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New aspects by ring opening polymerization of a spiro ketenacetal

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Summary

The ring opening polymerization of 3,9-bismethylene-2,4,8,10-tetraoxa-spiro[5,5]undecane was investigated. It was shown that this bifunctional ketenacetal undergoes a radical homo- and copolymerization forming crosslinked polymers with a high degree of ring opened units. Using other initiators than radicals it is possible to get statements about the electronical state of ketenacetal functions in saturated heterocycles.

Introduction

In 1964 ORTH described 3.9-bis-methylene-2,4,8,10-tetraoxa-spiro-[5,5]undecane as a viscous material, polymerising spontaneously in contact with the air (1). Therefore he did not investigate this compound further, but there were also no references in the literature until today. Recognising this molecule as a parent compound of bifunctional ketenacetals, we turned to this new field of polymer chemistry regarding the ring opening polymerization of cyclic ketenacetals. The present paper deals with the synthesis, characterization and polymerization of 3,9-bis-methylene-2,4,8,10-tetraoxa-spiro[5,5]undecane.

Experimental part

3,9-bisbromomethyl-2,4,8,10-tetraoxa-spiro[5,5]undecane $\underline{1}$

13,6 g (100 mmol) 2.2.-bishydroxymethyl-propane-1.3-diol, 33,8 g (200 mmol) bromoacetaldehyde dimethyl acetal and a trace of p-toluenesulfonic acid were added to a 250 ml flask with stirrer and water separator. Then the mixture was heated to a temperature of 130-140°C (oil bath) until the theoretical amount of methanol was collected over a period of about 20 minutes. After stirring for 30 min at 80°C, the pale yellow and viscous liquid was cooled to 0°C to become crystalline. The crude product was obtained after recrystallisation from benzene/hexane (1:5) as colourless needles.
yield: 28.6 g (≙ 82.6 % of th.); m.p.: 103°C

IR(KBr): 2985, 2952 and 2865 (CH), 1162 and 1128 (C-O-C), 731 (C-Br).
^{13}C NMR ($CDCl_3$): δ = 31.4 (CH_2-Br), 32.4 ($\mathbf{C}(CH_2O)_4$), 68.7 and 70.3(CH_2-O)
99.3 ($(RO)_2$CH-)

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$C_9H_{14}Br_2O_4$ (346.0) Calc. C 31.24 H 4.08 Br 46.18
Found C 31.77 H 3.69 Br 45.02

3,9-bismethylene-2,4,8,10-tetraoxa-spiro[5,5]undecane 2

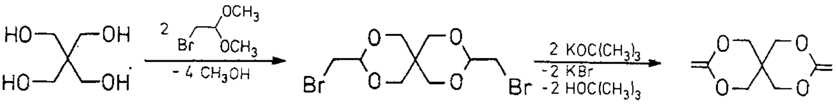
In a 250 ml 3-neck flask with stirrer, condenser and dropping funnel 13.2 g (120 mmol) potassium butoxide was dissolved in 80 ml of dry tetrahydrofurane (THF). Under a week stream of nitrogen and stirring 17.3 g (50 mmol) 1, dissolved in 80 ml dry THF, was added dropwise to the solution within 30 min. After this, the obtained mixture was stirred for another 6h at 65°C under nitrogen.
After cooling to room temperature the precipitated KBr was separated and washed with 3 portions of dry THF. The solvent was removed in vacuum and the residue allowed to crystallize at 0°C. Under strict exclusion of moisture the product was obtained as colourless needles from hexane/benzene (9:1).
yield: 4.9 g (≙ 52 % of th.), m.p.: 53°C

IR(nujol): 1678 ($C{=}CH_2$, s), 1466 and 1378 (C-O-C).
^{13}C NMR (THF-d_8): $\delta = 36.7$ ($\mathbf{C}(CH_2O)_4$), 68.0 ($={\mathbf{C}}H_2$), 69.6 ($\mathbf{C}H_2O$), 161.4 ($\mathbf{C}{=}CH_2$)

$C_9H_{12}O_4$ (184.2) Calc. C 58.92 H 6.56
Found C 58.75 H 6.68

Results and discussion

In 1982 (2) BAILEY found, that 2-methylene-1.3-dioxane undergoes a ring opening polymerization after radical attack with a ring opening degree of avarage 85%. That is the reason why we postulated, that 2 must have similar properties of polymerization, because of it is similar structure. The monomer was synthezised according to the following equation:



(1)

In contrast to (1), 2 represents a crystalline, colourless solid, which is stable against oxygen, but very sensitive to moisture. It can be kept under nitrogen for a long time without any change.
Falling back on (1) and (3), we expected a ring-opening polymerization mainly by using radical initiators. Because of the bifunctionality preferably crosslinked polymers have to result. Table 1 show the experiments carried out to get information about the reactivity of this bifunctional ketenacetal.

