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Polymerization of cyclic monomers

9. Synthesis and radical polymerization of spirocyclic 2-vinylcyclopropanes

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Summary

6,6-Diethyl- (**1a**) and 6-methyl-6-propyl-5,7-dioxa-4,8-dioxo-1-vinylspiro[2.5]octane (**1b**) were synthesized by the acetalization of 2-vinylcyclopropane-1,1-dicarboxylic acid with 2- or 3-pentanone. The new monomers were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The radical polymerization of the monomers **1a** and **1b**, in addition of 6,6-methyl-5,7-dioxa-4,8-dioxo-1-vinylspiro-[2.5]octane (**1c**) and (exo/endo)-7-ethoxycarbonyl-2-oxo-7-vinyl-bicyclo[4.1.0]-heptane (**1d**), was carded out in bulk with 2,2`-azoisobutyronitrile (AIBN) as the initiator. The polymer yield with **1d** was only low. The polymerization of the monomers **1a** and **1c** resulted in cross-linked polymers, whereas in case of the polymerization of monomer **1b** soluble polymers in a high yield were obtained.

Introduction

2-Vinylcyclopropanes are interesting monomers which undergo radical ring-opening polymerization resulting in polymers mainly bearing a 1,5-ring-opened unit[1,2]), because they demonstrate less polymerization shrinkage than other vinyl monomers, such as methacrylates. In comparison to methacrylates, 2-vinylcyclopropanes are less reactive[3]). It is well known that cyclic monomers, such as bicyclic orthoesters or spiro orthocarbonates, show a high ring-opening tendency[4]). Although it is not possible to generalize the connection between the ring-opening tendency and a spirocyclic monomer structure, we synthesized derivatives with a spirocyclic or bicyclic structure in order to influence the monomer reactivity of 2-vinylcyclopropanes.

Previously, we reported about the synthesis and polymerization of hybrid 2-vinylcyclopropanes[5]) and cross-linking 2-vinylcyclopropanes[6]). This paper briefly describes the synthesis and radical polymerization of spirocyclic and bicyclic 2-vinylcyclopropanes **1a-d**:

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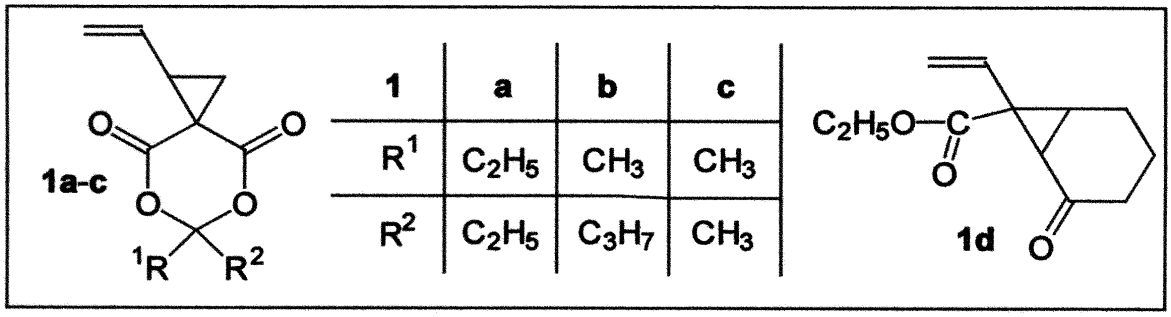


Experimental

Materials

Dichloromethane, hexane, and tetrahydrofurane (THF) were dried over molecular sieves. 2-Vinylcyclopropane-1,1-dicarboxylic acid[7] and 1,1-bis(methoxycarbonyl)-2-vinylcyclopropane (**BMCVCP**) were prepared according to the literature[8]. Isopropenyl acetate, 2- and 3-pentanone, and 6,6-methyl-5,7-dioxa-4,8-dioxo-spiro[2.5]octane were used without further purification. 2,2`-azo-isobutyronitrile (AIBN) was purified by recrystallization. Acetic anhydride was distilled over sodium acetate. All chemicals were purchased from Fluka.

