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Investigations on synthesis and polymerization of difunctional 7-membered cyclic ketenacetals

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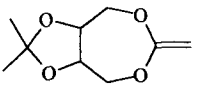
Summary

The synthesis of difunctional seven-membered cyclic ketenacetals was investigated and the new monomers were characterized by IR-, NMR-spectroscopy, and elemental analysis. It was shown that the bifunctional ketenacetal 5 undergoes a radical homopolymerization forming crosslinked polymers with a high degree of ring-opened units. The copolymerization of the difunctional ketenacetal 5 with the monofunctional ketenacetal 1 leads only to low molecular polymers.

Introduction

For a number of industrial applications it is necessary to find monomers that undergo either zero shrinkage or expansion on polymerization /1,2/.
In our former article we described the copolymerization of 1 with 2. Low contents of 2 (2-5wt-%) give highly viscous or gel-like polymers with 0.2 or 2.6 % shrinkage. But these polymers have too low glass transition temperatures for many applications such as in dental medicine /3/.
This is the reason for our further investigation to find monomers that undergo a low volume change during their polymerization and form polymers with higher T_g-values.
Therefore the present paper deals with the synthesis of difunctional cyclic ketenacetals.



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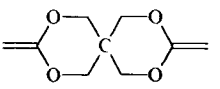

2

Experimental part

Bromoacetaldehyddiethylacetal, 1,4-cyclohexadione, cis-2-butene-1,4-diol, butane-1,4-diol, ethane-1,2-diol and pyruvic acid are commercially available.

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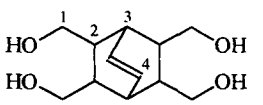
2-Bromomethyl-4,7-dihydro-1,3-dioxepine was synthesized according to the procedure by Anteunis and Becu in the yield of 80% /4/. 2,2-Dimethyl-4,7-dihydro-1,3-dioxepine was produced via acetalization of cis-2-butene-1,4-diol with acetone (yield: 86%) /5/. The synthesis of 2-bromomethyl-5,6-dihydroxy-1,3-dioxepane, 2,2-dimethyl-5,6-dihydroxy-1,3-dioxepane and monomer 1 is in accordance with the procedure described in ref. /3/. 1,2-Bis(mercaptoethoxy)ethane (Bis-SH 12) was synthesized as described in /6/.
A general procedure for the preparation of ketenacetals is given in /7/.
The synthesis of 5,5'-[1,2-ethanediylbis(oxy-2,1-ethanediylthio)]bis[2,2-dimethyl-1,3-dioxepane] 6 and 4-methylene-9-ethoxy-3,5,8,10-tetraoxabicyclo[5,3,0]decane 11 are analogous to the known procedure /6- 8, 11/.

5,6,7,8-Tetrakishydroxymethylbicyclooct-2-ene 3
In a three-necked flask with stirrer and extraction head 5g of $LiAlH_4$ was suspensed in 150 ml dry tetrahydrofuran (THF). In the soxhlet thimble 15g of bicyclooct-2-en-5,6,7,8-tetraacidanhydride was placed. After 12h the extraction was discontinued. The suspension was cooled in an ice bath, and then ethyl acetate was added dropwise up to the end of hydrogen evolution. The crude product was dried in a porcelain basin and then extracted with ethanol for 12h. The extract was concentrated to a small volume. The product precipitated and was dried.
Yield: 7-7.9 g (67-79 % of th.)

$C_{12}H_{20}O_4$ (228.24 g·mol^{-1}) calc.: C 63.14 H 8.83

found: C 63.09 H 8.91



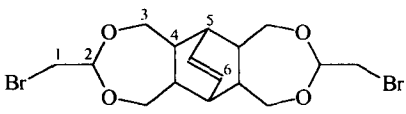
3

IR (KBr): 3247 (OH); 3042 (C=C); 2947, 2916, 2890 (CH); 1053,1037 (C-O) cm^{-1}
^{13}C NMR (62 MHz, d^6-DMSO): 61.31 C_1; 44.38 C_2; 35.75 C_3; 132.42 C_4 ppm

3,9-Bis(bromomethyl)-5a,6,6a,7,11,11a,12,12a-octahydro-1*H*,5*H*-6,12-ethenobenzo-[1,2-e; 4,5-e']bis[1,3]dioxepine 4
The acetalation of 5,6,7,8-tetrakishydroxymethylbicyclooct-2-ene with bromoacetaldehyddiethylacetal is according to previously described preparation of acetals/ketals /7/.
Yield: 3.4 g (70% of th.)