In all cases the homopolymerization of 2 leads to insoluble, colourless polymers (**2a**-**2e**). The IR-spectrum (Fig.1) demonstrates, that there must be a ring opening because of the signal at 1744 cm^{-1} which corresponds to the ester-carbonyl-group.

Table 1

polymer	initiator	solvent	comonomer	conditions
2a	1 wt.-% ketal$^{1)}$	CH_2Cl_2	-	RT, UV, 5h
2b	1 wt.-% AIBN	toluene	-	100°C, 2.5h
2c	1 wt.-% AIBN	-	-	RT → 70°C,1h
2d	1 wt.-% Et_3OSbCl_6	CH_2Cl_2	-	RT, 10 min
2e	1 wt.-% $BF_3.Et_2O$	CH_2Cl_2	-	-78°C → RT
2f	10 wt.-% $NaOCH_3$	THF	-	RT → 65°C, 5h
2g	1 wt.-% $C_{10}H_8Na^{2)}$	CH_2Cl_2	-	RT, 3h
2h	1 wt.-% ketal	-	$C_8H_{15}NO_2{}^{3)}$	RT, UV, 5h
2i	1 wt.-% ketal	-	$C_4H_6O_2{}^{4)}$	RT, UV, 5h

1) 2.2-dimethoxy-2-phenyl-acetophenone
2) naphthyl-sodium in THF-solution
3) N,N-dimethyl-amino-ethyl-methacrylate (double excess)
4) vinylacetate (tenfold excess)

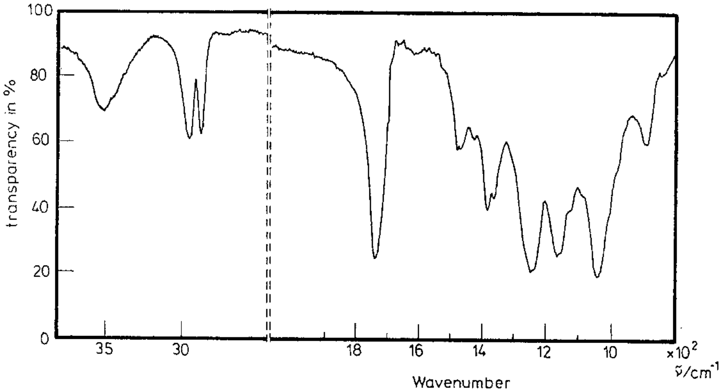
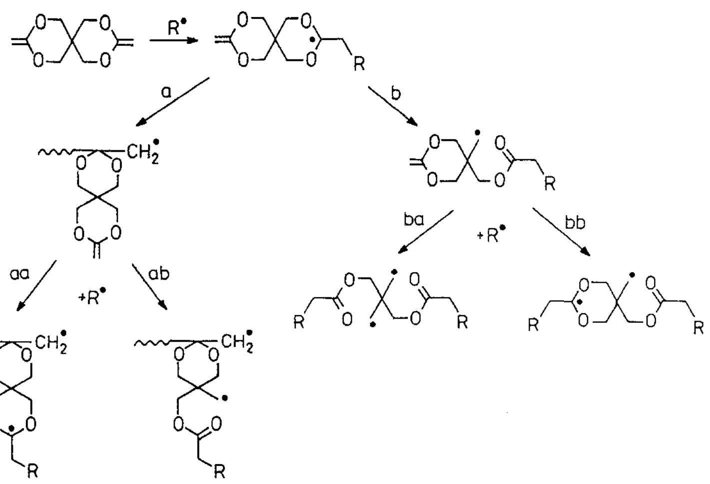


Fig.1 IR spectrum of **2a(2b)** in KBr

The ^{13}C solid state NMR spectrum (Fig.2) showes the structural elements containing in the crosslinked polymers.