Synthesis

Synthesis of 6,6-dialkyl-5,7-dioxa-4,8-dioxo-1-vinylspiro[2.5]octanes **1a** and **1b** *(general procedure)*:

A stirred suspension of 2-vinylcyclopropane-1,1-dicarboxylic acid (3.12 g, 20 mmol) in acetic anhydride (2.40 g, 24 mmol) and sulfuric acid (3 drops, 96 %) was treated at ~5 °C with 3(2)-pentanone (1.90 g, 22 mmol). The mixture was allowed to heat up to room temperature and stirred overnight. The solution was poured into a heterogeneous mixture of 50 mL of dichloromethane and 10 mL of water. After separation of the organic layer, the aqueous layer was extracted with dichloromethane. The combined organic solutions were washed twice with a saturated sodium hydrogen carbonate solution, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by distillation.

6,6-Diethyl-5,7-dioxa-4,8-dioxo-1-vinylspiro[2.5]octane (**1a**): The distillation in vacuum resulted in a colorless liquid (64% yield), b.p. (0.05 mbar): 111 °C.

IR (neat): 686 (w), 718 (w), 740 (w), 830 (w), 847 (w), 884 (w), 903 (m), 928 (m), 977 (s), 1042 8m), 1057 (m), 1070 (m), 1162 (m), 1189 (s), 1212 (s), 1272 (s; sh), 1326 (s), 1349 (s), 1365 (s), 1438 (m), 1465 (m), 1634 (w), 1743 (s; sh), 1764 (s), 2887 (m), 2946 (m), 2983 (s), and 3089 cm^{-1} (w).

^1H NMR ($CDCl_3$): δ = 1.00 and 1.06 (2t;2x3H,CH_3), 1.94-1.99 (2m;2x2H,CH_3-$\underline{CH_2}$-), 2.19-2.23 and 2.33-2.37 (m;2x1H,CH_2-cyclopr.), 2.76 (q;1H,CH-cyclopr.), 5.35 and 5.43 (2d;2x1H,CH_2=), 5.72-5.83 (m;1H,-CH=).

^{13}C NMR ($CDCl_3$): δ = 6.63 and 7.85 (CH_3), 24.99 (CH_2-cyclopr.), 30.10 and 32.64 ($CH_3\underline{CH_2}$-), 31.64 (CO-$\underline{C}$-CO), 42.87 (CH-cyclopr.), 108.87 (O-C-O), 121.85 (=CH_2), 131.52 (CH=), 165.28 and 167.68 (C=O).

6-Methyl-6-propyl-5,7-dioxa-4,8-dioxo-1-vinylspiro[2.5]octane **1b**): The vacuum distillation yielded a colorless liquid of the diastereomeric mixture (1:1) (58% yield), b.p. (0.05 mbar): 94 °C.

IR (neat): 631 (w), 704 (w), 741 (w), 831 (w), 847 (w), 929 (m), 970 (s), 996 (m), 1032 (s), 1073 (m), 1159 (s), 1190 (s), 1244 (s), 1283 (s), 1322 (s, b), 1380 (s), 1438 (m), 1468 (m), 1634 (w), 1732 (s; b), 2877 (m), 2966 (s; sh), and 3089 cm^{-1} (w).

^{1}H NMR ($CDCl_3$): δ = 0.91 and 0.98 (2t;3H,$\underline{CH_3}CH_2$-), 1.42-1.52 and 1.53-1.63 (m;2H,$CH_3\underline{CH_2}$-), 1.68 and 1.72 (s;3H,$\underline{CH_3}$-C-O), 1.88-1.94 (m;2H,$CH_3CH_2\underline{CH_2}$-), 2.18-2.23 and 2.32-2.38 (m;2x1H,CH_2-cyclopr.), 2.71-2.80 (m;1H,CH-cyclopr.), 5.32 and 5.46 (2d;2x1H,CH_2=), and 5.71-5.81 (m;1H,-CH=).