$C_{16}H_{22}Br_2O_4$ (438.096 g·mol^{-1}) calc.: C 43.86 H 5.06

found: C 43.75 H 5.13



4

IR (KBr): 3042 (C=C); 2948, 2919, 2875 (CH); 1127, 1032 (C-O-C); 747 (C-Br) cm^{-1}
^{13}C NMR (62 MHz; $CDCl_3$): 32.06 C_1; 105.94 C_2; 73.65 C_3; 44.47 C_4; 36.54 C_5; 132.11 C_6 ppm

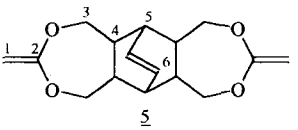
3,9-Bismethylen-5a,6,6a,7,11,11a,12,12a-octahydro-1*H*,5*H*-6,12-ethenobenzo-[1,2-e;-4,5-e']bis[1,3]dioxepine 5

In a three-necked flask with stirrer, condenser and dropping funnel, a solution of 3.3 g (30 mmol) potassium tert.butylate was dissolved in 50 ml dry THF. Under a weak stream of inert gas a solution of 5 g (11.4 mmol) 4 in 200 ml dry THF was added dropwise in 30 min to the ice-cooled mixture. Then it was heated up to 60°C and stirred for 6h. After cooling to room temperature the precipitated potassium bromide was filtered off and washed with dry THF. The solvent was removed under reduced pressure and the resulting crude product was recrystallized from dry benzene/heptane (1:1) to yield colorless needles (F_P = 103°C).

Yield: 1.78 g (56.5 of th.)

$C_{16}H_{20}O_4$ (276.28 g•mol^{-1}) calc.: C 69.55 H 7.29

found: C 69.59 H 7.36



5

IR (KBr): 2941, 2924, 2912, 2899 (CH); 1670 (C=C); 1470, 1352 (alkC-O-C); 1211, 1102, 1045 (C-O-C) cm^{-1}

^{13}C NMR (62 MHz, d^6-DMSO): 72.3 C_1; 164.9 C_2; 73.2 C_3; 44.1 C_4; 39.1C_5; 132.5 C_6 ppm

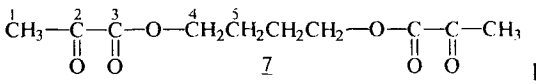
2-Oxopropionic-acid-4-(2-oxopropionyloxy)butylester 7

In a 100 ml flask with magnetic stirrer and water separator, 0.05 mol butane-1,4-diol and 0.1 mol pyruvic acid in 80 ml chloroform were heated with a little amount of Amberlyst 15 until the water separation finished. The excess of solvent was distilled off and the residue was distilled in vacuum.

Yield: 7.37 g (64% of th.); b.p. (0.35 torr): 134°C

$C_{10}H_{14}O_6$ (230.152 g•mol^{-1}) calc.: C 52.18 H 6.13

found: C 52.23 H 6.12

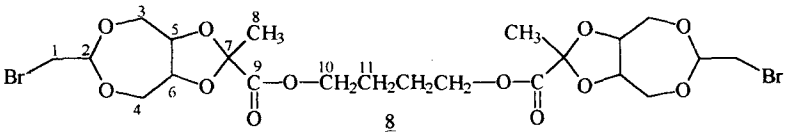


7

^{13}C NMR (62 MHz; $CDCl_3$): 26.3 C_1; 191.3 C_2; 160.4 C_3; 65.2 C_4; 24.6 C_5 ppm

6-(Bromomethyl)-tetrahydro-2-methyl-1,3-dioxolo[4,5-e][1,3]dioxepin-2-carboxylic-acid-1,4-butanediylester 8

The acetalation is in accordance with the described procedure.

