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Synthesis and characterization of new polymethacrylate bearing cyclopropane ring as side group

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Abstract

A cyclopropanation reaction of allylmethacrylate (**1**) with ethyldiazoacetate (**2**) lead to the formation of 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid ethyl ester (**3**) as a mixture of cis/trans isomers in molar ratio 2:1. The cis isomer could be selectively hydrolyzed by use of Pig liver esterase (PLE). An isolated *cis*-2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid (**4**) exhibited optical activity. The monomer **3** was easily polymerized using AIBN and benzopinacol as free radical initiators at 65 and 130 °C, respectively. ^{1}H NMR and FT-IR analyses confirmed the presence of the chemically stable cyclopropane ring in both monomer and polymers. The obtained polymers were also characterized by GPC and DSC measurements. A depolymerization behaviour was observed heating the polymers at 200–250 °C. The regeneration of starting cis/trans isomers of **3** can be taken as a proof of the high thermal stability of the cyclopropane ring.

Keywords: Cyclopropanation; Enzymatic hydrolysis; Depolymerization

1. Introduction

The polymerization behaviour of several cyclopropane-containing vinyl compounds has been described in many publications [1–6]. Their free radical polymerization results in polymers with mainly 1,5-ring-opened units, whereby radical stabilizing substituents or electron-withdrawing groups can increase the radical polymerizability and the ring-opening ability. For those specific systems in which the ring opening occurs, the cyclopropane-containing monomers show lower volume shrinkage during polymerization compared with other classes of vinyl compounds such as methacrylates. Moreover, 2-vinylcyclopropane-1,1-dicarboxylates are stable in the presence of humidity, acidic and basic impurities, and inorganic fillers. For this reason this kind of monomers have been considered in order to develop new materials for photopolymerization systems or dental application. However, in comparison with methacrylates, vinylcyclopropanes are less reactive [7], which restricts their practical applications. Up to now, no investigations have been carried out concerning the free radical polymerization behaviour of methacrylated cyclopropane rings. The present work deals with the synthesis and characterization of a new methacrylic monomer and polymer bearing cyclopropane ring as side group. Our purpose was to check the possibility of ring-opening reaction in the presence of free radicals or at relatively high temperature.

2. Experimental part

2.1. Materials and methods

All solvents of p.a. quality (Riedel de Haen, Fluka) were stored over molecular sieves of 3 or 4 Å. All other chemicals were purchased from Merck, Fluka and Aldrich and used without further purification.

Thin layer chromatography was performed on Merck Kieselgel plates 60-F254. Flash chromatographic separation was carried out on normal phase silica gel disposable RediSep® columns using Isco Combi*Flash* Companion 4×chromatograph equipped with UV (254 nm) detector. ^{1}H NMR spectra were recorded with a Bruker DRX500 NMR spectrometer with tetramethylsilane as internal standard in chloroform-*d* ($CDCl_3$) as solvent. FT-IR spectra were measured using a Nicolet 5SXB FT-IR spectrophotometer. Gel permeation chromatography (GPC) measurements were performed with *N*,*N*-dimethyl

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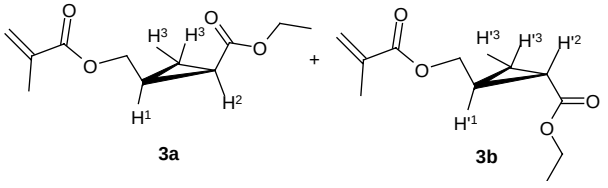
formamide (DMF) as the eluent at 25 °C using a PSS apparatus with a Shodex refractive index (RI) detector and a TSP UV2000 UV–vis detector at 25 °C under the following conditions: PSS-SDV (5 μm, 10^3 Å, 8×50 mm^2 column) and 3 PSS-SDV (5 μm, 8×300 mm^2 with 10^2, 10^3, 10^4 Å porosity) columns and DMF eluent containing LiCl at a flow rate of 1.0 ml min^{-1}. The calibration curves for GPC analysis were obtained using polystyrene standards (374–10^6 D). Differential scanning calorimetry (DSC) was carried out with a Perkin–Elmer DSC 822. The second heating data are presented, heating rate 10 °C min^{-1}. The molecular modelling calculations were performed using the software PC Spartan Pro 1.07*, with the semi-empirical methods AM1 and PM3 being used for geometry optimization.

