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.
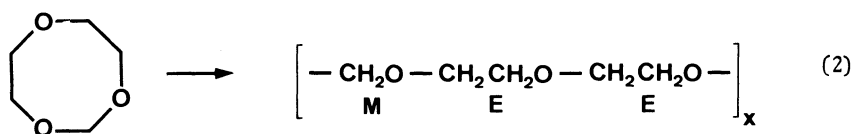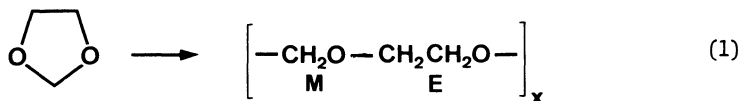
INTRODUCTION

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)-(1o). 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

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

$$\text{(I)}\qquad b = 1,2,3,4,5$$
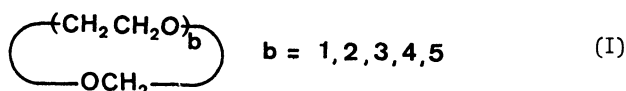
Dioxolane(b=1)gives a polymer, which can be regarded as a 1:1 alternating
copolymer of formaldehyde (M) and ethylene oxide (E). b=2 means trioxocane;
obviously the structure of this polymer corresponds to a 1:2 ratio form-
aldehyde-ethylene oxide (11)-(13).

$$\longrightarrow \quad \left[-CH_2O - CH_2CH_2O - \right]_x \qquad (1)$$
$$\underset{M}{} \qquad \underset{E}{}$$

$$\longrightarrow \quad \left[-CH_2O - CH_2CH_2O - CH_2CH_2O - \right]_x \qquad (2)$$
$$\underset{M}{} \qquad \underset{E}{} \qquad \underset{E}{}$$
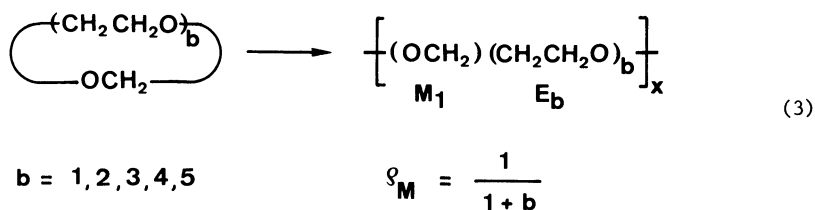
Thus, it should be possible to synthesize in this way regular copolymers of
formaldehyde and ethylene oxide with various sequences. This topic will be the
subject of the first part of this paper. In the second part acetals of seve-
ral other diols and their polymerization behaviour will be described.

OLIGOETHYLENE 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 con-
ducted 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, CH_2Cl_2 as solvent, and reaction temperatures between -25^oC
and $+3o^oC$. 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 homo-
logues series of cyclic oligomers is formed. In the case of TGF (I; b=3)
cyclic oligomers up to a polymerization degree of DP=2o (that means macro-
cycles with up to 22o ring atoms) were identified and quantitatively deter-
mined by means of high resolution gel permeation chromatography. The con-
centrations of the cyclic oligomers at equilibrium can be quantitatively
described by the Jacobson-Stockmayer-Semlyen theory (19). The cyclic oligo-
mers with DP up to 8 were isolated by preparative GPC (17)(18). With in-
creasing 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 1oo,ooo. The chain propa-
gation 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 studies 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.