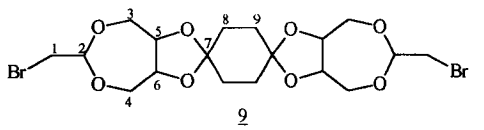


8

^{13}C NMR (62 MHz,$CDCl_3$): 29.1 C_1; 102.3 C_2; 68.5 C_3, C_4; 76.6 C_5, C_6; 105.8 C_7; 26.7 C_8; 169.3 C_9; 64.3 C_{10}; 24.9 C_{11} ppm

6,6"-Bis(bromomethyl)octahydrodispiro[1,3]dioxolo[4,5-e][1,3]dioxepin-2,1'-cyclohexane -4,2"-[1,3]dioxolo[4,5-e][1,3]dioxepine 9

Yield: 4.25 g (62% of th.)



9

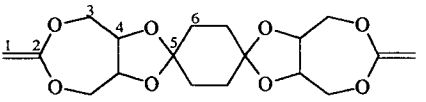
^{13}C NMR (62 MHz, $CDCl_3$): 30.9 C_1; 102.3 C_2; 66.8 C_3, C_4; 75.6 C_5, C_6; 109.5 C_7; 33.5 C_8, C_9 ppm

6,6'-Bis(methylen)octahydrodispiro[1,3-dioxolo[4,5-e][1,3]dioxepin-2,1'-cyclo-hexane-4', 2"- [1,3]dioxolo[4,5-e][1,3]dioxepine] 10

Yield: 1.46 g (~ 65 % of th.)

$C_{18}H_{24}O_8$	(368.292 g·mol^{-1})	calc.:	C	58.69	H	6.57
		found:	C	58.55	H	6.89

IR (KBr-plates): 3033, 1676 (C=C); 2936, 2880 (CH); 1479, 1379 (alkC-O-C); 1255, 1125,1052 (C-O-C); but 1742 (C=O) cm^{-1}



10

^{13}C NMR (62 MHz; $CDCl_3$): 69.1 C_1; 162.74 C_2; 66.9, 66.0 C_3; 73.7 C_4; 107.7 C_5; 25.1 C_6; but 170.3 (C=O) ppm

Radical polymerization

A 5 ml sealed polymerization tube containing 0.3 g monomer 5 and 1.5 wt.-% 2-phenyl-2,2-dimethoxyacetophenone (BDMK) as initiator in dry THF was photoirradiated by a Hg-lamp (250 W) for 6 h. The polymer precipitated in hexane.

The copolymerization experiment was carried out under the same conditions. The monomer mixture of 1 and 5 contains 75 wt.-% of 1 and 25 wt.-% of 5.

Results and Discussion

For the synthesis of difunctional cyclic ketenacetals we carried out extensive experiments. We assumed we could prepare the cyclic ketenacetals with simple diketones or tetraols. This was the basic idea for our starting materials.

3,9-Bis(bromomethyl)-5a,6,6a,7,11,11a,12,12a-octahydro-1*H*,5*H*-6,12-ethenobenzo-[1,2-e; 4,5-e']bis[1,3]dioxepine 4 was synthesized by an acetal exchange reaction of bromoacetaldehyddiethylacetal with 5,6,7,8-tetrakis-hydroxymethylbicyclooct-2-ene 3. The following dehydrobromination of 4 with potassium tert. butylate in dry THF gave the monomer 5 in a 56 % yield. The IR- and the ^{13}C NMR spectra (Fig. 1) are in agreement with the monomer structure.

5 polymerizes in THF with BDMK as initiator and yields a colorless polymer insoluble in common solvents. The IR-spectrum of the polymer (Fig. 2) shows the characteristic signals of the C=O group at 1736 cm^{-1} for the ring-opening structure and that of the C=C group at 1672 cm^{-1}.

