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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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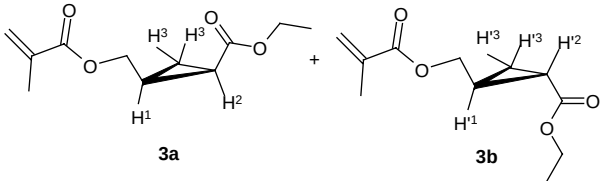
formamide (DMF) as the eluent at 25 °C using a PSS apparatus with a Shodex refractive index (RI) detector and a TSP UV2000 UV–vis detector at 25 °C under the following conditions: PSS-SDV (5 μm, 10^3 Å, 8×50 mm^2 column) and 3 PSS-SDV (5 μm, 8×300 mm^2 with 10^2, 10^3, 10^4 Å porosity) columns and DMF 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