$$\mathrm{(CH_2CH_2O)_b \atop OCH_2} \longrightarrow \left[(OCH_2)(CH_2CH_2O)_b \right]_x \qquad (3)$$
$$\underset{M_1}{} \qquad \underset{E_b}{}$$

$$b = 1,2,3,4,5 \qquad \varrho_M = \frac{1}{1+b}$$

$$(II)$$

Therefore, these polymers can be considered to be copolymers with regular
sequences of 1 CH_2O-unit (M) and 1-5 C_2H_4O (E) units. They comprise a homo-
logous 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 51o nm undergoes a blue shift and
a new maximum at 26o 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 $K_c = 3.5 \pm 1.1$ 1/mol and for the monomer $K_c = 3.8 \pm 2.1$/mol.
With the same method, Garito and Wayland (26) calculated an equilibrium con-
stant of $K_c = 1.1 \pm o.o5$ 1/mol (in CCl_4) for the iodine-1,4-dioxane complex
and of $K_c = o.7$ 1/mol (in CCl_4) for iodine-1,3-dioxane. For the complex for-
mation between iodine and crown ethers K_c values of approximately 5 1/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)-(3o).
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_2H_4O
unit. Similarly, we have found 2-2.5 molecules urea per C_2H_4O unit, i.e.
o.66-o.83 molecules per chain atom. For C9-C19 paraffins, o.76-o.82 mole-
cules urea are found per carbon atom (32). Thus, a polymer of TGF having
the sequence

$$\left[-CH_2O-(CH_2CH_2O)_3- \atop M \qquad\qquad E_3 \right]_x \qquad (4)$$
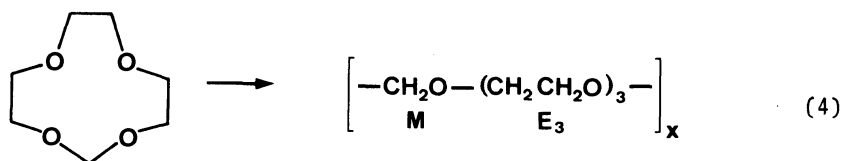
TGF

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 1o-12.

$$\left[-CH_2O-(CH_2CH_2O)_4- \atop M \qquad\qquad E_4 \right]_x \qquad (5)$$
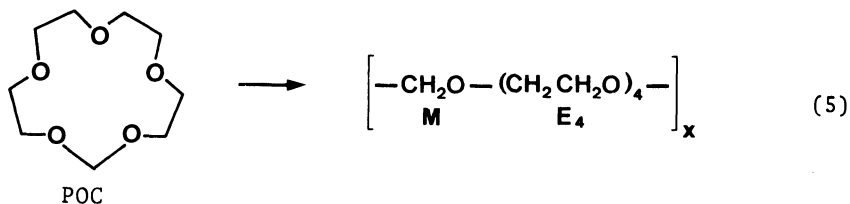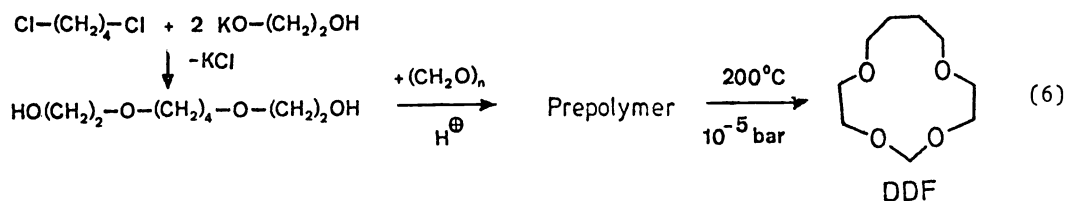
POC

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 dif-
fractions are very different from urea but consistent with those of the
urea-poly(ethylene oxide) inclusion complexes. The composition of the in-
clusion 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 poly-
mers 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 $HgCl_2$ (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
o.1-o.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 $LiClO_4$, 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 CH_2O 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 o.1
M HCl at room temperature is reduced to 5o% after 25o min. The degradation
is statistical and can be described using the known kinetic equations.