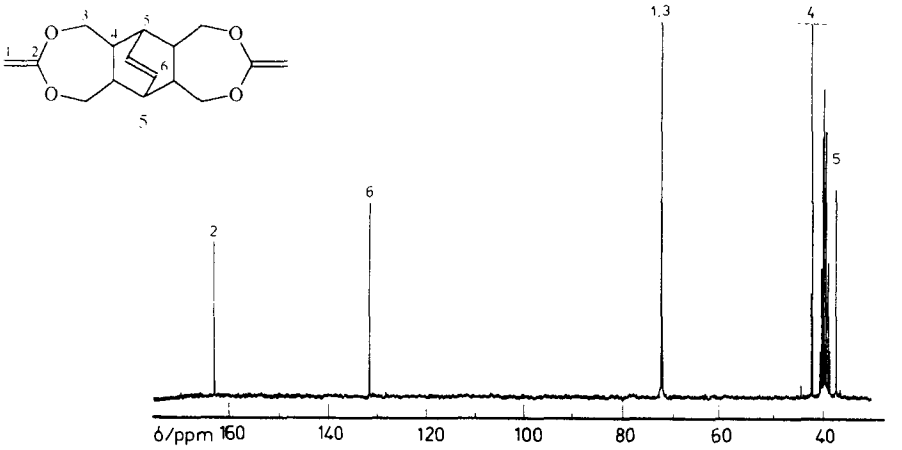
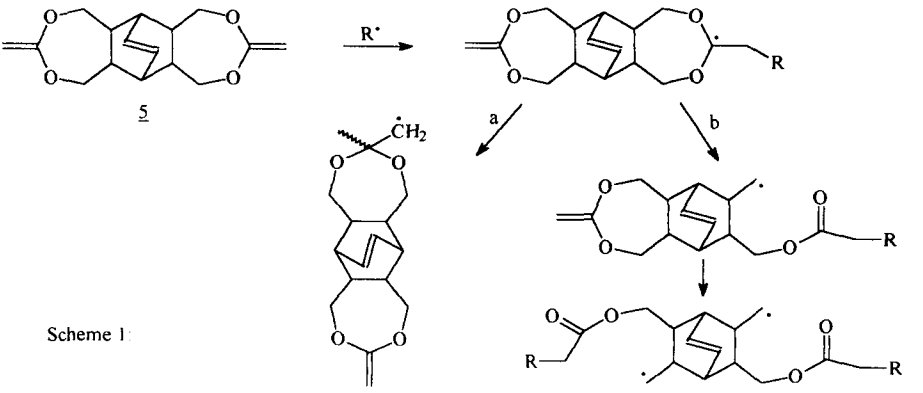


Fig. 1: ^{13}C NMR spectrum (62 MHz, d^6-DMSO) of 5

There are two ways to react after radical attack (see Scheme 1):
Firstly, the vinyl ether-like polymerization without ring-opening (way a). The resulting non-opened units are mainly present in the network, but of course it is possible that the second intact ketenacetal group can add another starting radical or a growing chain end. Secondary, in the reverse case the ring-opening step starts first (way b) followed by two possible ways, too. In each case the reaction has to lead to a crosslinked polymer. Because of the insolubility of the polymer we are not able to distinguish the degree of ring-opening, but the amount must be high because of the intensive C=O signal in the IR-spectrum (Fig. 2).



Scheme 1

The DSC-curve of the homopolymer of 5 showed at first an exothermic peak and then we found the glass transition temperature at 89°C. We explain the occurrence of the exothermic peak by a secondary thermal polymerization of a part of the C=C residual groups.