^{13}C NMR ($CDCl_3$): δ = 13.88 and 14.05 ($\underline{CH_3}CH_2$-), 16.10 and 17.40 ($CH_3\underline{CH_2}$-), 24.48 and 24.58 (CH_2-cyclopr.), 25.09 and 26.43 ($\underline{CH_3}$-C-O), 31.66 (CO-$\underline{C}$-CO), 42.16 and 42.97 ($CH_3CH_2\underline{CH_2}$-), 42.67 (CH-cyclopr.), 106.32 and 107.25 (O-C-O), 121.57 and 121.69 (=CH_2), 131.17 and 131.73 (CH=), 165.02, 165.19, 167.28 and 167.44 (C=O).

6,6-Dimethyl-5,7-dioxa-4,8-dioxo-1-vinylspiro[2.5]octane **1c** was synthesized by the reaction of 2-vinylcyclopropane-1,1-dicarboxylic acid with isopropenyl acetate analogous to S. Danishefsky et al.[9]. (exo/endo)-7-Ethoxycarbonyl-2-oxo-7-vinyl-bicyclo[4.1.0]heptane (**1d**) was prepared according to the literature[10].

Polymerization

The radical bulk polymerizations were carried out in sealed glass tubes as previously described[11]. The obtained solution polymerizates were precipitated in a mixture of methanol with water (9:1). The polymer was filtered off and then dried to constant weight in vacuum. The polymer yield was calculated from the gravimetrically determined yield of the dried polymers.

Poly(**1a**) (AIBN, bulk): IR (KBr): 692 (w), 750 (m), 877 (w), 968 (s), 1046 (m), 1100 (m), 1158 (m), 1249 (s), 1372 (s), 1438 (m), 1466 (m), 1634 (w), 1742 (s), 1764 (s; sh), 2889 (m), 2947 (m), and 2984 cm^{-1} (m).

Poly(**1b**) (AIBN, solution): IR (KBr): 708 (w), 747 (w), 884 (w), 955 (s), 1031 (m), 1069 (m), 1103 (m), 1170 (m), 1253 (s), 1368 (m), 1387 (m), 1435 (m), 1742 (s), 1710 (s), 2876 (m), 2935 (m), and 2964 cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ = 0.91-0.96 (m;3H,$\underline{CH_3}CH_2$-), 1.39-1.44 (m;2H,$CH_3\underline{CH_2}$-), 1.58 (s;3H,$\underline{CH_3}$-C-O), 1.92-1.98 (m;2H,$CH_3CH_2\underline{CH_2}$-), 2.31-2.73 (m;4H,-$\underline{CH_2}$-CH=), and 5.38-5.48 (m;2H,-CH=). ^{13}C NMR ($CDCl_3$): δ = 12.77 ($\underline{CH_3}CH_2$-),15.59 ($CH_3\underline{CH_2}$-), 27.38 ($\underline{CH_3}$-C-O), 40.05, 41.21, and 43.12 ($CH_3CH_2\underline{CH_2}$-/-CH_2-), 53.71 (CO-$\underline{C}$-CO), 106.42 (O-C-O), 128.16 (=CH_2-), and 167.24 (C=O).

Poly(**1c**) (AIBN, bulk): IR (KBr): 699 (w), 949 (s), 978 (m), 1035 (m), 1092 (m), 1202 (s), 1269 (s), 1394 (s), 1438 (m), 1742 (s), 1762 (s; sh), 2947 (w) and 3002 cm^{-1} (w). ^{13}C NMR (solid-state, CP-MAS)): δ = 29.5 (CH_3), 41.2 (CH_2), 54.7 (CO-$\underline{C}$-CO), 106.3 (O-C-O), 129.1 (=CH_2-),167.7 and 168.7 (C=O).