2.1.1. 2-(2-Methyl-acryloyloxymethyl)-cyclopropane carboxylic acid ethyl ester (*3*)

Allylmethacrylate (**1**) (2.52 g, 0.02 mol) was dissolved in 10 ml hexane containing 0.11 g (0.0012 mol) CuCN and 0.05 g 3,5-di-*tert*-4-butylhydroxytoluene (BHT) as stabilizer. This mixture was heated under reflux while a solution of 2.74 g (0.024 mol) ethyl diazoacetate in 10 ml hexane was added in such a rate as to maintain stable evolution of N_2. When the addition was completed, the mixture was refluxed for further 30 min. The mixture was then cooled, filtered and concentrated at room temperature. Purification was performed by flash chromatography on a normal phase silica gel disposable RediSep® 120 g column using a mixture hexane ethyl acetate 6:1 as eluent. Two side components were found and identified by ^{1}H NMR as diethyl fumarate and diethyl maleate. The yield of the desired product **3** as a mixture of cis:trans isomers was 1.06 g (25%). R_f—value (hexane/ethyl acetate = 6:1) = 0.76.



^{1}H NMR (500 MHz, $CDCl_3$ [ppm]): δ = 6.06 (s, 1H, CH_2=), [6.03 (s, 1H, CH'_2=)], 5.52 (s, 1H, CH_2=), [5.49 (s, 1H, CH'_2=)], [4.53 (dd, *J* = 5.99 Hz, 1H, OCH'_2], 4.11–4.03 (m, 1H, OCH_2 [1H, OCH'_2] and 2H, $COOCH_2CH_3$ [2H, $COOCH'_2CH_3$]), 3.97 (dd, *J* = 6.93 Hz, 1H, OCH_2), 1.89 (s, 3H, CH_2=C(CH_3)), [1.87 (s, 3H, CH_2=C(CH'_3)], 1.76 (m, 1H, H^2 and [m, 1H, H'^2]), [1.67 (m, 1H, *J* = 6.31 Hz, H'^1], 1.57 (m, 1H, *J* = 4.42 Hz, H^1), 1.22–1.18 (m, 3H, O–CH_2CH_3 [3H, O–CH_2CH_3'] and [2H, H'^3]), 1.10 (m, 1H, H^3), 0.87 (m, 1H, H^3).

^{13}C NMR (125 MHz, $CDCl_3$, [ppm]): δ = 173.70 ($COOCH_2CH_3$), [172.49 ($C'OOCH_2CH_3$)], 167.60 (CH_2=C(CH_3)COO) and [CH_2=C(CH_3)$C'OO$], 136.54 (CH_2=$C(CH_3)$), [136.76 CH_2=C' (CH_3)], 126.13 (CH_2=), [125.74 $C'H_2$=], 66.34 (OCH_2CH^1), [63.49 $OC'H_2CH'^1$], 61.03 (OCH_2CH_3) and [OCH_2CH], 20.82 (OCH_2CH^1 in cyclopropane), [19.84 $OCH_2C'H'^1$ in cyclopropane], 18.67 (CH^2COO in cyclopropane), 19.02 (CH_2=C(CH_3)) and [CH_2=C($C'H_3$)], [18.06 $C'H'^2COO$ in cyclopropane], 14.59 (OCH_2CH_3) and [$OCH_2C'H_3$], 13.39 (CH^3 in cyclopropane), [12.37 ($C'H'^3$ in cyclopropane)].

^{13}C NMR (125 MHz, $CDCl_3$, DEPT [ppm]): δ = 66.34 (+), [63.49 (+)], 61.03 (+), 20.82 (−), [19.86 (−)], 19.02 (−), [18.06 (−)], 18.67 (−),14.59 (−), 13.39 (+), [12.37 (+)]. During this reaction two isomers in a ratio of about 2:1 were formed, what possible to calculate from the position of CH_2= protons. The signals in ^{1}H and ^{13}C NMR spectra of the second (less abundant) isomer are set in brackets [H′] or [C′].

