RECENT RESULTS IN THE POLYMERIZATION OF MACROCYCLIC ACETALS

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Abstract - The cationic polymerization of oligoethylene glycol acetals of the general formula I with 11-, 14- and 17-membered rings yields highpolymers and a homologous series of macrocyclic oligomers. Earlier results are reviewed. It is shown that in this way copolymers with a regular sequence of 1 oxymethylene unit and 1-5 oxyethylene units are obtained. Some physical properties of these polymers are described, in particular the complex formation with iodine, alkaline salts and the inclusion compounds with urea. In the second part some other cyclic acetals and their polymerization are discussed. By polymerization of 1,3,6,11-tetraoxacyclotridecane highpolymers are formed, the structure of which corresponds to a regular terpolymer. 1,3-dioxacycloundecane is also polymerizable. An equilibrium is attained consisting of polymer and cyclic oligomers but without the monomer. 2,3-benzo-1,4,7,9-tetraoxacycloundecane-2 only forms cyclic dimers but no polymers. With 4H,7H-1,3-dioxepin the polymerization proceeds exclusively by ring opening and the double bond is retained. This monomer also forms a cyclic dimer.

INTRODUCTION

It has long been known that oxacyclic compounds are polymerizable under ring opening (1), but these observations has attracted only few interest at that time. Systematic studies of this type of polymerization started around the nineteen sixties. Since then, several groups are involved in the kinetics, reaction mechanisms and thermodynamics of the ring-opening polymerization mostly of tetrahydrofurane and dioxolane. During the last years, many papers on the synthesis and polymerization of several other cyclic ethers, monocyclic and bicyclic acetals have been published (for review articles see (2) and (3)).

This paper will be restricted to monocyclic acetals of formaldehyde. The most simple compound of this type is dioxolane, which has been extensively studied for its homo- and copolymerization behaviour (4)-(10). We have been interested in the question whether the higher homologues of dioxolane can be polymerized, and which polymeric structures would be obtained. Therefore, we
ROLF C. SHULZ et al.

synthesized a series of cyclic oligoethylene glycol acetics having the general structure I.

\[
\begin{align*}
\text{OCH}_2
\end{align*}
\]

(1)

Dioxolane \((b=1)\) gives a polymer, which can be regarded as a 1:1 alternating copolymer of formaldehyde \((M)\) and ethylene oxide \((E)\). \(b=2\) means trioxocane; obviously the structure of this polymer corresponds to a 1:2 ratio formaldehyde-ethylene oxide \((11)-(13)\).

\[
\begin{align*}
-\text{CH}_2\text{O}--\text{CH}_2\text{CH}_2\text{O}--
\end{align*}
\]

(1)

Thus, it should be possible to synthesize in this way regular copolymers of formaldehyde and ethylene oxide with various sequences. This topic will be the subject of the first part of this paper. In the second part acetals of several other diols and their polymerization behaviour will be described.

