Transition Metal Catalyzed Polymerization of 1,3,5-Trioxane

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Übergangsmetall-katalysierte Polymerisation von 1,3,5-Trioxan

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1. Introduction

The cationic ring-opening polymerization of cyclic ethers plays an important role in synthetic polymer chemistry.[1] Typical examples are the synthesis of polyether, cf. polyTHF,[2] or of polyoxymethylene consisting mainly of CH_2O-units. Polymers of the latter type were investigated for the first time by Staudinger et al. at the beginning of the last century.[3] Starting materials for these polymers are essentially formaldehyde, 1,3,5-trioxane, or 1,3,5,7-tetraoxane. For practical reasons and in particular in industrial applications 1,3,5-trioxane is used which can be obtained by drying an extraction mixture of the trimerization process of formalin. This extraction mixture (technical trioxane) is also containing 1,2-dichlororethane (ca. 60 %) as a solvent and water impurities of about 1 %. Trioxane can be polymerized in the solid, molten, or dissolved state and even in suspension and is - in contrast to formaldehyde - only cationically polymerizable.[4] Typical catalysts are Lewis acids like $BF_3 \cdot OEt_2$,[5-7] Brœnsted acids of all types,[8,9] or *tert*-butyl perchlorate,[9] some of which are used in an industrial process. Also transition and main group metal halides or acetonates (*vide infra*) have been employed as catalysts for the cationic polymerization of trioxane.[10]

Initial mechanistic studies were carried out in the early sixties where it was concluded that the presence of formaldehyde is crucial for the polyacetal formation. It was proposed that in the first step of the polymerization, trioxane is attacked by a cationic initiator resulting in the cleavage of a C-O bond and the formation of a carbocationic chain terminus.[4,6] The ring opening is supposed to be followed by a rapid decomposition into formaldehyde monomers and a methylenic carbocation. In the second phase, the concentration of free formaldehyde becomes sufficiently high to render an alternative path possible. In this phase the concentration of free formaldehyde remains constant since its formation and consumption are in equilibrium and polymer formation is observed. Also, by insertion of formaldehyde into activated trioxane, tetraoxane may be formed as a transient by-product.[11] The polymerization process itself is fundamentally highly dynamic: chain growth and formaldehyde liberation from the cationic chain end are continuously taking place, contrasting e.g. the basically irreversible polyolefin formation from 1-alkenes. In theory thus a statistic mixture of polyacetal chains is formed with an average length solely determined by the ratio of initiator and formaldehyde units. In practice, chain transfer takes place through reactions with impurities and an inherent hydride shift reaction.[4,12-14,39] It is assumed that in the latter process, the cationic chain end pol-OCH_2^+ abstracts H^- from a chain fragment pol-OCH_2O-pol (or monomer) to generate a terminus pol-OCH_3 and pol-OCH^+O-pol, which may decompose to a further terminus pol-OC(=O)H and a cation like pol-OCH_2^+, or become a branching point. Reversible reaction of a cationic chain end with an oxygen chain fragment leads to an oxonium species and ultimately to transacetalization and redistribution of the chain length. To obtain high molecular weight polyacetals a high purity monomer basis is a prerequisite. Typical for cationic polymerization, hydrolytic impurities like water act as chain transfer reagents: reaction of the chain end pol-OCH_2^+ with water will result in the formation of pol-OCH_2OH and H^+ which will act as an initiator and start a new chain.

Also contrasting polyolefins, polyacetals of the type pol-OCH_2OH will thermally decompose to the monomer formaldehyde as such hemiacetals are labile compounds. Before thermally processing, the polymer needs to be stabilized. This is achieved through end capping, transforming the hemiacetal into e.g. an ester (reaction with acetic anhydride) (Delrin® by Dupont), or through copolymerization of trioxane with small amounts (<5 % by weight) of cyclic oxygen hetereocycles containing at least C_2-entities, like ethylene oxide, dioxetane (Hostaform® by Celanese) or dioxepane (Ultraform® by BASF). The resulting copolyacetal then contains units of the type copol-OCH_2O-$(CH_2)_n$-$(OCH_2)_mOH$ ($n \geq 2$). Thermal treatment will decompose the initial formed hemiacetal chain end thereby liberate formaldehyde until reaching a comonomer unit and thus leaving back a now thermally stable endcapped polyacetal of the type copol-$OCH_2O-(CH_2)_n-OH$. It is therefore advantageous for a catalyst system to induce the copolymerization of trioxane and other oxygen heterocycles.

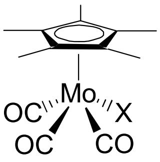
Transition metal catalysts generally offer the advantage to control polymerization reactions and the properties of the resulting polymers by varying the electronic conditions and the steric bulk of the metal centers and ligands, respectively. Although such complexes have been widely tested as catalysts for several kinds of polymerization reactions, like ROMP,[15] olefin polymerization,[16,17] or the copolymerization of carbon monoxide with olefins,[18,19] investigations are only emerging in which such catalysts were employed to initiate the ring opening polymerization of oxygen containing heterocycles.[20-24] In earlier days, some have been probed with success for the polymerization of trioxane. These involve in particular acetylacetonato complexes of molybdenum,[25] cobalt, and other transition metals. In the case of molybdenum some investigations propose a trioxane polymerization reaction through an insertion mechanism: trioxane formally inserts into a Mo-alkoxide bond. In later investigations, this was questioned.[26]