FT-IR (diamond): 2982, 2158 (alkyl), 1716 (C=O), 1638 (CH=CH), 1151 (C–O–C), 1043 (C–C, cyclopropane), 1452, 1380, 1319, 1295,1095, 1012, 940, 815, 658 cm^{-1}.

2.2. Polymerization procedure

All polymerization experiments were carried out under nitrogen atmosphere. The polymers were precipitated into appropriate solvents, filtered off and dried under vacuum at room temperature. The detailed experimental procedure is given for poly-**1** as a typical example.

2.2.1. Poly-*1*

A solution of 0.2 g (0.9 mmol) 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid ethyl ester (**3**) (isomeric mixture) and 1.5 mg (0.009 mmol) of AIBN in 2.3 ml of toluene was flushed with nitrogen for 20 min and heated at 65 °C during 4 h. Polymerization was terminated by cooling the reaction mixture in an ice bath. The solution was dropped into 30 ml of hexane. The obtained polymer was filtered off and after reprecipitation from toluene into diethyl ether was dried under vacuum at room temperature. Yield: 0.11 g (55%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = [4.30 (s, broad, 1H, $C(CH_3)C(O)O–CH'_2$], 4.09 (s, 2H, $CHC(O)O–CH_2CH_3$ and [2H, $CHC(O)O–CH'_2CH_3$], 3.99 (s, 1H, CH_2–$C(CH_3)C(O)O–CH_2$), 3.89, 3.80 (s, s, 2H, $C(CH_3)C(O)O–CH_2$), 1.89, 1.76 (s, s, 1H, in cyclopropane C*H*–COOEt and [1H, in cyclopropane C*H′*–COOEt], 1.67, 1.56 (s, 1H, in cyclopropane OCH_2–C*H′* and [s, 1H, in cyclopropane OCH_2–C*H′*]), 1.22 (s, 3H, O–CH_2CH_3 and [3H, O–CH_2CH_3']), 1.07 [s, 1H, in cyclopropane CH'_2], 0.98 (s, 1H, in cyclopropane CH_2), 0.83 (s, 1H, in cyclopropane CH'_2 and 3H, CH_2–$C(CH'_3)$) ppm. The signals of polymer from second isomer are set in brackets [H′].

FT-IR (diamond): 2982, 2158 (alkyl), 1718 (C=O), 1162 (C–O–C), 1042 (C–C, cyclopropane), 1448, 1375, 1320, 1266, 1179, 1267, 1093, 983, 859 cm^{-1}.

2.2.2. Enzymatic hydrolysis of 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid ethyl ester

0.38 g (1.8 mmol) of **3** (isomeric mixture) were dissolved in 1 ml of acetone and poured into 100 ml of a phosphate buffer solution (pH 7). 0.2 ml of Pig liver esterase (PLE) suspension in 3.2 M ammonium sulphate solution (activity 142 U mg^{-1}) was added. The resulting change in pH value was compensated with 0.05 N NaOH. After 24 h the aqueous phase was acidified with 1 N HCl and extracted with diethyl ether (3×20 ml). The ethereal phase was dried over anhydrous $MgSO_4$, filtered and

evaporated under vacuum. After purification by flash chromatography on a normal phase silica gel disposable RediSep® 12 g column with a mixture of hexane ethyl acetate 6:1 as eluent, 0.09 g of 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid (**4**) as a colourless liquid were obtained. The yield was 50% R_f—value (hexane/ethyl acetate = 6:1) = 0.38. $[\alpha]_{589}^{20} = -3.7^{\circ}$ dm^{-1} g^{-1} cm^{-3} (in diethyl ether).

^{1}H NMR (500 MHz, $CDCl_3$ [ppm]): $\delta = 6.07$ (s, 1H, CH_2=), 5.55 (s, 1H, CH_2=), 4.11 (m, 1H, OCH_2), 3.74 (m, 1H, OCH_2), 1.89 (s, 3H, CH_2=C(CH_3), 1.81 (m, 1H, H^2) 1.59 (m, 1H, J = 4.76 Hz, H^1), 0.95 (m, 1H, H^3), 0.81 (m, 1H, H^3).