The activation energy of 1o6.6 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/1o^{-5} bar; n_D^{2o} = 1.4572). The product was reacted with paraform-
aldehyde 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 5o%;b.p. 57-58°C/2.6x1o^{-5} bar; n_D = 1.4584).

$$Cl-(CH_2)_4-Cl \;+\; 2\; KO-(CH_2)_2OH$$

$$\downarrow \; -KCl$$

$$HO(CH_2)_2-O-(CH_2)_4-O-(CH_2)_2OH \quad \xrightarrow[H^\oplus]{+(CH_2O)_n} \quad Prepolymer \quad \xrightarrow[10^{-5}\,bar]{200°C} \qquad (6)$$
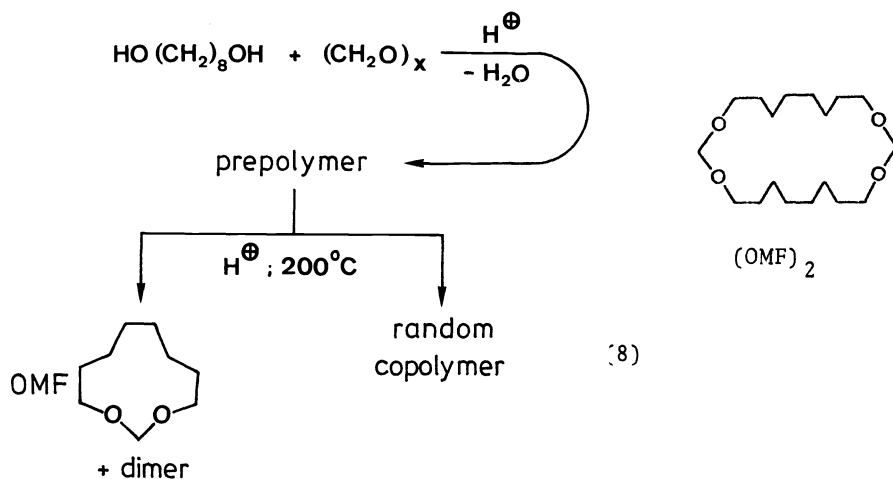
DDF

The ^{1}H-NMR spectrum of DDF shows a sharp singlett at 4.73 ppm assigned to the
protons of the formal group (C_2). A multiplett between 3.63 and 3.87 ppm is
attributed to the protons of carbon atoms 4,5,7,1o,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}C-NMR spectrum (22.63 MHz):
96.43 ppm (C_2); 69.59 ppm (C_4,C_{13}); 69.4 ppm (C_5,C_{12}); 68.49 ppm (C_7,C_{1o});
25.7o ppm (C_8,C_9). 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 CH_2Cl_2 using CF_3-SO_3H as a catalyst
(monomer concentration: o.16-2.9o mol/l; initiator concentration: o.o1-o.o5
mol%; T=0°C). Polymerization rates are similar to TGF. Like with TGF, poly-
merization 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
2o,ooo. The ^{1}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:

$$\longrightarrow \quad +[(OCH_2)(OC_2H_4)(OC_4H_8)(OC_2H_4)]_x \qquad (7)$$

$$+[M — E — B — E]_x$$

DDF
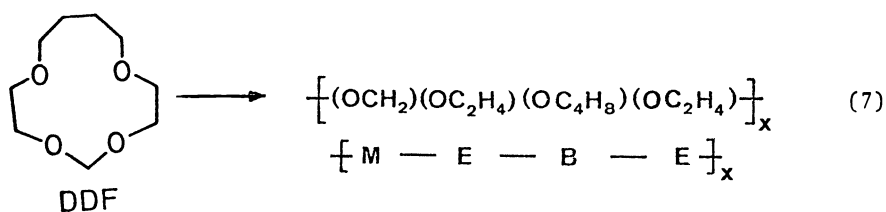
that means a terpolymers with regular sequences comprised of 1 oxymethylene
(M), 2 oxyethylene (E) and 1 oxybutylene (B) units.