Measurements

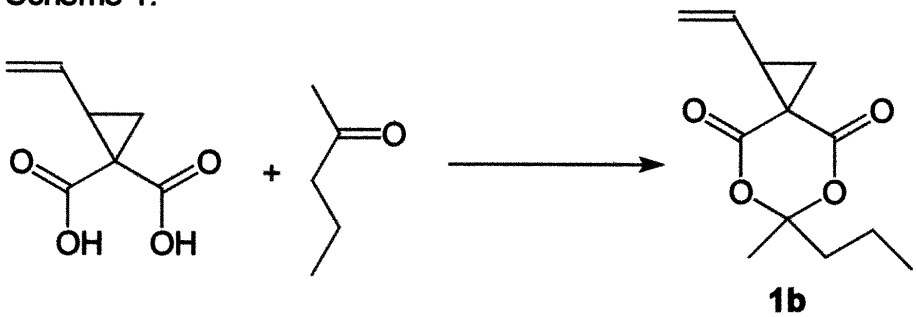
NMR measurements were recorded on a DPX-400 spectrometer (Bruker, ^{1}H: 400 MHz, ^{13}C: 100 MHz) using tetramethylsilane (TMS) as the standard and $CDCl_3$ or dimethylsulfoxide-d_6 as the solvent. The ^{13}C CP/MAS spectrum was

recorded on a Bruker AMX 400 spectrometer operating with a ^{13}C resonance frequency of 100.6 MHz equipped with a solid state probe. Cross polarization (CP) technique, with 4.5 µs pulses under Hartmann-Hahn conditions: 5ms; recording time with ^{1}H decoupling: 26.5 ms, was used. The sample spinning at the magic angle (MAS) was carried out at 5.7 kHz. A FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weights of the polymers and their distribution (MWD) were determined by gel permeation chromatography (GPC), using THF as the eluent, a UV-detector Spectra 100, and columns calibrated with poly(styrene) standards. The glass transition temperature (T_G) was determined by differential scanning calorimetry (DSC) measurements using a Perkin-Elmer DSC-7 thermal analyzer. Scanning rates of 10 °C/min were used.

Results and discussion

The new monomers **1a** and **1b** were synthesized by acetalization of 2-vinyl-cyclopropane-1,1-dicarboxylic acid with 2- or 3-pentanone shown in Scheme 1 for monomer **1b**:

Scheme 1:



1b

The monomers **1a** and **1b** are colorless compounds. In the refrigerator, the monomer **1a** tends to crystallize. The characterization of the vinylcyclopropanes was carried out by ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The spectra data are in agreement with the expected structure. For example, the 2-vinylcyclopropane unit is supported by the presence of multiplets, assignable to CH and CH_2 of the cyclopropane ring at δ = 2.7-2.8 ppm and 2.3-2.4 ppm, or duplets assignable to the vinyl group at δ = 5.3 and 5.4 ppm in the ^{1}H NMR spectrum. Typically for the spirocyclic group is the signal at δ = 31.6 ppm in the ^{13}C NMR spectrum, assignable to the spiro carbon atom.

The bulk polymerization of monomers **1a-d** was carried out in the presence of AIBN (2.0 mol-%) at 65 °C for 15 h. In case of the monomers **1a** and **1c**, the polymerization resulted in solids, which were insoluble in common organic solvents. The monomer conversion was nearly quantitative. In case of the bulk polymerization **1b**, a soluble polymer was obtained with a number-average molecular weight of 147000 g/mol in 89% yield. In contrast to this, the polymer yield for monomer **1d** was only about 4%. Poly(**1b**) is well soluble in chloroform, acetone, chlorobenzene, toluene or N,N-dimethylformamide and less soluble in ethyl acetate or THF. In order to obtain soluble polymers, the polymerization of