FT-IR (diamond): 2957 (alkyl), 1695 (broad, C=O), 1637 (CH=CH), 1155 (C–O–C), 1014 (C–C, cyclopropane), 1454, 1319, 1295,1088, 1014, 942, 815 cm^{-1}.

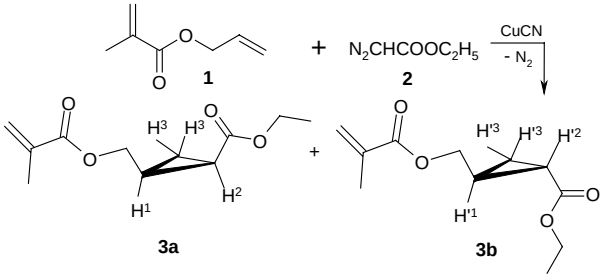
2.3. Depolymerization experiments

The depolymerization was performed by heating up 40 mg samples in sealed testing tubes immersed into a preheated oil bath.

3. Results and discussion

3.1. Monomer synthesis and characterization

Cyclopropanation of allylmethacrylate (**1**) was achieved by slightly modified procedure described in literature [8] utilizing ethyl diazoacetate (EDA) as a cyclopropanating agent and CuCN as a catalyst. A new cyclopropane-containing monomer 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid ethyl ester (**3**) was obtained as a mixture of two isomers (**3a**, **3b**) in relatively low yield (25%) accompanied by the diethyl esters of fumaric and maleic acids as side products via carbene dimerization.



Our efforts to improve the yield of desired product **3** by replacement of catalyst (CuCN was changed to $Pd(Ac)_2$) or solvent (instead of hexane, THF and DMF were also employed) did not result in substantial improvement. Nevertheless, isomer mixture was easily separated from maleic and fumaric esters with flash-chromatography, but no eluent could be proposed for separation of cis/trans isomers **3a** and **3b**. The monomers were finally obtained as colourless liquids. The characterization was carried out using ^{1}H, ^{13}C NMR and FT-IR spectroscopy.

In the ^{1}H NMR spectrum the existence of 1,2-disubstituted cyclopropane ring was proved by signals at $\delta = 1.76$ (H^2 and H'^2), 1.57 (H^1), 1.67 [H'^1],1.10 (H^3) and 0.87 ppm (H^3).

Surprisingly, the observed NMR coupling constants (J) for isomers **3a**,**b** indicate that the cis product **3a** is preferred. For the isomer **3a**, formed in higher amount, J of the proton H^1 at 1.57 ppm in the cyclopropane ring was evaluated as 4.42 Hz. In contrast, the corresponding proton at 1.67 ppm in the less abundant isomer, **3b**, had $J = 6.31$ Hz. Thus, the relative molar ratio of isomers, evaluated by integration of ^{1}H NMR signals, was about 2:1 for **3a** and **3b** correspondingly (Fig. 1). The signals in ^{1}H NMR spectra corresponding to the less abundant isomer **3b** are printed as [H′].

The energy of geometry optimized cis and trans configurations of the final products with the semi-empirical methods AM1 and PM3 did not show any significant difference between the isomers. The heat of formation for cis isomer **3a** was −141.3 kcal mol^{-1} (AM1) and −137.8 kcal mol^{-1} (PM3). It was very similar to calculated heat of formation for trans isomer **3b** with values of −142.3 kcal mol^{-1} (AM1) and −137.4 kcal mol^{-1} (PM3), respectively.

The presence of cyclopropane group was also supported by six corresponding signals in the ^{13}C NMR spectrum at 20.82, CH^1 [19.84, $C'H'^1$]; 18.67, CH^2 [18.06, $C'H'^2$]; 13.39, CH^3 and [12.37, $C'H'^3$]. The signals of the less abundant isomer are set in square brackets. A weak C–C vibration at 1043 cm^{-1} in the FT-IR spectrum also proves the proposed structure [3].