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 1o-2o%; 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.

$$HO(CH_2)_8OH \ + \ (CH_2O)_x \xrightarrow[- H_2O]{H^{\oplus}}$$

prepolymer

$$H^{\oplus}; 200°C$$

OMF

random copolymer   (8)

(OMF)$_2$

+ dimer

The structure of OMF is confirmed by its IR and NMR spectra (^{1}H-NMR: 4.66
ppm (s); 3.66-3.86 ppm (m); 1.56 ppm;)(^{13}C-NMR (22.63 MHz):96.43 ppm (C_2);
7o.5o ppm (C_4;C_{11}); 28.52; 25.66; 23.84 ppm (C_5-C_{10})). OMF differs from TGF
only by a lower oxygen content. It can therefore be considered as a homo-
logue of 1,3-dioxocane. A space-filling model reveals that there are con-
formations 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 2o°C in CH_2Cl_2 ($[M]_o$ o.1 to o.7 mol/1)
with different catalysts($[I]$ o.5 to $2x1o^{-3}$ mol/1). Using BF_3-etherate, the
polymerization proceeds slowly and reaches the stationary state after 48 h,
while with CF_3SO_3H 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}H and ^{13}C NMR spectra are consistant 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
1o,ooo. 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 pro-
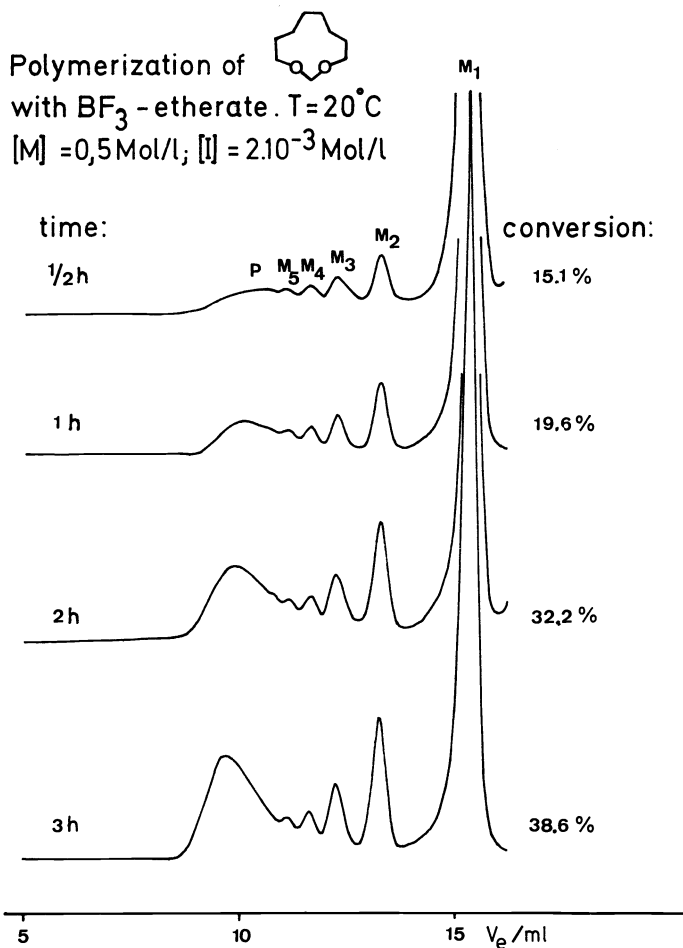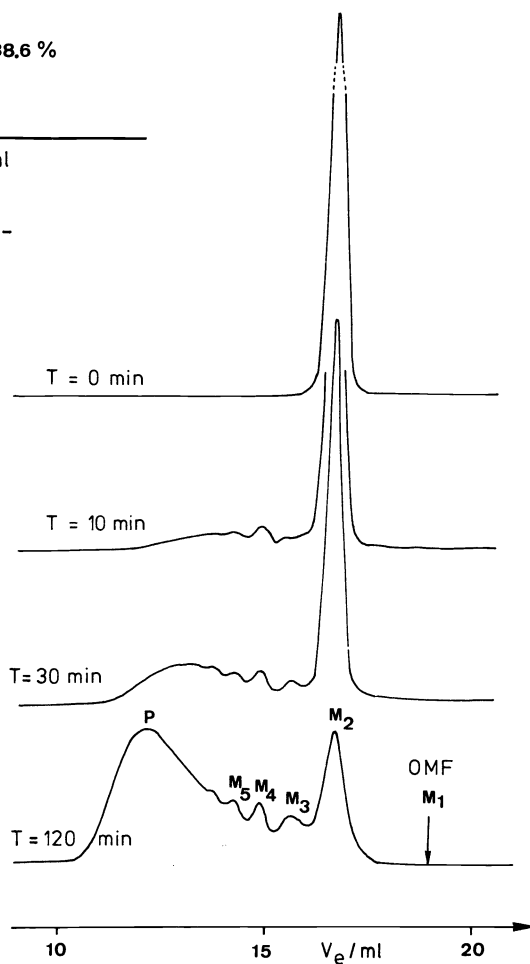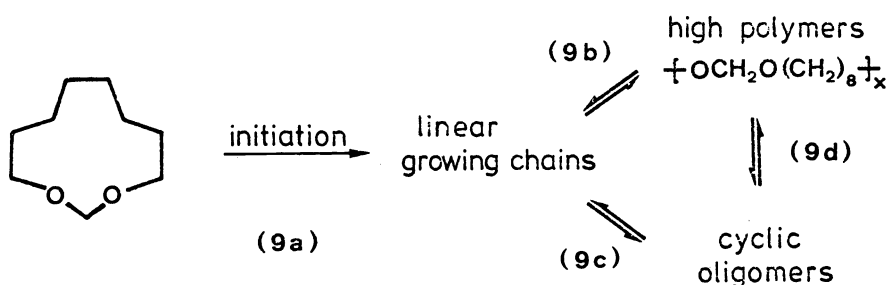pagation reaction (9b) competes with the cyclisation reactions forming