We initiated a larger research effort with the objective to find robust organometallic catalysts for the metal controlled polymerization of trioxane, and to investigate the catalyzed polymerization process in more detail as a comprehensive understanding is far from reached (*vide supra*). In this paper, it is demonstrated that η^5-cyclopentadienylmolybdenum complexes are able to induce the ring opening polymerization of 1,3,5-trioxane even in the presence of some water. Also trioxane could be copolymerized with 1,3-dioxepane by these complexes, which is important since such copolymers provide higher thermal stability than homopolymers through the above described endcapping. With endcapped polyacetal resins thermal or basic decomposition is impeded. The course of the polymerization was monitored by NMR (Nuclear Magnetic Resonance) spectroscopy and it turned out that it was accompanied by a redox process. The experimental evidence points toward a non-metal centered polymerization process, i.e. the initiation only can be controlled through tuning of the metal-ligand entity.

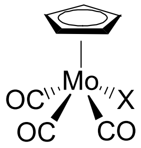
In a final chapter, the above-mentioned catalyst **2a** was also tested in the polymerization of the extraction mixture. An expensive intermediate purification step could be economized, if it were possible to polymerize technical trioxane with this catalyst without drying and purification, which is of great interest for the industrial production of polyoxymethylene.

2. Results and Discussion

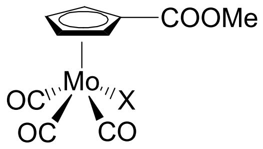
Several years ago Beck et al. reported on the organometallic strong Lewis acid $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^+$ stabilized by weakly coordinating anions like BF_4^-, $CF_3SO_3^-$, or MF_6^- (M = P, As, Sb).[27-30] A comparable complex with $CF_3CO_2^-$ as anion was briefly described by F. J. Lalor et al.[31] The first mentioned authors established that the BF_4^- anion in $(\eta^5\text{-}C_5H_5)Mo(CO)_3BF_4$, was easily replaced for cyclic ethers like oxirane, oxetane, tetrahydrofuran or 1,4-dioxane to give cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Mo(CO)_3$ ether]$[BF_4]$. In particular the oxirane and dioxane complexes proved to be very labile and returned above -40 °C to the starting complex and the corresponding ethers. Under certain conditions the oxirane ring in the complex was subjected to consecutive reactions. In addition, the oxetane complex slowly decomposed in the presence of acetone under formation of 2,2-dimethyl-1,3-dioxolane. In the case of the tetrahydrofuran and dioxane complexes, the cleavage of an ether C-O bond was not observed.[32] These findings show that such molybdenum complexes interact in a defined manner with oxygen heterocycles, and prompted us to investigate whether the same (**2a**–**c**) or related complexes (**1a**, **3a, 4a-c**) are suitable systems for studying the ring opening polymerization (ROP) of trioxane (Chart 1). Due to the different substitution patterns of the cyclopentadienyl rings these complexes differ in their Lewis acidity. Also the influence of various weakly coordinating anions was taken into consideration.



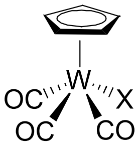
1a



2a-c



3a



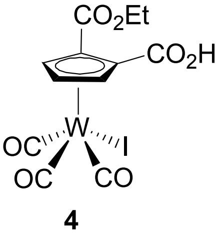
4a-c

a: X = F_3CSO_3; **b**: X = F_3CCO_2; **c:** X = BF_4

Chart 1. Differently substituted η^5-cyclopentadienylmolybdenum and –tungsten complexes.

2.1. Synthesis and Characterization of the Molybdenum- and Tungsten Complexes

The molybdenum- and tungsten complexes were prepared as described in the literature, [28,29,31,33] except for **3a** which has been made accessible by somewhat modified standard methods. [34] It was obtained as a bordeaux red solid, sensitive to aerial oxygen and readily soluble in polar to medium polar organic solvents. To the best of our knowledge until hitherto no structural information of complexes of the type **1a**, **2a**-**c**, **3a**, and **4a**-**c** are available. To get insight into the molecular motif, **2a** (Chart 1) and the intermediate complex **4** (Chart 2) were chosen for an X-ray structural investigation. In Table 1 and 2 selected bond distances and bond angles of the piano stool complexes **2a** and **4** are summarized. The corresponding ORTEP plot of **2a** with atom labeling is depicted in Figure 1. Two independent molecules are found in the triclinic unit cell. In agreement with the weak coordination of the trifluoromethane sulfonate anion to the central molybdenum atom a slightly longer Mo-O distance (2.212(2) Å) was established compared to a standard Mo-O single bond with bond length of 2.138 and 2.194 Å as in the molybdenum acetylacetonato complex.[35] The distance between the cyclopentadienyl centroid and molybdenum (1.987 Å) differs not significantly from other molybdenum(II) complexes such as $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (2.012 Å).



4

Chart 2. Tungsten iodo complex **4**.