Due to the fact that the isomers **3a** and **3b** could not be separated using flash-chromatography, enzymatic hydrolysis was applied as a potential selective stereospecific hydrolytic method [3,9]. The two main products obtained after Pig liver esterase (PLE) catalyzed hydrolysis of **3a**,**b** were easily separated by flash-chromatography. The trans isomer **3b** was completely hydrolyzed. In contrast, the cis isomer **3a** was hydrolyzed only at the carboethoxy group and 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid (**4**) was obtained as product. The compound **4** showed cis configuration in respect to carboxylic and methacrylic groups. This was proved by ^{1}H NMR coupling constant of proton H^1 at 1.59 ppm in the cyclopropane ring of **4** ($J = 4.76$ Hz). CH_2= protons were only slightly shifted to 6.07 and 5.55 ppm compared to the signals of **3a** in contrast with the H^2 signal of cyclopropane ring that was shifted from 1.76 ppm in **3a** to 1.81 ppm in **4**. Thus, stereospecific enzymatic hydrolysis could be proposed as a method for separation of the isomers **3a** and **3b**.

Polarimetric measurements, carried out after the enzymatic catalyzed hydrolysis, clearly indicated the cleavage of optically inactive **3a**,**b** into an optically active acid (**4**) with specific optical rotation $[\alpha]_{589}^{20} = -3.7^{\circ}$ dm^{-1} g^{-1} cm^{-3} (in diethyl ether). Hence, PLE acted as an enantio and stereo selective hydrolyzing agent toward the cyclopropane esters.

3.2. Polymerization

The structural characteristics of polymers were verified from ^{1}H NMR and FT-IR measurements. Broad signals in the ^{1}H NMR spectrum at 1.76, 1.67, 1.56, 1.07, 0.98 and 0.83 ppm proved that the obtained polymer contains a 1,2-substituted cyclopropane structure. A weak C–C vibration at 1042 cm^{-1} in the FT-IR spectrum also confirmed that the polymer main

