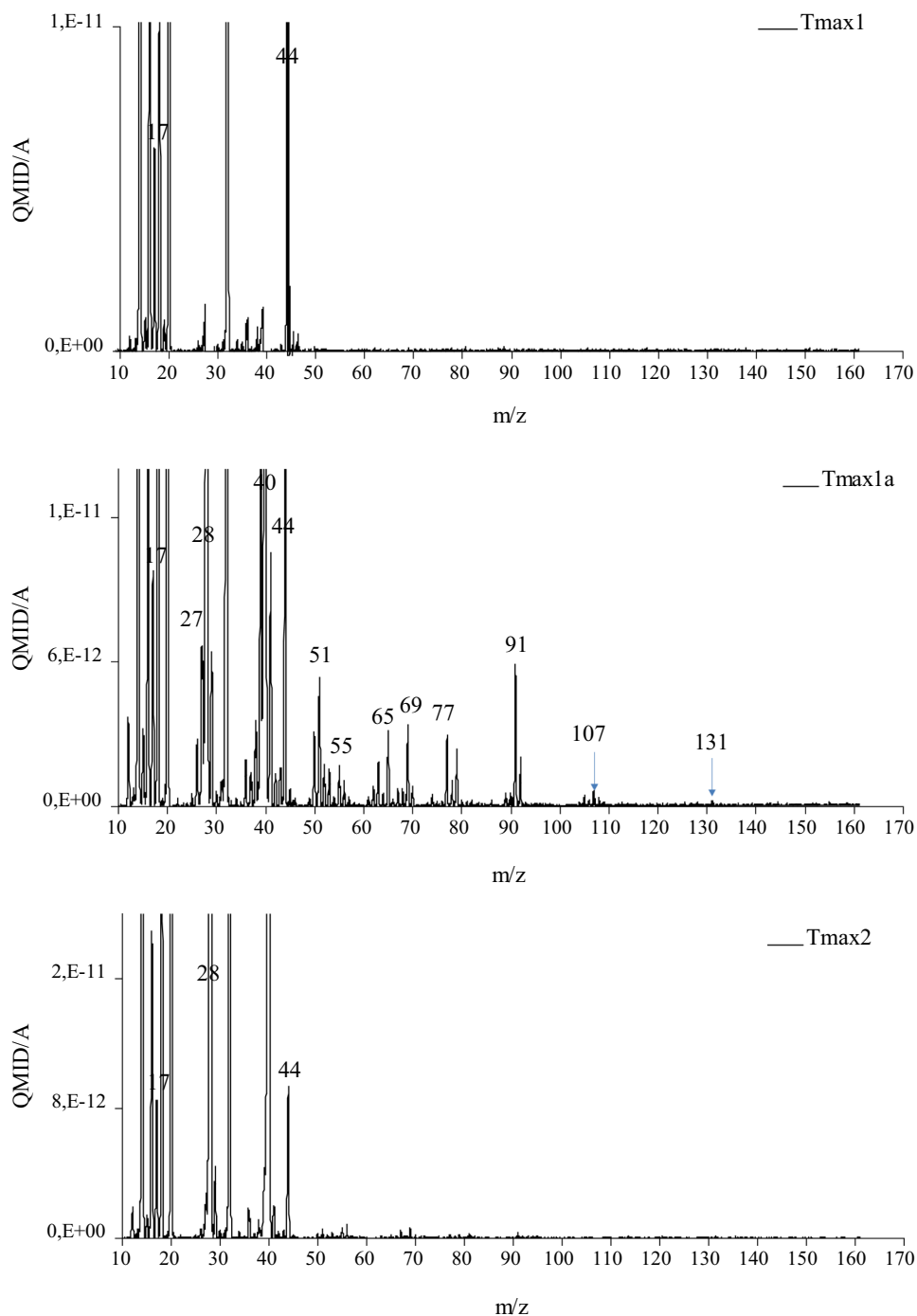


Figure 8 The FTIR spectra received under the decomposition process of the copolymers (a synthetic air atmosphere).

interesting is that in the DSC curves for the tested copolymers, only the endothermic signals are present. It suggests mainly the cleavage of the bonds in the structure of the copolymers. This indicates a

different course of the decomposition of homopolymers and copolymers in an oxidizing atmosphere. In the case of the copolymers, the presence of oxygen inhibits the formation of free radical intermediates.

Figure 9 The m/z ions characteristic for the gaseous decomposition products of the copolymers (a synthetic air atmosphere).