$[(\eta^5\text{-}C_5H_3(CO_2C_2H_5)_2)W(CO)_3I]$ which is an intermediate product for the preparation of $[(\eta^5\text{-}C_5H_3(CO_2C_2H_5)_2)W(CO)_3OTf]$ (**4d**) is available from $[C_5H_3(COOC_2H_5)_2W(CO)_3]Na$ and iodine at room temperature. Complex **4** was obtained by adventitious hydrolysis of $[(\eta^5\text{-}C_5H_3(CO_2C_2H_5)_2)W(CO)_3I]$ in dichloromethane within two weeks as orange crystals, sensitive to aerial oxygen and moisture. The structure of **4** (Figure 2) is very similar to that of the piano stool complex **2a**. Four independent molecules of **4** are found in a monoclinic unit cell. A hydrogen bond was established between O(6) and HO(5).

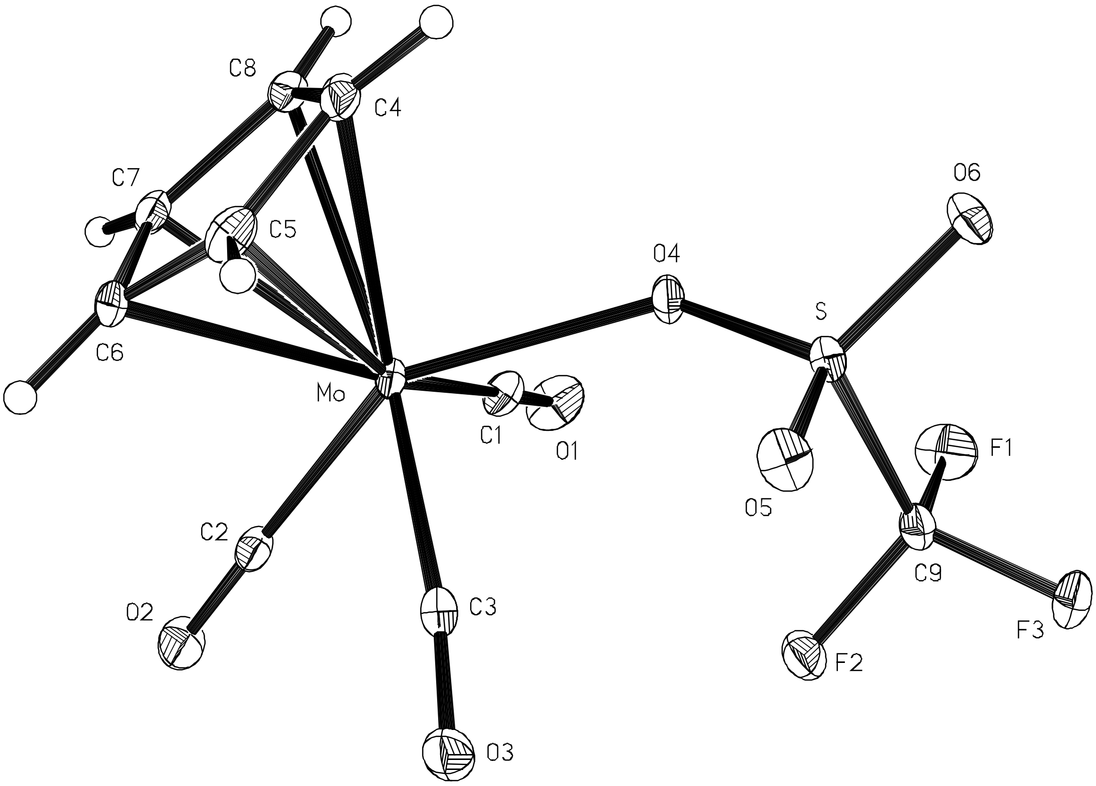

C8
C4
C7
C5
C6
O6
O4
S
Mo
C1
O1
F1
O5
C2
C9
O2
C3
F3
F2
O3

Figure 1. ORTEP plot of **2a** shown at the 20 % probability level.