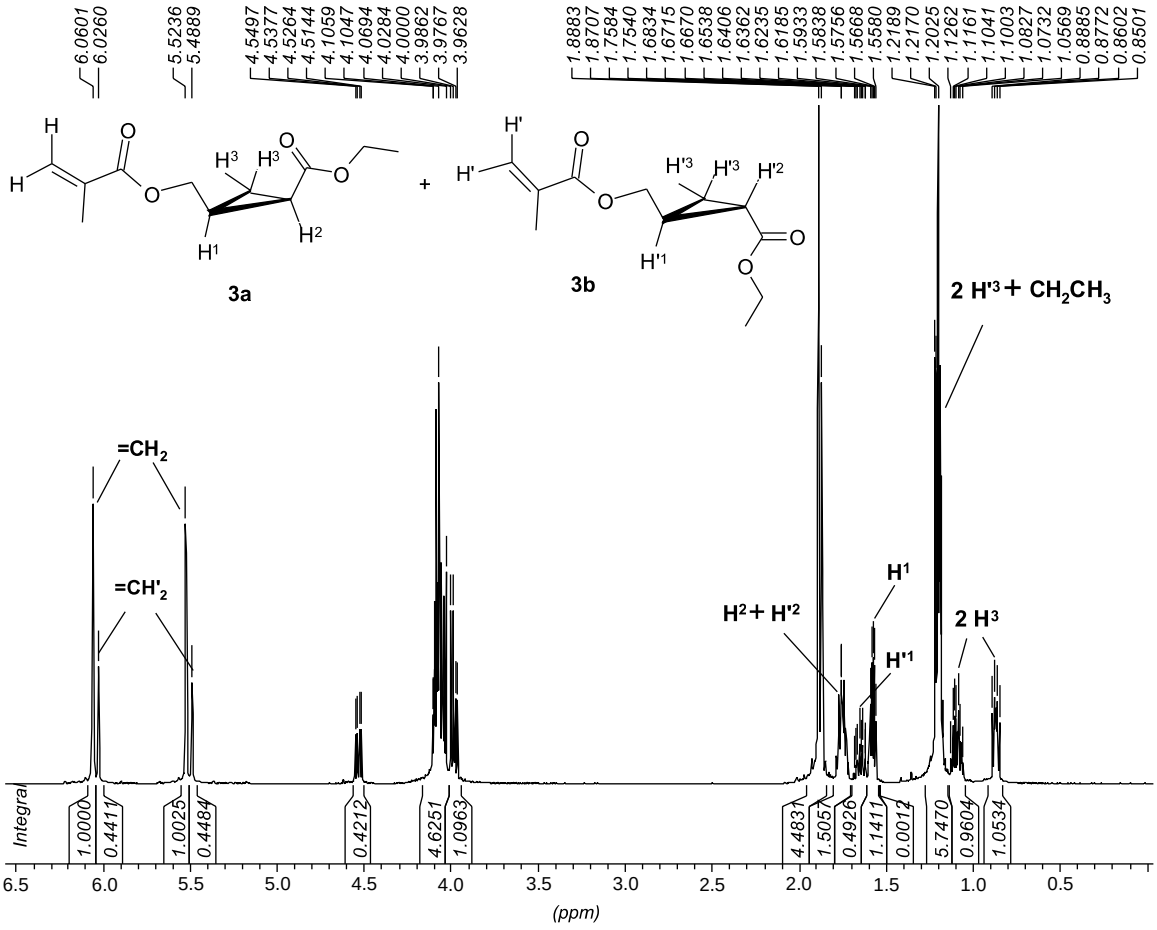


Fig. 1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid ethyl ester, mixture of isomers (**3a**, **3b**), region 0.1–6.5 ppm.

chain is bearing cyclopropane ring. No residual stretching vibration at 1638 cm^{-1} corresponding to the double bond of the monomer as well as chemical shifts at 6.06 [6.03] and 5.52 [5.49] ppm corresponding to CH_2= protons could be detected in the spectra of the polymers.

In order to evaluate the influence of the polymerization temperature on the cyclopropane ring stability, the radical polymerization of monomer **3** (isomeric mixture) was performed in solution at 65 and 130 °C using AIBN and 1,1,2,2-tetraphenyl-1,2-ethanediol (benzopinacol) as free radical initiators, respectively. In accordance with our previous results [10], benzopinacol could be proposed as a substitute of *tert*-butyl peroxide for radical polymerization initiation at high temperature. The diarylhydroxymethyl radicals formed from the initiator do not react directly with the monomer under addition (typical mechanism for peroxides or azocompounds), but in a secondary reaction by hydrogen transfer forming two benzophenone molecules and two monomer radicals that initiate the polymerization [11]. Among the advantages in using this C–C-bond splitting high temperature initiator, there is the fact that it is possible to avoid oxidation side reactions on relatively unstable chemical functionalities. This could be the case for the free radical polymerization of cyclopropane containing monomers iniated at high temperature using peroxides. Moreover, with aromatic pinacols, it is possible to get polymers with hydrogen atoms at the end of the chain, i.e. 'end-group free' polymers.

The obtained polymers showed good solubility in $CHCl_3$, CH_2Cl_2, DMSO, DMF and benzene at room temperature. The molecular weight was investigated through gel permeation chromatography (GPC) analyses using DMF as eluent. Table 1 summarizes the experiments performed and the characterizations of the polymers.

The monomer **3** underwent high conversion to a good soluble polymer product with a relatively high molecular weight when polymerized in toluene solution at 65 °C using AIBN as a free radical initiator. Poly-**2**, obtained by solution polymerization in presence of benzopinacol, showed a lower molecular weight and a higher PDI value. Due to the different initiation mechanism and to a different kinetic equation [11], it is possible that benzopinacol is not the most appropriate initiator for this kind of monomer. However, the polymerization conditions were not fully optimized in this case and this polymerization experiment was solely conducted to evaluate the thermal stability of the cyclopropane ring during a reaction performed at a relatively high temperature. Anyway, the high polydispersity could be attributed to a high contribution of chain transfer

Table 1
Polymerization conditions and GPC, DSC data for the obtained polymers

Sample	Solvent	Initiator	T (°C)	Time (h)	Conversion (%)	$M_w \times 10^3$ (g mol^{-1})	$M_n \times 10^3$ (g mol^{-1})	PDI	T_g (°C)[a]
Poly-**1**[b]	Toluene	AIBN	65	4	55	800	300	2.6	30.1
Poly-**2**[b]	DMF	Benzopinacol	130	9	40	43	7	6.1	18.0

[a] Glass transition temperature obtained by DSC measurements. Second scan, heating rate: 10 °C min^{-1}.
[b] [Monomer] = 20 wt%, [initiator] = 1 mol%

reactions at 130 °C. All polymer samples exhibited good film formation ability. Mechanically stable transparent coatings were obtained on a glass surface even directly from the reaction mixture.