the monomers **1a-c** was also carried out in a solution. However, only in case of monomer **1b**, were well soluble polymers obtained (Tab. 1), whereas the solution polymerization of monomers **1a** and **1c** also resulted in cross-linked polymerizates. The gel formation started very quickly, for example, at a concentration of **1a** of 2.0 mol/L within about 10 minutes under the polymerization conditions described in Tab. 1. In comparison to **BMCVCP**, the polymer yield of monomer **1b** is a somewhat lower, whereas the molecular weight of poly(**1b**) is significantly higher than that of poly(**BMCVCP**). The higher glass transition temperature of poly(**1b**) (76 °C) can be explained on the basis of the more bulky structure of repeating units in poly(**1b**) in comparison to poly(**BMCVCP**) (T_G = 51 °C).

Tab. 1. Polymerization of monomer 1b and BMCVCP (2.5 mol/L) in chlorobenzene in the presence of AIBN (2.0 mol-%) at 65 °C

Monomer	Polymerization time (h)	Polymer yield (wt.-%)	M_n (g/mol)
1b	0.5	32	150100
BMCVCP	0.5	47	38960
1b	2.0	81	113600[a)]
BMCVCP	2.0	89	40600[b)]
1b	5.0	99	78500
BMCVCP	5.0	94	21620

[a)] T_G = 76 °C, [b)] T_G = 51 °C

Tab. 2. Copolymerization of monomer 1a with 1b ([1a]+[1b] = 2.5 mol/L) in chlorobenzene in the presence of AIBN (2.0 mol-%) at 65 °C; polymerization time: 0.5 h

[1a]/[1b] (mol/mol)	Polymer yield (wt.-%)	$M_n \times 10^{-4}$ (g/mol)	Polydispersity
2.5/1	-[a)]	-[a)]	-[a)]
1/1	51	290	7.21
1/3	46	5.35	1.59

[a)] Not determined, cross-linked polymer formed

The copolymerization of **1a** with **1b** resulted in well soluble copolymers at monomer ratio [**1a**]/[**1b**] equal or less than 1.0. Thereby, both the number-avera-

ge weight of the formed copolymers and their polydispersity increased with increasing content of **1a** in the starting monomer mixture (Tab. 2). This shows that the formation of insoluble poly(**1a**) is probably caused by cross-linking of the polymer chains via chain transfer reactions of **1a** monomer units.

Basically, 2-vinylcyclopropanes undergo radical polymerization to result in a polymer consisting of a 1,5-ring-opened unit (Scheme 2). The ^{1}H NMR spectra of the soluble poly(**1b**) obtained in the presence of AIBN clearly indicate the formation of the 1,5-adduct units. Typical signals of poly(**1b**) assignable to the ring-opened structure are peaks at 2.31-2.73 (-$\underline{CH_2}$-CH=) and 5.38-5.48 ppm (-CH=). Furthermore, in the ^{13}C NMR spectra of poly(**1b**) the signals at 53.71 (CO-C(<)-CO) and 128.16 ppm (=CH-) confirm the ring-opening mechanism and the solid state ^{13}C CP/MAS NMR spectrum of the cross-linked poly(**1c**) is also in agreement with the expected ring-opened structure (Fig. 1).