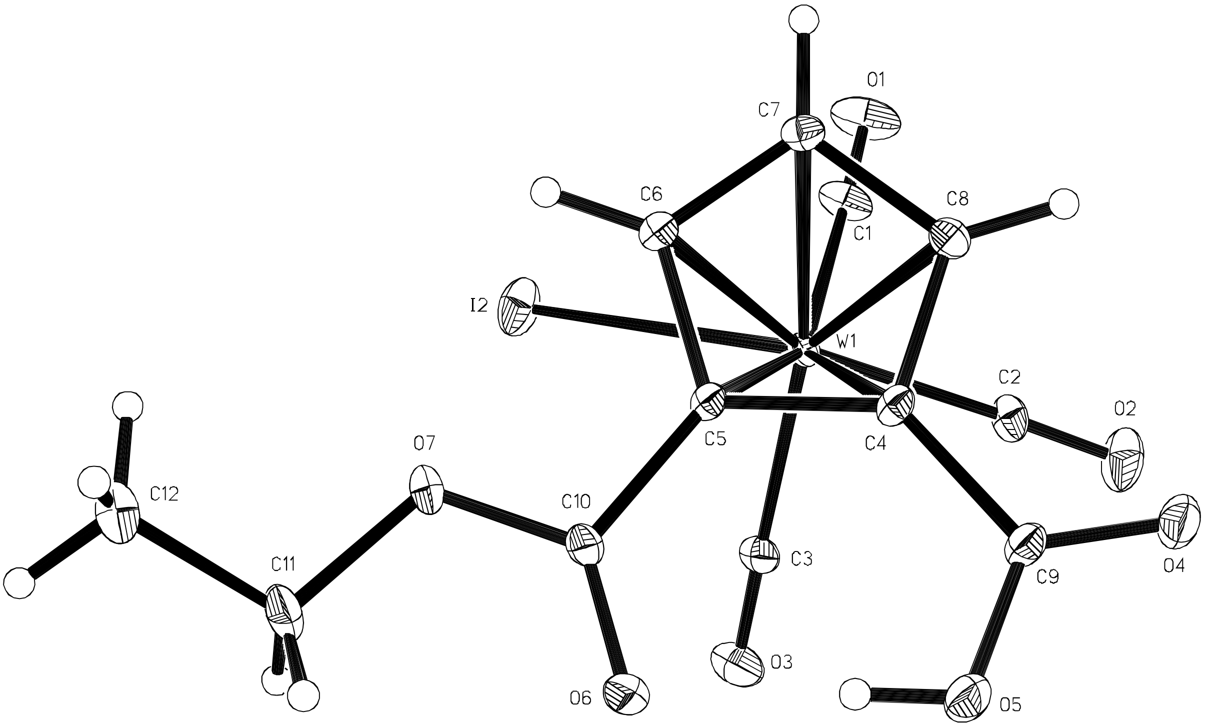

O1
C7
C6
C8
C1
I2
W1
C2
O2
C5
C4
O7
C12
C10
C9
O4
C11
C3
O3
O6
O5

Figure 2. ORTEP plot of **4** shown at the 20 % probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a.

	2a
Mo-C(2)	1.989(3)
Mo-C(3)	2.020(3)
Mo-C(1)	2.060(3)
Mo-O(4)	2.212(2)
O(1)-C(1)	1.113(4)
O(2)-C(2)	1.145(4)
O(3)-C(3)	1.136(4)
S-O(4)-Mo	136.62(13)
O(1)-C(1)-Mo	178.6(3)
O(2)-C(2)-Mo	178.9(3)
O(3)-C(3)-Mo	172.9(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4.

	4
W(1)-C(2)	1.995(8)
W(1)-C(3)	2.030(8)
W(1)-C(1)	2.033(8)
W(1)-I(2)	2.8274(6)
O(1)-C(1)	1.102(11)
O(2)-C(2)	1.117(10)
O(3)-C(3)	1.121(10)
O(4)-C(9)	1.193(10)
O(5)-C(9)	1.319(10)
O(6)-C(10)	1.205(11)
O(7)-C(10)	1.316(9)
O(7)-C(11)	1.459(10)
C(4)-C(9)	1.493(9)
C(10)-O(7)-C(11)	117.6(7)
O(1)-C(1)-W	174.8(8)
O(2)-C(2)-W	177.2(8)
O(3)-C(3)-W	178.1(8)

2.2. Initiation of the Polymerization of 1,3,5-Trioxane with Catalysts 1a, 2a-c, and 3a

Molten trioxane (6 mL, 76.6 mmol) was treated at 80 °C with $1.2 \cdot 10^{-2}$ mmol of the respective catalyst **1a, 2a-c,** and **3a** dissolved in 1 mL of dichloromethane. The induction time, which is the period between the addition of the catalyst and the visible formation of the polymer, varied between seven seconds and 75 minutes. Catalysts **2a** and **3a** were most active, the one with the lowest activity was **2b**. Complexes **1a** and **2c** revealed a medium activity. The induction time increases in the sequence **3a** ~ **2a** < **1a** < **2c** < **2b** (Figure 3), which means that the Lewis acidity of the metal center takes influence on the reaction. The decreasing induction times are congruent with the increasing electron withdrawing effect of