**OLIGOEHYLNE GLYCOL ACETALS OF TYPE I**

Compounds having the general structure I with \(b=3,4\) and \(5\) can be prepared by a two-step synthesis starting from paraformaldehyde and the appropriate oligoethylene glycol \((14)\). Polymerization studies of these monomers were conducted simultaneously and independently by Yamashita et al \((15)\) and by our group in Mainz \((16)\). The results of both groups are largely consistent. Because the polymerization of these compounds has been already described in detail \((17)-(21)\) only the most important facts will be summarized quite briefly and then some new results on the properties of the polymers shall be added. Different reaction conditions can be applied for the polymerization of I. In our experiments we used preferentially trifluoromethane sulfonic acid as catalyst, \(\text{CH}_2\text{Cl}_2\) as solvent, and reaction temperatures between \(-25^\circ\text{C}\) and \(+30^\circ\text{C}\). The conversion was determined by HP-GPC. This technique has the advantage of a simultaneous determination of monomer consumption and of polymer as well as oligomer formation. For all three monomers the reaction comes to an equilibrium state and a mixture of monomer, polymers and a homologues series of cyclic oligomers is formed. In the case of TGF \((I; b=3)\) cyclic oligomers up to a polymerization degree of \(DP=20\) (that means macrocycles with up to 220 ring atoms) were identified and quantitatively determined by means of high resolution gel permeation chromatography. The concentrations of the cyclic oligomers at equilibrium can be quantitatively described by the Jacobson-Stockmayer-Semlyen theory \((19)\). The cyclic oligomers with \(DP\) up to 8 were isolated by preparative GPC \((17)-(18)\). With increasing of the monomer concentration the molecular weights of the polymers
increase and the formation of the oligomers decreases. The high molecular fractions have molecular weights of up to about 100,000. The chain propagation mechanism was studied by the ion-trapping technique described by Penczek et al. (22)(23). The formation of cyclic oligomers in addition to the polymers can be explained by competing back-biting and end-biting reactions on the one hand and by propagation reactions on the other hand. A general kinetic scheme for the ring-chain-competition and mathematical methods to their quantitative treatment were recently published by Penczek et al (24). Our results are consistent with these models.

The chemical structure of the polymers was studied in detail by means of IR, $^1$H- and $^{13}$C-NMR spectroscopy. It was found that the composition of the polymer was, in all cases, identical with that of the monomer. Furthermore, it was ascertained that no re-arrangement reactions occur and thus the polymer units are correctly described by the general formula II.

\[
\begin{align*}
\text{(CH}_2\text{CH}_2\text{O)}_b & \quad \rightarrow \quad \left[ \frac{(\text{OCH}_2)}{\text{M}_1} \left(\text{CH}_2\text{CH}_2\text{O)}_b \right) \frac{\text{E}_b}{x} \right] \\
b &= 1, 2, 3, 4, 5
\end{align*}
\]

Therefore, these polymers can be considered to be copolymers with regular sequences of 1 CH$_2$O-unit (M) and 1-5 C$_2$H$_4$O (E) units. They comprise a homologous series of copolymers which cannot be prepared by other routes. The polymers are colourless, wax-like or highly viscous materials. They are readily soluble in many organic solvents, as well as in water. Thus, their solubility properties are similar to that of poly(ethylene oxide), and also some other properties, for instance the reaction with iodine. Addition of monomeric or poly-TGF to a dilute solution of iodine in CCl$_4$ leads to a colour change. The maximum absorbance of 510 nm undergoes a blue shift and a new maximum at 260 nm is formed. According to the Rose-Drago equation (25), an equilibrium constant for the polymer-iodine interaction can be determined. For poly-TGF we found $K_C = 3.5 \pm 1.1$ l/mol and for the monomer $K_C = 3.8 \pm 2.1$ l/mol.

With the same method, Garito and Wayland (26) calculated an equilibrium constant of $K_C = 1.1 \pm 0.05$ l/mol (in CCl$_4$) for the iodine-1,4-dioxane complex and of $K_C = 0.7$ l/mol (in CCl$_4$) for iodine-1,3-dioxane. For the complex formation between iodine and crown ethers $K_C$ values of approximately 5 l/mol (in n-hexane) have been determined (27).

It is known that poly(ethylene oxide) like low molecular weight paraffins and alcohols, forms crystalline inclusion complexes with urea (28)-(30). Like with low molecular weight compounds, there is a definite molar ratio of the host to guest molecules. Bailey and France (31) calculated from the crystal lattice parameters, that for a high molecular weight poly(ethylene oxide) the ratio should be approximately 2 molecules urea per one C$_2$H$_4$O unit. Similarly, we have found 2-2.5 molecules urea per C$_2$H$_4$O unit, i.e. 0.66-0.83 molecules per chain atom. For C9-C19 paraffins, 0.76-0.82 molecules urea are found per carbon atom (32). Thus, a polymer of TGF having the sequence
should have a molar ratio urea: base unit of about 7-9, the polymeric POC (I; \( b=4 \)) with the following sequence a ratio of 10-12.