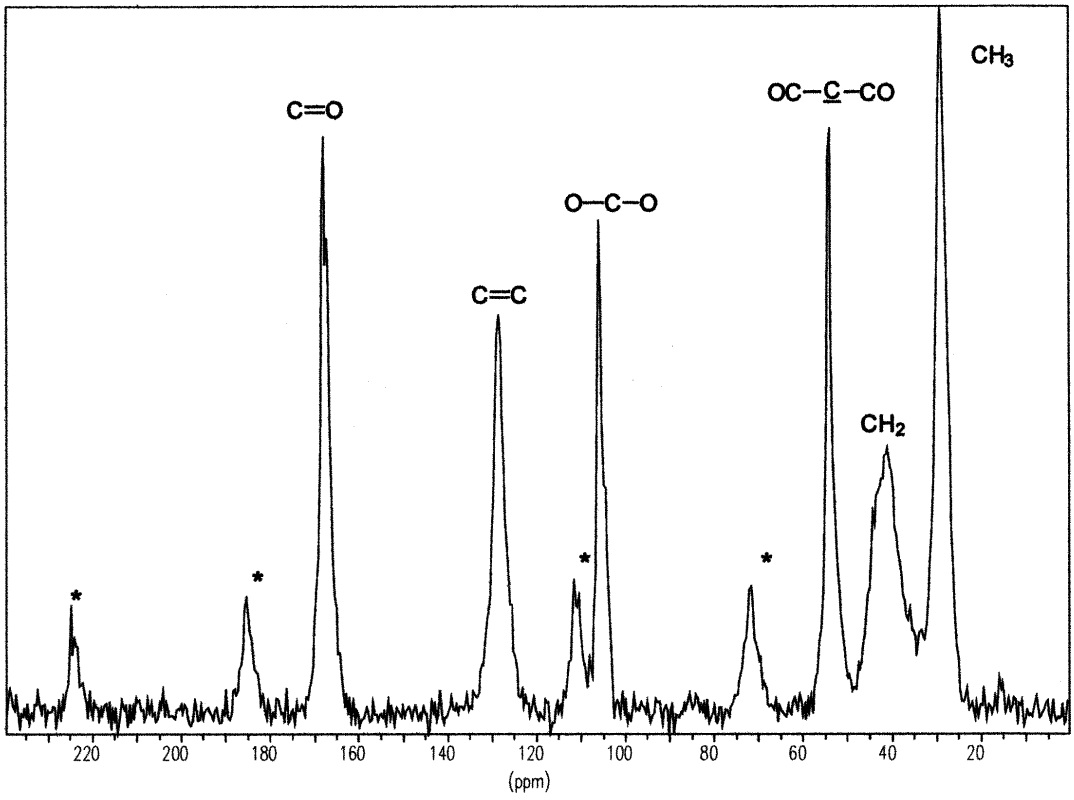
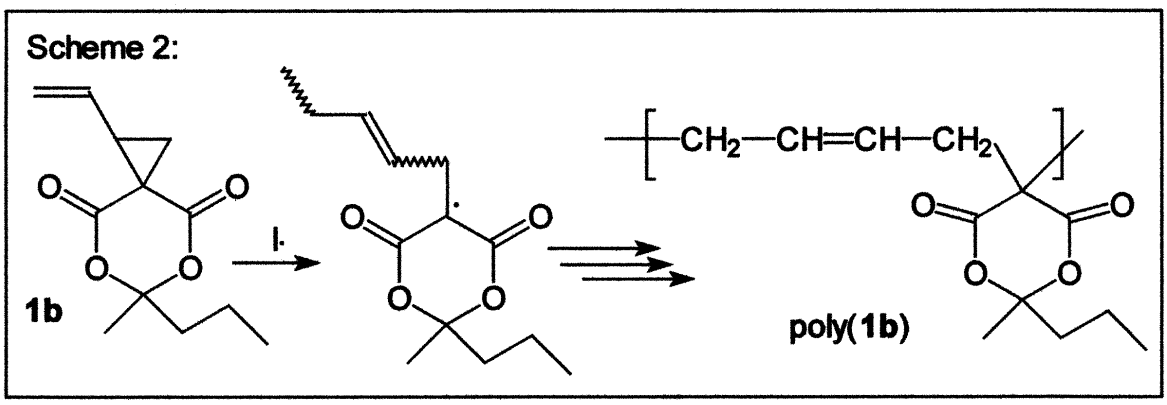


Fig. 1. Solid-state ^{13}C NMR spectrum of poly(1c) (* = spinning side band)



Finally, it should be mentioned that during the bulk polymerization of **1b** a volume shrinkage of about 7.5 % occurs, which also confirms the ring-opening mechanism of the polymerization of **1b**.

Acknowledgement

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