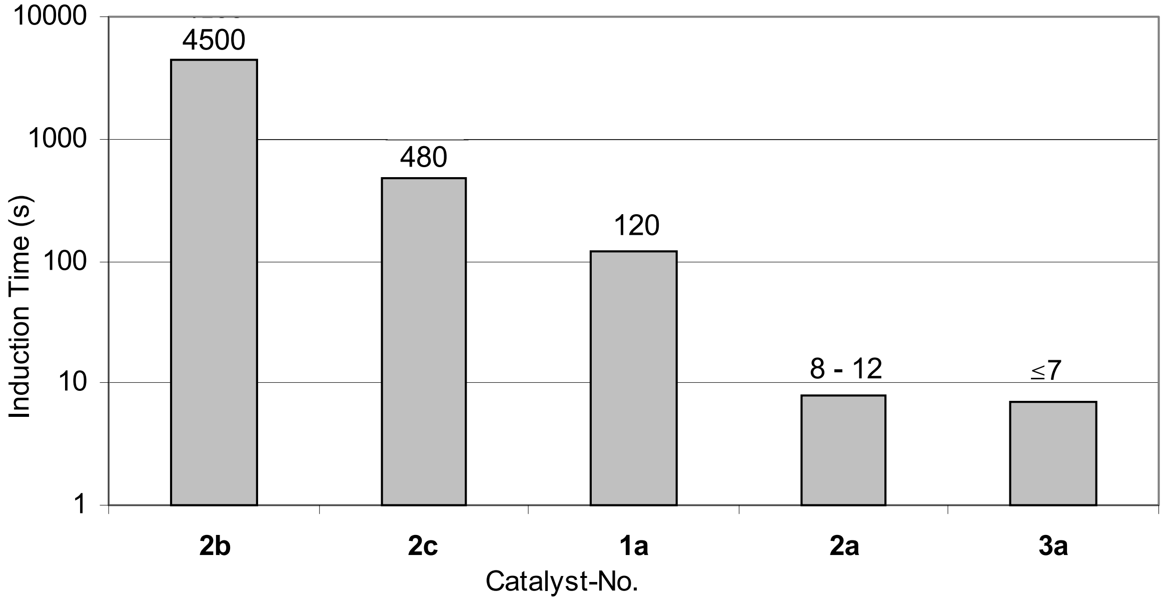


Figure 3. Different activities of catalysts **1a**, **2a-c**, and **3a** in the polymerization of 1,3,5-trioxane at 80 °C (no solvent was used).

the cyclopentadienyl ligands $C_5Me_5 < C_5H_5 < C_5H_4CO_2Me$.[36] In this context the anion also plays an important role as the induction time increases in the series **2a** < **2c** < **2b**. It may thus be anticipated, that in the first step trioxane will – like shown for other oxygen heterocycles – reversibly coordinate to the Lewis acidic metal center, displacing the weakly coordinating anion and probably form a contact or solvent separated ion pair (Scheme 1). The coordination will lead to a charge redistribution in trioxane and eventually induce a polymerization reaction (*vide infra*). Apparently, the opening of the trioxane ring is rate determining and coordination is fast and reversible since the induction time follows the Lewis acidity.

2.3. Polymerization of 1,3,5-Trioxane with Catalysts 4a-c

Molten trioxane (6 mL, 76.6 mmol) was treated at 65 °C with $3.05 \cdot 10^{-2}$ mmol of **4a**, $6.82 \cdot 10^{-2}$ mmol of **4b**, and $4.60 \cdot 10^{-2}$ mmol of **4c** dissolved in 1 mL of dichloromethane. The induction times varied between 1.5 and 120 minutes. Catalyst **4a** was most active, **4c** revealed a medium and **4b** a low activity. In this context also the anion plays an important role and the induction time increased in the series **4a** < **4c** < **4b** (Chart 1 and Figure 4).

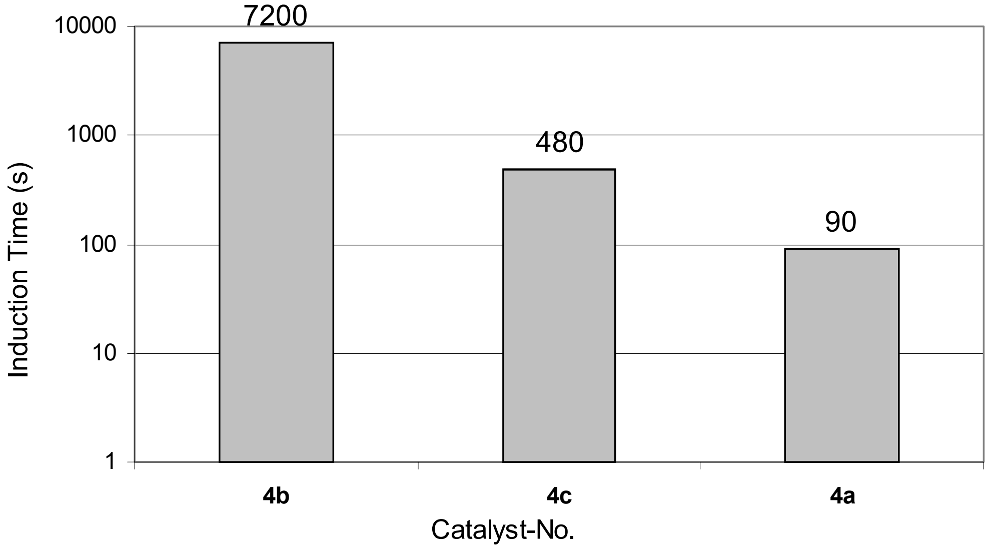


Figure 4. Different activities of catalysts **4a-c** in the polymerization of 1,3,5-trioxane at 65 °C (no solvent was used).

2.4. Formaldehyde in the 1,3,5-Trioxane Polymerization

Complex **2a** was selected to study the polymerization reaction in the presence of formaldehyde. Some decades ago it was elucidated that during the induction period in the polymerization of 1,3,5-trioxane with BF_3 as a catalyst[4,6,11] only formaldehyde and its oligomers are formed. Allegedly a “ceiling concentration” of monomeric formaldehyde is necessary to start the polymerization process (*vide supra*).[6] This was later confirmed by Curioni et al.[11] Furthermore it was found possible to reduce or avoid the induction time by adding a certain amount of gaseous formaldehyde to the reaction mixture prior to the addition of the catalyst. In the present investigation with catalyst **2a** ($1.2 \cdot 10^{-2}$ mmol) the addition of about 4.16 mmol (6.5 mol%) of gaseous formaldehyde to 64 mmol of trioxane resulted in a reduction of the induction time to approximately 1.5 minutes, compared to an induction period of 4 minutes without formaldehyde. The experiments were performed with equal amounts of trioxane and 1,1,2,2-tetrachloroethane as solvent at 80 °C. The observations may be interpreted in terms of an interaction of the molybdenum complex and formaldehyde. Formaldehyde is a much better donor and sterically smaller than trioxane and will coordinate both stronger and faster to Lewis acids, and may even displace coordinated trioxane. Again an ion pair of some kind may be formed (Scheme 1) from which polymerization is initiated. It is conjectured, that the cationic initiator of the type $CpMo(CO)_3OCH_2^+$[anion] is more readily formed than a corresponding complex from trioxane (Scheme 1) and hence polymer formation is observed faster.