If a saturated methanolic solution of urea is mixed at room temperature with poly-TGF or poly-POC, needle-like crystals are formed, which have melting points about 3-4°C higher than urea. Their wide-angle x-ray diffractions are very different from urea but consistent with those of the urea-poly(ethylene oxide) inclusion complexes. The composition of the inclusion complexes can be determined from the nitrogen content. For poly-TGF the expected ratio urea:base unit of 9.5-9.6 was found, and for poly-POC a ratio of 13-15. Because of the similarities of the macrocyclic acetals with crown ethers, it appeared interesting to study their complex formation with alkali salts. Yamashita et al. (33) and our group found that the polymers are not suitable as phase transfer catalysts. However, it has been known that ethylene glycol ethers (34) and also high molecular weight poly-(ethylene oxide) form crystalline complexes with various alkali and earth alkali salts (35) and with HgCl₂ (36). We could now show that complex formation or association takes also place between poly-TGF and for example, KSCN, NaSCN and NaJ. Upon addition of these salts to a polymer solution the three proton signals at 4.68, 3.64 and 3.6 ppm are shifted downfield by 0.1-0.22 ppm. Furthermore it is noteworthy that salt addition to poly-TGF leads to a considerable increase of the glass transition temperature, e.g. from -63°C to -4°C with KSCN and to 0°C with NaSCN (at a molar ratio of 1:1, salt/base unit). With KJ or NaJ, at a molar ratio of 1:2, Tg increases to -6°C and -13°C, respectively. A similar increase of the glass transition temperature by interaction with salts, such as LiClO₄, has been described for poly(propylene oxide) (37).

In contrast to the polyethers, all of the polymers described here are acid-sensitive and are hydrolyzed under formation of CH₂O and oligoethylene glycols. Degradation occurs already on standing of the polymers at humid air in the presence of catalytic concentration of acid, and is enhanced by the formation of formic acid. The degradation in solution can be followed by viscometry, e.g., the specific viscosity of a poly-POC solution in 0.1 M HCl at room temperature is reduced to 50% after 250 min. The degradation is statistical and can be described using the known kinetic equations.
The activation energy of 106.6 kJ is of the same order as in other comparable hydrolytic decompositions of acetals.

**SOME OTHER CYCLIC ACETALS AND THEIR POLYMERIZATION**

Starting from 1,4-dichlorobutane we prepared 3,8-dioxaoctanediol-1,4 (yield 35%; b.p. 85°C/10⁻⁵ bar; \( n_D = 1.4572 \)). The product was reacted with paraformaldehyde following the general procedure of Astle (14) and yielding a pre-polymer from which 1,3,6,11-tetraoxacyclotridecane (DDF) was formed upon heating in vacuo (yield 50%; b.p. 57-58°C/2.6x10⁻⁵ bar; \( n_D = 1.4584 \)).

\[
\begin{align*}
\text{Cl}-\text{CH}_2-\text{Cl} + 2 \text{ KO-(CH}_2)\text{OH} & \xrightarrow{-\text{KCI}} \text{HO(=CH}_2\text{)}_2\text{O} \xrightarrow{\text{H}^+} \text{Prepolymer} \\
& \xrightarrow{200^°\text{C}} \text{10⁻⁵ bar} \text{DDF}
\end{align*}
\]

The \( ^1\text{H-NMR} \) spectrum of DDF shows a sharp singlett at 4.73 ppm assigned to the protons of the formal group (C₂). A multiplet between 3.63 and 3.87 ppm is attributed to the protons of carbon atoms 4,5,7,10,12 and 13, while another multiplet at 1.74 ppm is assigned to the protons of carbon atoms 8 and 9. The following signals are observed in the \( ^13\text{C-NMR} \) spectrum (22.63 MHz): 96.43 ppm (C₂); 69.59 ppm (C₄,C₁₃); 69.4 ppm (C₅,C₁₂); 68.49 ppm (C₇,C₁₀); 25.70 ppm (C₈,C₉). The monomer is a highly viscous colourless and odourless liquid that freezes to a glassy mass upon cooling to -15°C. It is soluble in organic solvents as well as in water.