Polymerization of [structure]
with BF_3 - etherate. T = 20°C
[M] = 0,5 Mol/l; [I] = 2.10^{-3} Mol/l

time:

1/2 h — 15.1 %

1 h — 19.6 %

2 h — 32.2 %

3 h — 38.6 %

conversion:

P M_5 M_4 M_3 M_2 M_1

5   10   15 V_e /ml

Fig. 1. HP-GPC during the poly-
merization of OMF

T = 0 min

T = 10 min

T = 30 min

T = 120 /min

P M_5 M_4 M_3 M_2 OMF M_1

10   15 V_e / ml   20

Fig. 2. HP-GPC during the poly-
merization of the cyclic dimer of
OMF in CH_2Cl_2 $[M_2]_0$ = 62×10^{-3} mol/l;
$[CF_3SO_3H]$ = 0.6×10^{-3} mol/l;
temp. 20°C.

high polymers

(9b)

$+OCH_2O(CH_2)_8+_x$

initiation   linear
                  growing chains

(9d)

(9a)   (9c)   cyclic
                                                   oligomers

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 de-
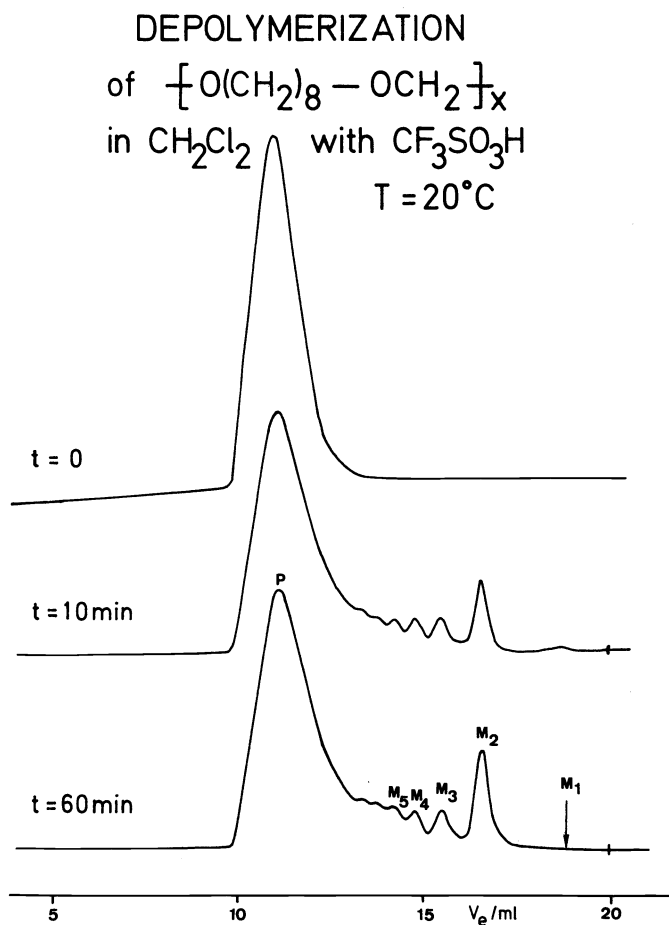tected using the ion trapping method of Penczek (22,23).