To probe whether a copolymerization of 1,3,5-trioxane and evolved formaldehyde (*vide supra*) takes place, a controlled copolymerization was carried out of trioxane and ^{13}C labeled formaldehyde that was generated by thermal decomposition of ^{13}C labeled paraformaldehyde. In this experiment, the formaldehyde gas evolved was fed under the above-mentioned conditions to a mixture of equal amounts of trioxane and tetrachloroethane at 80 °C. The polymer which was obtained after addition of $1.2 \cdot 10^{-2}$ mmol of catalyst **2a** was analyzed by MALDI (Matrix Assisted Laser Desorption Ionisation) and SIMS (Single Ion Mass Spectrometry). Molecular fragments with mass differences of m/z = 30 and 31 Da were obtained, indicating that indeed a copolymer was formed and not two coexisting homopolymers (see Figure 5 and Figure 6). This observation is consistent with the conception that formaldehyde which may be formed in the process is participating in the polymerization of trioxane (Scheme 1).[7]

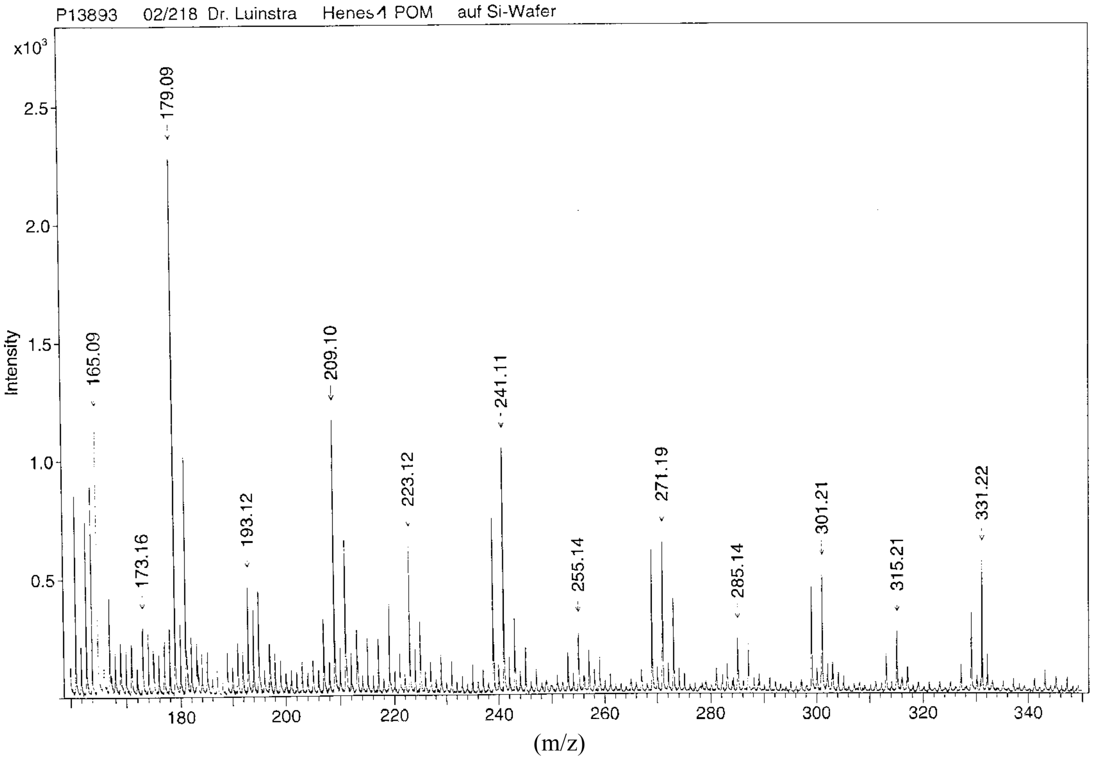


Figure 5. SIMS Spectrum of a Polyoxymethylene Homopolymer.