Therefore, mainly decomposition rather than chemical reactions takes place in the presence of oxygen.

Simultaneous TG-FTIR-QMS analysis in a synthetic air atmosphere

The FTIR gas spectra for the copolymers collected from $T_{5\%}$ to $T_{\max 1}$ show the presence of the following

absorption bands: the stretching vibrations of the = C-H and $C_{Ar} = C_{Ar}$ at 3025 cm^{-1} and 3058 cm^{-1} , the stretching vibrations for the compounds with the C = O groups at $1733\text{--}1735\text{ cm}^{-1}$ with a low intensity band at 1774 cm^{-1} (copolymers 1 and 2) or 1785 cm^{-1} (copolymer 3), the stretching vibrations of the C = C at $1621\text{--}1623\text{ cm}^{-1}$, the deformation vibrations of the C-H at $1440\text{--}1370\text{ cm}^{-1}$, the stretching vibrations of

the C–O at 1297–1051 cm^{-1} and the out of plane deformation vibrations of the = C–H and $C_{Ar} = C_{Ar}$ at 912–1000 cm^{-1} and 690–800 cm^{-1} , respectively [53–55]. The presence of these absorption bands may indicate the emission of ester fragments and a lower molecular mass compounds containing unsaturated bonds, aromatic rings and/or carbonyl groups in the structure. In addition, at this temperature range, a low emission of CO_2 (2358–2333 cm^{-1}) is also observed. At $T_{\text{max}2}$, mainly the emission of CO_2 and H_2O is confirmed, Fig. 8 [56, 57, 59].

The QMS spectra collected at $T_{\text{max}1}$, $T_{\text{max}1a}$ and $T_{\text{max}2}$ for the selected copolymer (copolymer 2) are presented in Fig. 9. As it is well visible, the appearance of the following m/z ions: 14, 15, 16, 17, 18, 20, 27, 36, 39, 44 at $T_{\text{max}1}$ is confirmed. However, at $T_{\text{max}1a}$, the number of m/z ions is significantly increased, which is related to the release of the main decomposition products during heating. At $T_{\text{max}1a}$, the presence of the m/z ions characteristic for the emission of benzyl methacrylate monomer is observed (m/z 39, 41, 65, 69, 79, 90, 91, 107, 131) [58]. In addition, the QMS spectra show the presence of m/z ions: 27, 29, 37, 38, 39, 40, 41, 42, 43, 50, 51, 52, 53, 54, 55, 56, 57, 58, 65, 67, 68, 69, 70, 77, 79, 91, 92 which are derived from decomposition products such as citronellyl methacrylate, citronellal and 2-methylpropenal. At $T_{\text{max}2}$, mainly the emission of H_2O (m/z 16, 17, 18), CO_2 (m/z 44) and CO (m/z 28) is visible [58] which indicate on the combustion processes of the formed residues [60, 61].

Conclusions

The more environmentally friendly polymeric materials with a high conversion of the double bonds evaluated based on the FTIR and ^{13}C CPMAS/NMR spectra and with an excellent solvent and chemical resistance were prepared in the UV polymerization of benzyl methacrylate monomer and methacrylate monomer synthesized in the esterification of natural, terpene alcohol (citronellol) and methacryloyl chloride. The DSC analysis proved the glass transition temperature of these copolymers in the range of 15.8–19.9 °C. The TG/DTG analysis indicated that the copolymers containing up to 50 mass% of citronellyl methacrylate were characterized by a thermal resistance above 200 °C (inert conditions) and above 185 °C (oxidizing conditions). In addition,

the FTIR and QMS analyses of the gaseous decomposition products confirmed that the decomposition of the copolymers was complex and included the depolymerization reactions and intermediate products decomposition reactions combined with possible radical reactions under inert and oxidizing conditions. This led to the emission of a mixture of the following gaseous products: benzyl methacrylate, citronellyl methacrylate, 2-methylpropenal, citronellal and a higher molecular mass compounds due to the possible radical reactions in an inert atmosphere. During the oxidation conditions, the formation of the same, major volatiles as in the inert atmosphere was observed. It suggested that the presence of oxygen did not affect the decomposition process of the tested copolymers. As additional gaseous decomposition products, only small amounts of CO, CO_2 and H_2O as a result of the combustion process of the residues were observed.

Summing up, these novel environmentally friendly poly(citronellyl methacrylate)-*co*-poly(benzyl methacrylate) copolymers due to their properties can be applied as the materials working in corrosive conditions, potential protective coatings or as materials for other uses in everyday life.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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