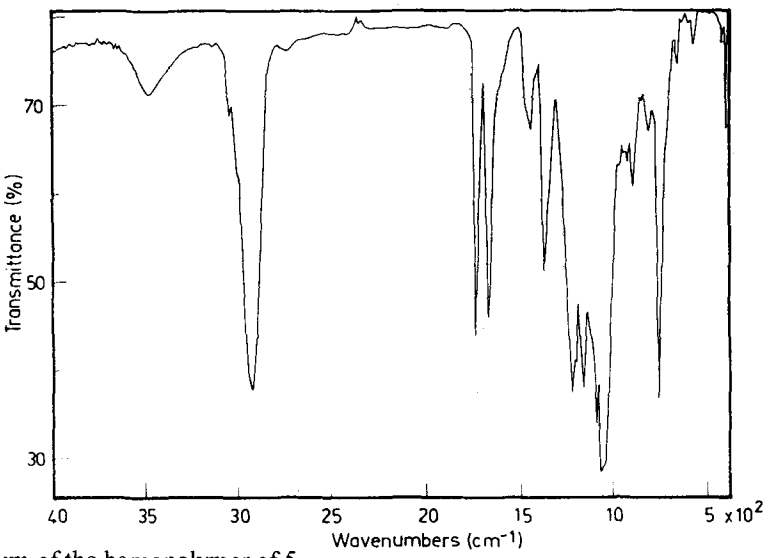


Fig. 2: IR-spectrum of the homopolymer of 5

The copolymerization of 5 and 1 (25 : 75 wt.-%) led only to a low-molecular polymer (VPO: $M_n \sim 2500$ g·mol^{-1}) in a slight yield (15%). As main product we isolated the intact monofunctional ketenacetal 1. By means of the DSC we determined the glass transition temperature of the copolymer at 67°C. Further investigations on the copolymerization of 5 with other monomers (MMA, 2-methylene-4-phenyl-1,3-dioxolane) are in preparation.

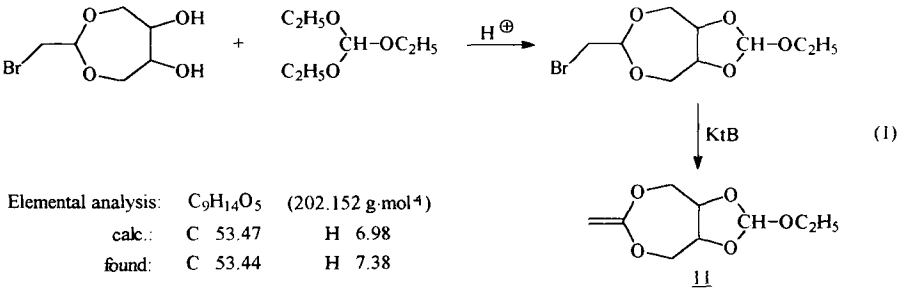
The results of these copolymerization are not satisfactory. Therefore we want to synthesize another novel synthetic bifunctional ketenacetals. In our previous investigations we found that it was possible to synthesize 4-methylene-9-spiro-1'-cyclohexane-3,5,8,10-tetraoxabicylo[5,3,0]decane via acetalation of 2-bromomethyl-5,6-dihydroxy-1,3-dioxepine with cyclohexanone. The yield was 85% /9/. So we thought that the synthesis of a difunctional cyclic ketenacetal with cyclo-1,4-hexadione was possible.

The ketalization of 2-bromomethyl-5,6-dihydroxy-1,3-dioxepane with cyclo-1,4-hexadione gave a colorless amorphous product. For the compound 9 we could not find any solvent for recrystallization and therefore it was washed only with abs. ethanol. The elemental analysis showed good agreement with the calculated values. The dehydrobromation of 9 gave a slightly yellow product. The IR- and the ^{13}C NMR spectra showed the characteristic peaks for 10, but also the signals of the C=O group. That we can only explain by the existence of a ring-opened constituent.

Comparatively, the ketalization of 2,5-hexadione with ethane-1,2-diol or 2,2-dimethyl-5,6-dihydroxy-1,3-dioxepane led to colorless crystalline products. The structure could be proved via NMR- and IR-spectroscopy. In contrast to these model compounds the

ketalization with 2-bromomethyl-5,6-dihydroxy-1,3-dioxepane gave a liquid which decomposed during distillation.