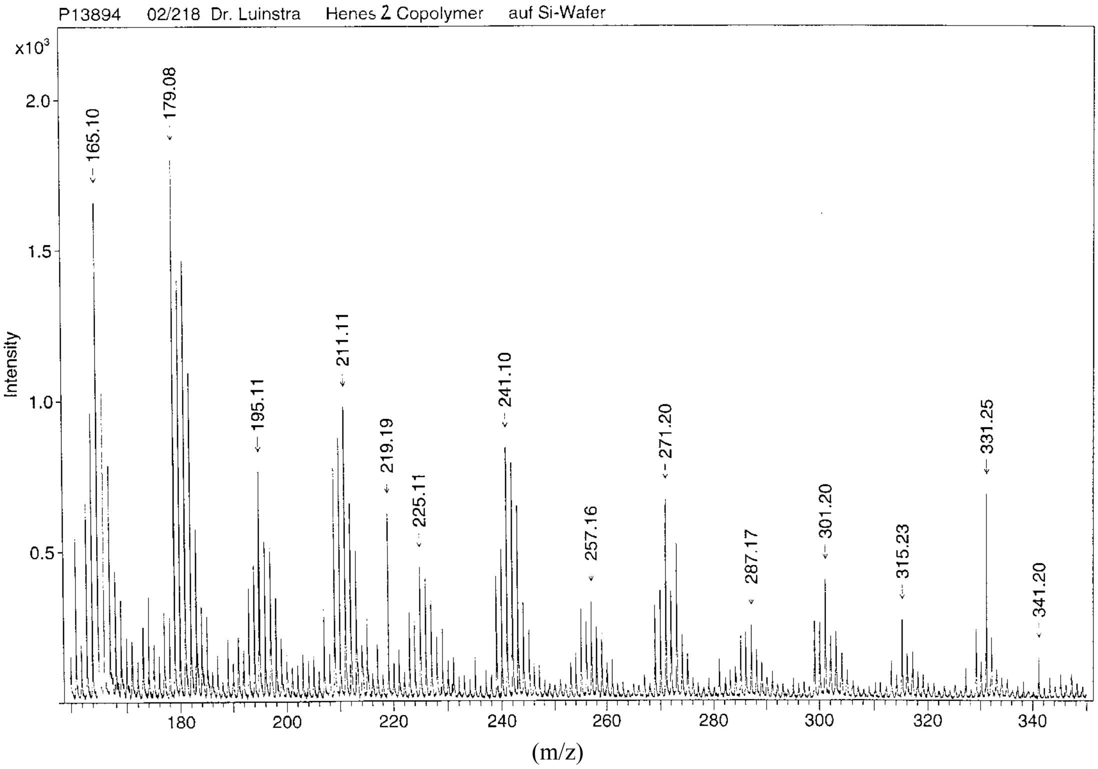


Figure 6. SIMS Spectrum of a ^{12}C Trioxane / $H^{13}CHO$ Copolymer.

To get a further insight into the transition metal catalyzed polymerization of trioxane, ^{1}H NMR spectra of the reaction mixture were recorded at several times at 45 °C using **2a** as catalyst. Conclusive NMR data were obtained if 15.2 mg of trioxane and 40 mg of catalyst **2a** (molecular ratio 1 : 0.60) were dissolved in 0.60 mL of tetrachloroethane. To calibrate the intensities of the ^{1}H NMR resonances during the reaction, which was conducted in an NMR tube at 45 °C, hexamethylbenzene (HMB, 4.5 mg) was present as internal standard. The ratio of the protons in trioxane : **2a** : HMB was 2 : 1 : 1. The first spectrum in Figure 7 (t = 0) shows the above-mentioned solution. Immediately after the addition of the catalyst a weak