Glass transition temperatures were investigated by DSC measurements (Table 1). The obtained T_g for poly-**2** (18.0 °C) was lower compared with poly-**1** (30.1 °C) what we could explain considering a certain influence of the higher

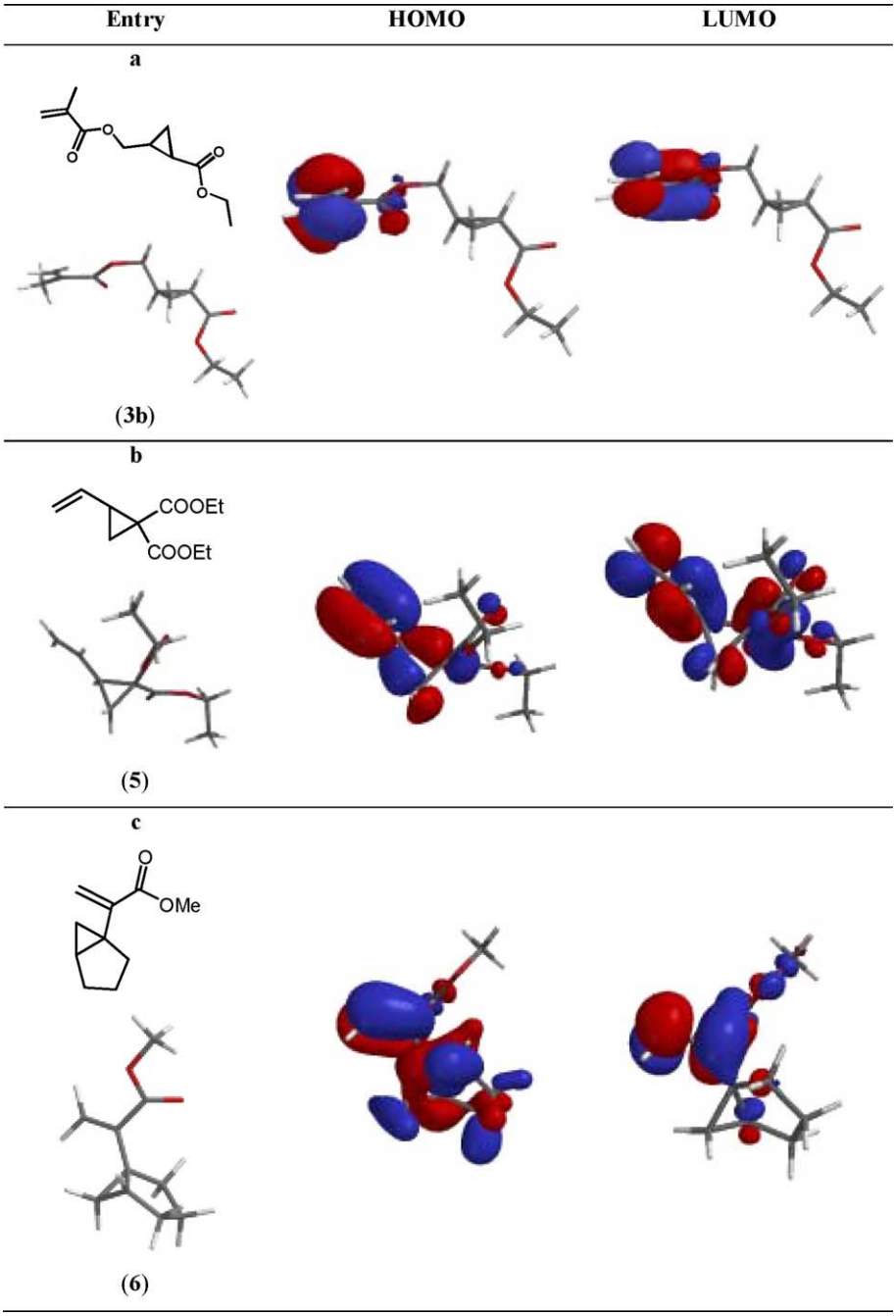


Fig. 2. Geometry optimized models and localization of frontier orbitals (HOMO–LUMO) of the monomers **3b**, **5**, and **6** calculated with the semi-empirical method AM1*.

polydispersity (PDI = 6.1) and lower molecular weight of the former. All samples exhibited also sharp endothermic peaks in the region around 290–360 °C (348.4, 288.6, respectively for poly-**1**, and -**2**). The change of the samples colour from white to black confirmed an oxidative decomposition process at such temperatures. Keeping in mind the question about stability of cyclopropane ring, it should be noted that no further transitions were detected on DSC curves before full polymer chain decomposition.

On the other hand, a very effective depolymerization process was observed for all the polymer samples constantly heated at 200–250 °C.

The presence of the initial monomer **3a**,**b** could be easily recognised through ^{1}H NMR spectroscopy. Intensive signals at 6.06 [6.03] and 5.52 [5.49] ppm, assigned to the vinyl protons of the monomer, appeared after heating and could be the evidence of the monomer formation. Evolved compound was also separated from the polymer and its ^{1}H NMR spectrum was identical to the spectrum of **3a**,**b**. Therefore, cyclopropane ring was completely stable even at 200–250 °C.

3.3. Theoretical calculations

As it was found, in contrast to other very reactive cyclopropane-containing monomers, e.g. 1,1-diethoxycarbonyl-2-vinylcyclopropane (**5**) or methyl 2-(bicyclo[3.1.0]hex-1-yl)acrylate (**6**), the monomer **3** exhibited high chemical stability even in the presence of free radicals that could promote a ring-opening polymerization. To explain this dissimilar behaviour, the frontier orbital (HOMO–LUMO) model was employed. For free radical reactions we could expect that the radical would attack the