DEPOLYMERIZATION
of $+O(CH_2)_8 - OCH_2+_x$
in CH_2Cl_2 with CF_3SO_3H
T = 20°C

t = 0

t = 10 min   P

t = 60 min M_5 M_4 M_3 M_2 M_1

5   10   15 V_e/ml   20

Fig.3. HP-GPC during the
depolymerization of
poly-OMF in CH_2Cl_2
with CF_3SO_3H

The polymer structure can be described as a 1:1 alternating copolymer of oxymethylene and oxyoctamethylene sequences.

$$\left[-CH_2O-(CH_2)_8O-\right]_x \qquad (1o)$$

OMF
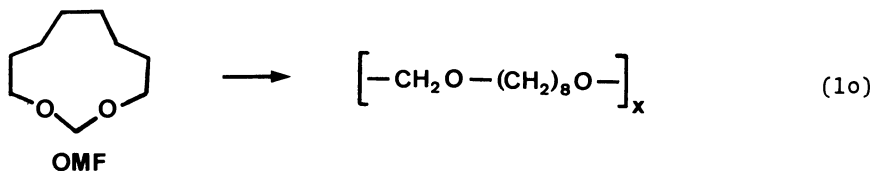
Thus, the oxygen content is only 5o% of the poly-TGF. Accordingly, the properties of this polymer are quite different from those described above. For instance, poly-OMF is only soluble in CH_2Cl_2, $CHCl_3$, benzene and toluene but insoluble in alcohol, ether and H_2O. This polymer is, in contrast to the above described polyetheracetals, a solid at ambient temperature, and forms spherulites upon cooling down the melt. The crystalline melting point is 49-5o°C, as determined by DTA analysis. The polymer forms complexes with iodine. Addition of poly-OMF to a violet solution of iodine in 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±3 1/mol (at λ_{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 CH_2Br_2 leads to a small yield of benzo-TGF (m.p. 84°C).
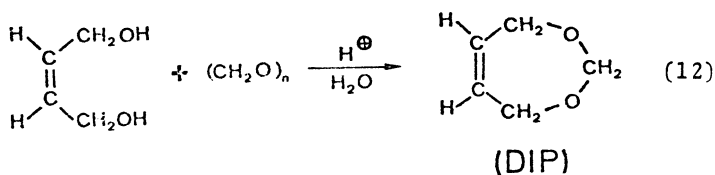