To assign the signals to the carbon-atoms we used the direct comparison with the ^{13}C NMR spectrum of 1. In this way we found that the signals at 30.5, 36.3, 62.5 and 102.2 ppm belong to the non-ring opened units of 2. The additional signals at 20.0 and 113.0 ppm and the very small carbonyl signal at 175.6 ppm indicate the presence of opened units in the network.

To form these structures the following mechanism is to discuss:



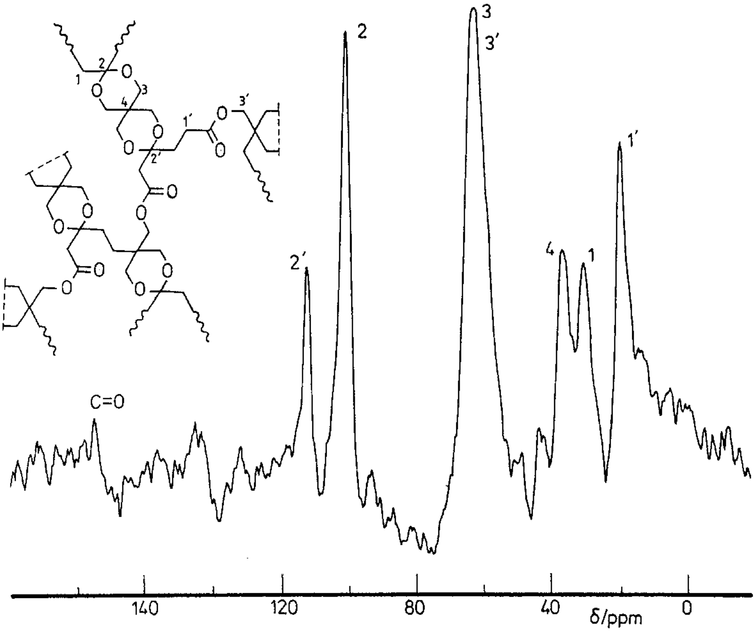


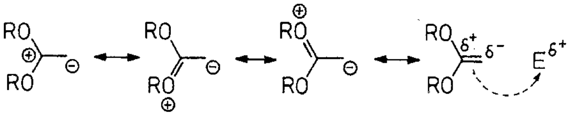
Fig.2 ^{13}C solid state spectrum of **2a** (400 MHz, standard, ext. adamantane)

There are two alternative ways to react after radical attack: 1) the chain growth without ring-opening (way **a**). The resulting non-opened units are mainly present in the network, but of course it is likewise possible, that the second intact ketenacetal group can add another starting radical or a growing chain end (way **ab**). In the reverse case the ring opening step is able to go on primary (way **b**) followed by two possible ways too. In every case the reaction has to lead to a crosslinked polymer. Because of the insolubility of the samples we are not able to distinguish the degree of ring opening, but the value must be high because of the intensive signals in the spectrum (see Fig.2).

Carrying out the polymerization in bulk we observed an explosive reaction with complete decomposition. (experiment **2c**). While the radical initiated polymerization elapses relative slowly, the cationic polymerization (**2d** and **2e**) take place immediately forming insoluble colourless polymers with similar properties like those polymers obtained from radical polymerizations. It is also remarkable that the polymerization can not slow down using low temperatures (**2e**).

According to our exceptions 2 does not react in the presence of bases undergoing an anionic mechanism (experiment **2f** and **2g**). Indeed bases are able to stabilize ketenacetals like BAILEY reported in (4).

However, the results of our experiments demonstrate that clearly, ketenacetals as electron-rich olefines accept electron deficient particles, like Et^+, BF_3 or radicals (cyano isopropyl radicals or benzoyl radicals) to start a polymerization. That is also the reason why electron-rich compounds are not able to release a polymerization.



(3)

In (5) we reported that N,N-dimethylamino-ethyl-methacrylate is an efficient comonomer to yield soluble oligomers of fast polymerising ketenacetals. 2 dissolves very good in the methacrylate. After irradiation in presence of 1 wt.-% ketal (Tab.1) a yellow transparent insoluble polymer was obtained. A similar result experiment **2i** gives.

Thus 2 represents an effective comonomer to reach crosslinked copolymers. It is really reasonable for commercial use to add 2 in a low ratio (1-5 wt.-%) to radical polymerizable and film formation monomers (e.g. styrene, vinylacetate) in order to get transparent and chemical resistent films, because both samples are very stable against acides and bases.

Further investigations regarding the copolymerization of monofunctional ketenacetals with the bifunctional ketenacetal 2 are in preparation.

Acknowledgement

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