Polymerizations were carried out in CH₂Cl₂ using CF₃SO₃H as a catalyst (monomer concentration: 0.16-2.90 mol/l; initiator concentration: 0.01-0.05 mol/l; T=0°C). Polymerization rates are similar to TGF. Like with TGF, polymerization yields a mixture of cyclic oligomers and polymers, but with a lower content of monomer and dimer at equilibrium than in the case of TGF. The polymers are colourless and wax-like materials and soluble in many organic solvents except ether and aliphatic hydrocarbons. The solubility in water is low. Molecular weights as determined by GPC are approximately 20,000. The \( ^1\text{H-NMR} \) spectrum shows signals identical with those of the monomer, and the IR spectra of monomer and polymer are also identical. We therefore conclude the following structure for the polymers:

\[
\begin{align*}
\text{DDF} & \xrightarrow{\text{M} - \text{E} - \text{B} - \text{E} - \text{M}} \left[\text{(OCH}_2\text{)(OC}_2\text{H}_4\text{)(OC}_4\text{H}_8\text{)(OC}_2\text{H}_4\text{)}}\right]_x
\end{align*}
\]
that means a terpolymers with regular sequences comprised of 1 oxymethylene (M), 2 oxyethylene (E) and 1 oxybutylene (B) units.

A further cyclic formal that has not yet been described is 1,3-dioxacyclo-undecane (OMF). It can be obtained in the usual way (14) from 1,8-octanediol and paraformaldehyde (yield 10-20%; b.p. 196°C; m.p. -62°C). A crystalline compound is formed as side-product and this was identified as the cyclic dimer of OMF.

\[
\text{HO(CH}_2\text{)}_8\text{OH} + (\text{CH}_2\text{O})_x \xrightarrow{\text{H}^+} \xrightarrow{\text{H}^+; 200°C} \text{(OMF)}_2
\]

The structure of OMF is confirmed by its IR and NMR spectra (\(^1\text{H-NMR}: 4.66 \text{ ppm (s); 3.66-3.86 ppm (m); 1.56 ppm;}) \(^{13}\text{C-NMR (22.63 MHz): 96.43 ppm (C}_2; 70.50 \text{ ppm (C}_4;\text{C}_{11}; 28.52; 25.66; 23.84 \text{ ppm (C}_5;\text{C}_{10})}).\) OMF differs from TGF only by a lower oxygen content. It can therefore be considered as a homologue of 1,3-dioxocane. A space-filling model reveals that there are conformations for this 13-membered ring without any torsional or angle strain, but the flexibility of this ring is considerably lower than for TGF.

Polymerizations were carried out at 200°C in CH\(_2\)Cl\(_2\) ([M]\(_0\) 0.1 to 0.7 mol/l) with different catalysts ([I] 0.5 to 2x10\(^{-3}\) mol/l). Using BF\(_3\)-etherate, the polymerization proceeds slowly and reaches the stationary state after 48 h, while with CF\(_3\)SO\(_3\)H the maximum yield of polymer is obtained already after 2 h, at the same reaction conditions. In the HP-GPC a series of oligomeric peaks is found in addition to a broad polymer peak (see Fig.1). However, in contrast to the polymerization reactions described above, the monomer is completely consumed in this case. The cyclic dimer is found as the major component in the oligomeric mixture; it is identical to the cyclic dimer found as by-product in the synthesis of OMF. It can be separated from the reaction mixture by sublimation, (m.p. of 82°C). In the field desorption mass spectrum, the expected molecular ion is found at \(^m/z\) 316. Likewise, \(^1\text{H and }^{13}\text{C NMR spectra are consistent with the structure of 1,3,12,14-tetraoxacyclodocosane (OMF)}\(_2\).\) This compound can be polymerized under the same conditions as OMF yielding polymers with average molecular weights of 10,000. Besides the polymers cyclic oligomers are formed but no trace of the monomer OMF is found (see Fig.2). We assume that, in the presence of the catalyst, monomeric OMF forms the linear growing chains (9a). The propagation reaction (9b) competes with the cyclisation reactions forming.
Polymerization of OMF with BF$_3$-etherate. $T=20^\circ$C