In the next experiment pyruvic acid was the starting compound. The diester was formed with ethane-1,2-diol and we obtained the ketalyzed ester as a by-product. Sterzycki described pyridinium tosylate as a good catalyst for deacetalization of 1,3-dioxolanes /10/. The ketalyzed ester could be synthesized with a 3- to 5-times excess of ethane-1,2-diol as the main product. But when we used the pyridinium tosylate as catalyst we observed no reaction. So when we used butane-1,4-diol for esterification of pyruvic acid we did not find the by-product. The following ketalization and dehydrobromination were in accordance with the described procedure. When triethyl orthoformiate was applied for the abstraction of water during the ketalization we obtained the following ketenacetal as the more stable main product (eq. 1). The role of the orthoester is not limited to the reaction with water, but it also takes part in the ketalization reaction itself /11/. After the dehydrobromination we could isolate the product 11 in 80% yield.

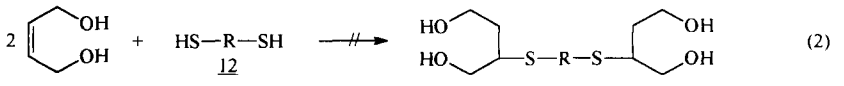


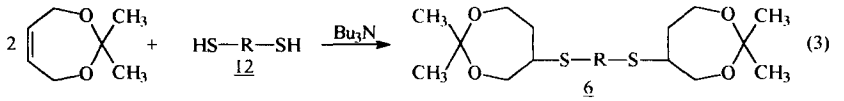
Elemental analysis: $C_9H_{14}O_5$ (202.152 g·mol^{-1})

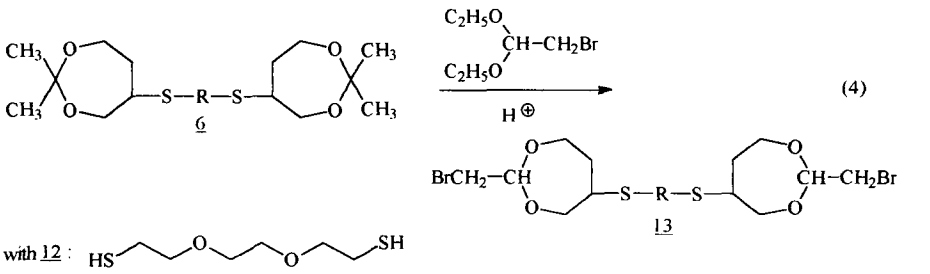
calc.: C 53.47 H 6.98

found: C 53.44 H 7.38

For the next ketenacetal preparation we used the SH-En-addition.The following equations illustrate the reaction path (eq. 2-4).







For these Michael addition reactions we used 1,2-bis(2-mercaptoethoxy)ethane (Bis-SH) 12 and tributylamine as catalyst /6/. At first we wanted to carry out the addition of a Br-containing En with a bifunctional thiol. With the following dehydrobromination we had a simple three-step synthesis of a cyclic difunctional ketenacetal. But the addition of 2-bromomethyl-4,7-dihydro-1,3-dioxepine with 12 gave a dark viscous product which was not distillible or characterizable. The addition of cis-2-butene-1,4-diol with the Bis-SH 12 was not possible as well (eq. 2). In comparison with this reaction the Michael addition of 2,2-dimethyl-4,7-dihydro-1,3-dioxepine led to a slightly yellow viscous product (eq.3). All peaks in the ^{13}C NMR spectrum would be exactly attributed to the structure. The typical band of the C=C group was missing in the IR-spectra. The transacetalization of 6 with bromoacetaldehyddiethylacetal gave a dark viscous product 13 which was not distillable or other isolated purely (eq. 4). But the elimination of acetone and ethanol was detectable by GC-analysis. To sum up, the SH-En addition analogous to the Michael addition is not a possible synthetic route to form difunctional cyclic ketenacetals.

Acknowledgement

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