$$(11)$$

benzo-TGF
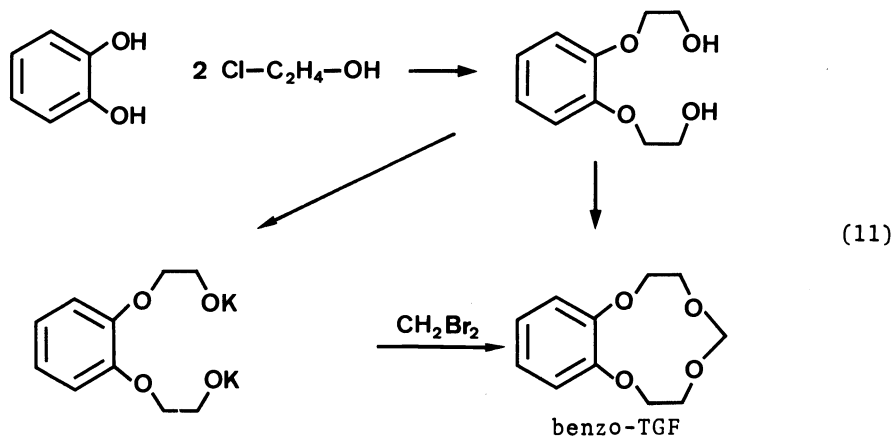
The structure was established by IR and NMR spectra. In the electron impact mass spectrum the expected molecular ion at m/Z 21o is found with relatively high abundance. At modified reaction conditions a higher melting compound (m.p. 167-168°C) was obtained and identified as the cyclic dimer of benzo-TGF. This compound has properties identical with that synthesized by Pedersen (39) by a different route and with lower yield.
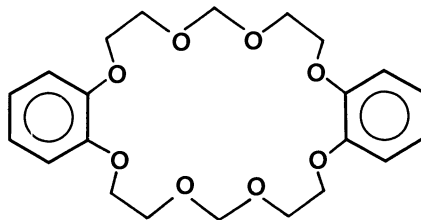
Like with OMF, the formation of the cyclic dimer appears to be sterically
favored. Unfortunately, it was not possible to polymerize either the monomer
or the dimer with cationic initiators. Addition of CF_3SO_3H or BF_3-etherate
to a CH_2Cl_2 solution of the monomer or the dimer leads to a violet coloration,
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 (4o), we obtained with good yield 4H,7H-
1,3-dioxepin (DIP) from cis-buten-(2)-diol-(1,4) and paraformaldehyde. DIP
is a liquid of unpleasant odour (b.p. $127^{\circ}C$; m.p. $-55^{\circ}C$; d_4^{20} = 1.o67; n_D =
1.456; ^{13}C-NMR (22.63 MHz): 129.9o ppm (C_5,C_6); 96.24 ppm (C_2); 66.86 (C_4,C_7).

$$H \underset{H}{\overset{CH_2OH}{\underset{C}{\overset{\parallel}{\underset{C}{\diagup}}}} CH_2OH} \quad + \quad (CH_2O)_n \quad \xrightarrow[H_2O]{H^{\oplus}} \quad \text{(DIP)} \qquad (12)$$

(DIP)

Hydrogenation of DIP with $Pd/BaSO_4$ in dioxane and bromination in CCl_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 $-78^{\circ}C$ and
$+ 22^{\circ}C$ leads only to varying amounts of oligomers, mainly dimers and trimers.
No polymer was found by HP-GPC when CH_2Cl_2, benzene, toluene and nitromethane
were used as solvents. In contrast, bulk polymerization under the same re-
action conditions, starts without induction period under formation of poly-
mer besides only small amounts of oligomers (see Fig.4 and 5). The molecular
weight of the polymer increases with decrasing temperature and concentration
of initiator. The polymers are plastic-like or rubber-like materials. They
are soluble in aromatic hydrocarbons, $CHCl_3$, CH_2Cl_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.
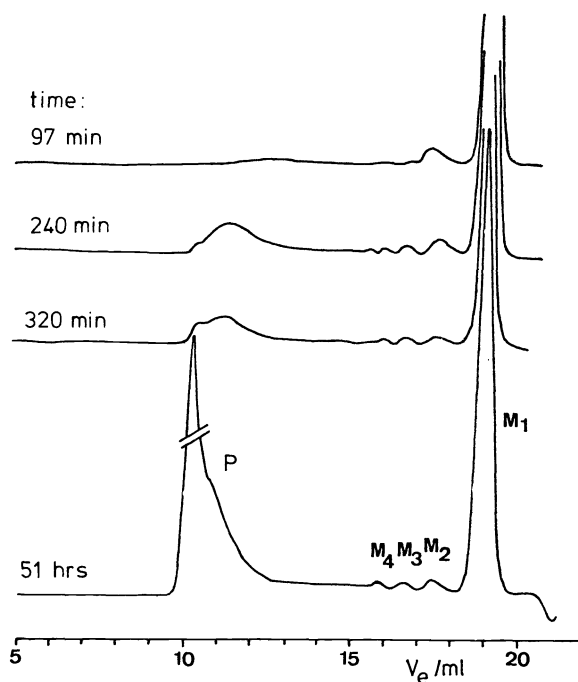
time:

97 min

240 min

320 min

M₁

P

M₄ M₃ M₂

51 hrs

5   10   15 V_e/ml   20

Fig. 4. HP-GPC during the
bulk polymerization of DIP
with BF_3-etherate
(o.3 mol%) at $-2o^oC$

%conversion

0.9 mol %

0.6 mol %

0.3 mol %

40

30

20

10

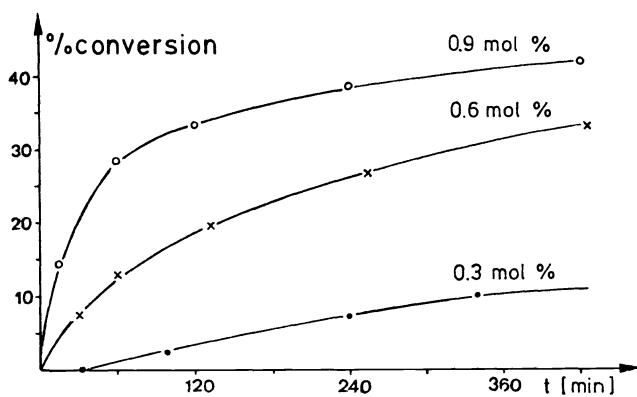120   240   360   t [min]

Fig.5. Time-conversion
curves of the bulk poly-
merization of DIP at $-2o^oC$
with o.3-o.9 mol% BF_3-
etherate

Catalytic hydrogenation leads to the consumption of 1 mol H_2 per base unit.
The ^{1}H-NMR spectrum of the hydrogenated product is identical with that of
polydioxepane. Bromine is added only to 8o-86% of the theoretical amount.
During bromination the polymeric reaction product precipitates and this may
be the reason for the incomplete conversion. Both ^{1}H and ^{13}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:

$$\longrightarrow \quad \left[-OCH_2 - OCH_2 - CH = CH - CH_2 - \right]_x \qquad (13)$$
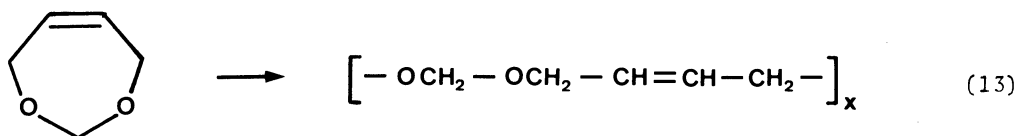
It is likely that the cis-configuration of the monomer is largely retained
in the polymer.As mentioned above, oligomers are also formed during the
polymerization. The cyclic structure of oligomers up to DP=6 could be con-
firmed. The cyclic dimer was isolated in high purity. It was identified as
(5Z, 12Z) ⁻1,3,8,1o-tetraoxacyclotetradecane-5,12-diene by elemental analysis,
NMR and mass spectrum.
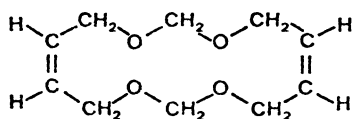
The same compound can also be obtained by a synthetic route described by
Nielsen et al.(41). These authors (42) recently published also a x-ray
structure analysis of this compound. It is assumed that the conformation found
for the crystalline state is also present in solution. Further studies on
the polymerization of DIP and the properties of the polymers are currently
being conducted.

ACKNOWLEDGEMENT

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