$[M]=0.5\text{ Mol/l}$; $[l]=2.10^{-3}\text{ Mol/l}$

<table>
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<tr>
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<tr>
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<td>32.2%</td>
</tr>
<tr>
<td>3h</td>
<td>38.6%</td>
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</table>

Fig. 1. HP-GPC during the polymerization of OMF

Fig. 2. HP-GPC during the polymerization of the cyclic dimer of OMF in CH$_2$Cl$_2$ $[M]=62x10^{-3}\text{ mol/l}$; $[CF_3SO_3H]=0.6x10^{-3}\text{ mol/l}$; temp. $20^\circ$C.
oligomers, mostly cyclic dimer (9c). The back-biting reactions (9d) form also cyclic oligomers but no monomer. Re-initiation of the cyclic oligomers is possible by protonation. By depolymerization of the isolated polymer an equilibrium is reached with the same oligomers but without the formation of monomer (see Fig.3). The end groups of the growing linear chains were detected using the ion trapping method of Penczek (22,23).

DEPOLYMERIZATION

of \[ \{O(CH_2)_8 - OCH_2\}_x \]
in \( \text{CH}_2\text{Cl}_2 \) with \( \text{CF}_3\text{SO}_3\text{H} \)

\( T = 20°C \)

- \( t = 0 \)
- \( t = 10\text{min} \)
- \( t = 60\text{min} \)

Fig.3. HP-GPC during the depolymerization of poly-OMF in \( \text{CH}_2\text{Cl}_2 \) with \( \text{CF}_3\text{SO}_3\text{H} \)
The polymer structure can be described as a 1:1 alternating copolymer of oxymethylene and oxyoctamethylene sequences.

\[
\text{OMF} \quad \rightarrow \quad [\text{CH}_{2}\text{O}-(\text{CH}_{2})_{8}\text{O}]_x
\]

Thus, the oxygen content is only 50% of the poly-TGF. Accordingly, the properties of this polymer are quite different from those described above.

For instance, poly-OMF is only soluble in \(\text{CH}_2\text{Cl}_2, \text{CHCl}_3\), benzene and toluene but insoluble in alcohol, ether and \(\text{H}_2\text{O}\). This polymer is, in contrast to the above described polyetheracetals, a solid at ambient temperature, and forms spherulites upon cooling down the melt. The crystalline melting point is 49-50°C, as determined by DTA analysis. The polymer forms complexes with iodine. Addition of poly-OMF to a violet solution of iodine in \(\text{CCl}_4\) leads to a red coloration. The equilibrium constant for this complexation was determined spectroscopically according to the Rose-Drago equation (25) to \(5 \pm 3\) 1/mol (at \(\lambda_{\text{max}} = 453\) nm).

In order to study the influence of substituents on the polymerization behaviour of cyclic acetals, 2,3-benzo-1,4,7,9-tetraoxacycloundecene-2 (benzo-TGF) which has not yet been described, was prepared. The synthesis was performed starting from 1,2-dihydroxybenzene which was converted with chloroethanol to 1,2-bis(2-hydroxy-ethoxy)benzene (38). Reaction of the potassium salt with \(\text{CH}_2\text{Br}_2\) leads to a small yield of benzo-TGF (m.p. 84°C).