molecule in the place with high density of highest occupied molecular orbital (HOMO). However, as it was calculated on an AM1* level, the monomer **3b**, did not show any localisation of HOMO as well as lowest unoccupied molecular orbital (LUMO) on the cyclopropane ring. These orbitals were located only on the double bond (Fig. 2(a)). In contrast, the well-known ring-opening polymerizable monomer **5**, exhibited localisation of HOMO orbital not only on the vinyl substituent, but also on the cyclopropane function (Fig. 2(b)). Finally, in the extremely reactive [5] compound **6**, a very high density of HOMO orbital was observed all across the cyclopropane ring (Fig. 2(c)), as well. Thus, theoretical calculations of HOMO–LUMO localisation could be utilized to predict, at least qualitatively, the behaviour of cyclopropane containing monomers.

4. Conclusions

2-(2-Methyl-acryloyloxymethyl)-cyclopropane carboxylic acid ethyl ester (**3**) was obtained as a mixture of two (cis/trans) isomers in molar ratio 2:1 through a copper catalysed cyclopropanation. Stereospecific hydrolysis with Pig liver esterase (PLE) could be employed for isomers separation. The isolated hydrolysis product, 2-(2-methyl-acryloyloxymethyl)-cyclopropanecarboxylic acid (**4**), exhibited optical activity. The monomer **3** was easily polymerized in conditions of free radical polymerization at 65 and 130 °C. Spectroscopic investigations verified that the main chain of all resulting polymers was bearing cyclopropane ring. A very effective depolymerization process, with regeneration of the starting monomer isomeric mixture **3a**,**b** and without any decomposition of the cyclopropane ring, was observed at 200–250 °C. Theoretical calculations of HOMO–LUMO orbital localisation could be utilized for stability prediction and rationalization of cyclopropane containing monomers. Due to the high stability of the cyclopropane ring in this specific monomer, we could not expect any low volume shrinkage during polymerization as a typical behaviour of this class of monomers.

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