The structure was established by IR and NMR spectra. In the electron impact mass spectrum the expected molecular ion at \(m/z\) 210 is found with relatively high abundance. At modified reaction conditions a higher melting compound (m.p. 167-168°C) was obtained and identified as the cyclic dimer of benzo-TGF. This compound has properties identical with that synthesized by Pedersen (39) by a different route and with lower yield.
Like with OMF, the formation of the cyclic dimer appears to be sterically favored. Unfortunately, it was not possible to polymerize either the monomer or the dimer with cationic initiators. Addition of \text{CF}_3\text{SO}_3\text{H} or BF_3-etherate to a \text{CH}_2\text{Cl}_2 solution of the monomer or the dimer leads to a violet coloration, that is presumably caused by complex formation, but no polymer was found by HP-GPC.

We therefore studied an unsaturated cyclic acetal. According to a procedure described by Brannock and Lappin (40), we obtained with good yield 4H,7H-1,3-dioxepin (DIP) from cis-butene-(2)-dial-(1,4) and paraformaldehyde. DIP is a liquid of unpleasant odour (b.p. 127°C; m.p. -55°C; \(\delta_4^2 = 1.067\); \(n_D = 1.456\); \text{^13C-NMR} (22.63 MHz): 129.90 ppm (C$_5$, C$_6$); 96.24 ppm (C$_2$); 66.86 (C$_4$, C$_7$).

\[
\begin{align*}
\text{H}_2\text{C}=\text{C}\text{CH}_2\text{OH} + (\text{CH}_2\text{O})_n \rightarrow \text{H}_2\text{C}=\text{C}\text{CH}_2\text{O} -(\text{CH}_2\text{O}) -\text{H}_2\text{O} \\
\text{(DIP)}
\end{align*}
\]

Hydrogenation of DIP with Pd/BaSO$_4$ in dioxane and bromination in CC$_4$ consume the theoretical amounts of H$_2$ and Br$_2$ respectively. Inspection of a space-filling model shows that there are 3 favorable conformations for this compound: chair, boat and twist.

It should be pointed out that the special feature of this monomer are the two possibilities for polymerization, namely at the double bond and at the acetal group. Polymerization experiments in solution with monomer concentrations of 2.7 -5.5 mol/l, with 1% BF$_3$-etherate at temperatures between -78°C and + 22°C leads only to varying amounts of oligomers, mainly dimers and trimers. No polymer was found by HP-GPC when CH$_2$Cl$_2$, benzene, toluene and nitromethane were used as solvents. In contrast, bulk polymerization under the same reaction conditions, starts without induction period under formation of polymer besides only small amounts of oligomers (see Fig.4 and 5). The molecular weight of the polymer increases with decreasing temperature and concentration of initiator. The polymers are plastic-like or rubber-like materials. They are soluble in aromatic hydrocarbons, CHCl$_3$, CH$_2$Cl$_2$, acetone, dioxane and tetrahydrofurane, but insoluble in alcohols and water. Chemical as well as spectroscopic methods were applied to identify the structure of the polymers.
Catalytic hydrogenation leads to the consumption of 1 mol $\text{H}_2$ per base unit. The $^1\text{H}$-NMR spectrum of the hydrogenated product is identical with that of polydioxepane. Bromine is added only to 80-86% of the theoretical amount. During bromination the polymeric reaction product precipitates and this may be the reason for the incomplete conversion. Both $^1\text{H}$ and $^{13}\text{C}$-NMR spectra
reveal that the polymerization occurs exclusively by ring opening of the acetal group and not by reaction at the double bond. Thus, the following structure can be concluded for the polymer:

It is likely that the cis-configuration of the monomer is largely retained in the polymer. As mentioned above, oligomers are also formed during the polymerization. The cyclic structure of oligomers up to DP = 6 could be confirmed. The cyclic dimer was isolated in high purity. It was identified as \((5Z,12Z)-1,3,8,10\text{-tetraoxacyclotetradecane-5,12-diene}\) by elemental analysis, NMR and mass spectrum.

The same compound can also be obtained by a synthetic route described by Nielsen et al. (41). These authors (42) recently published also a x-ray structure analysis of this compound. It is assumed that the conformation found for the crystalline state is also present in solution. Further studies on the polymerization of DIP and the properties of the polymers are currently being conducted.

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