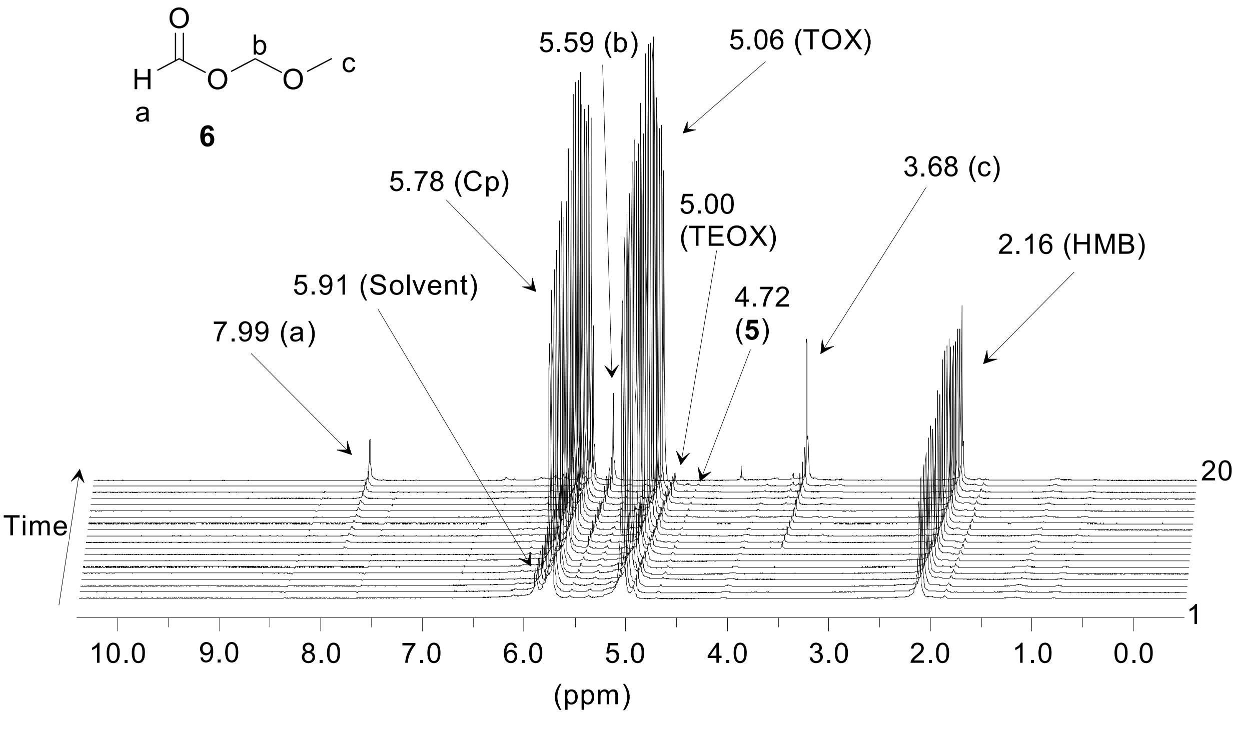


Figure 7. Degradation of 1,3,5-trioxane in the presence of catalyst **2a** monitored ^{1}H NMR spectroscopically. No. of spectra: 1: t = 0; 3: t = 00:01:07; 6: t = 00:03:41; 8: t = 00:05:08; 9: t = 00:59:49; 12: t = 01:18:35; 17: t = 01:40:32; 19: t = 05:52:13; 20: t = 12:55:07.

signal at 5.00 ppm emerges which is attributed to the formation of 1,3,5,7-tetraoxane[5,7,11] (Figure 8, top). At the same time the occurrence of another resonance at 4.72 ppm points to the appearance of polyoxymethylene. The weak intensity of this signal is due to the low solubility of the polyacetal in the used solvent, which leads to partial precipitation of the polymer. Within approximately one hour three further resonances at 7.99, 5.59, and 3.68 ppm appear with steadily increasing intensities. They can unequivocally be

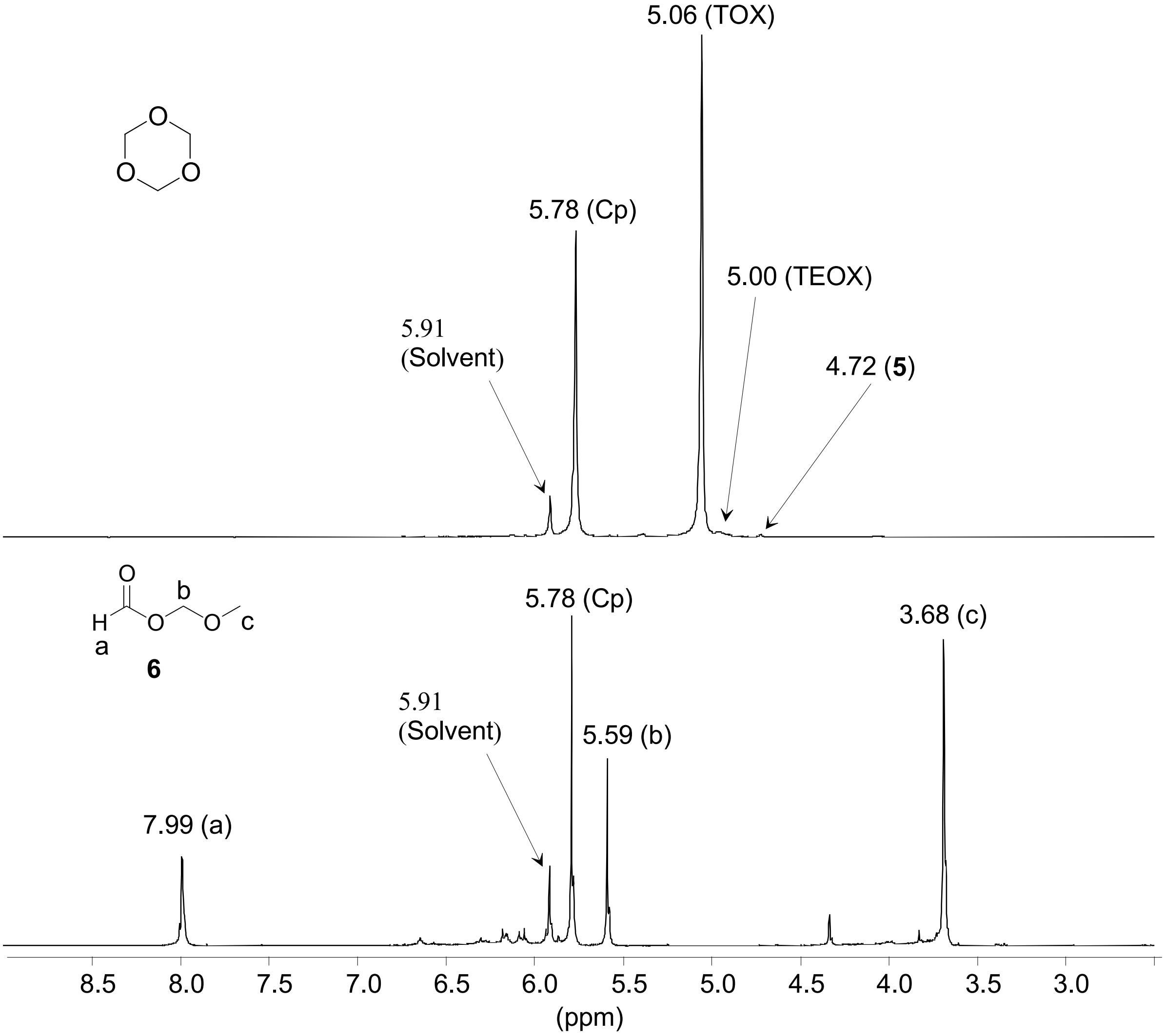
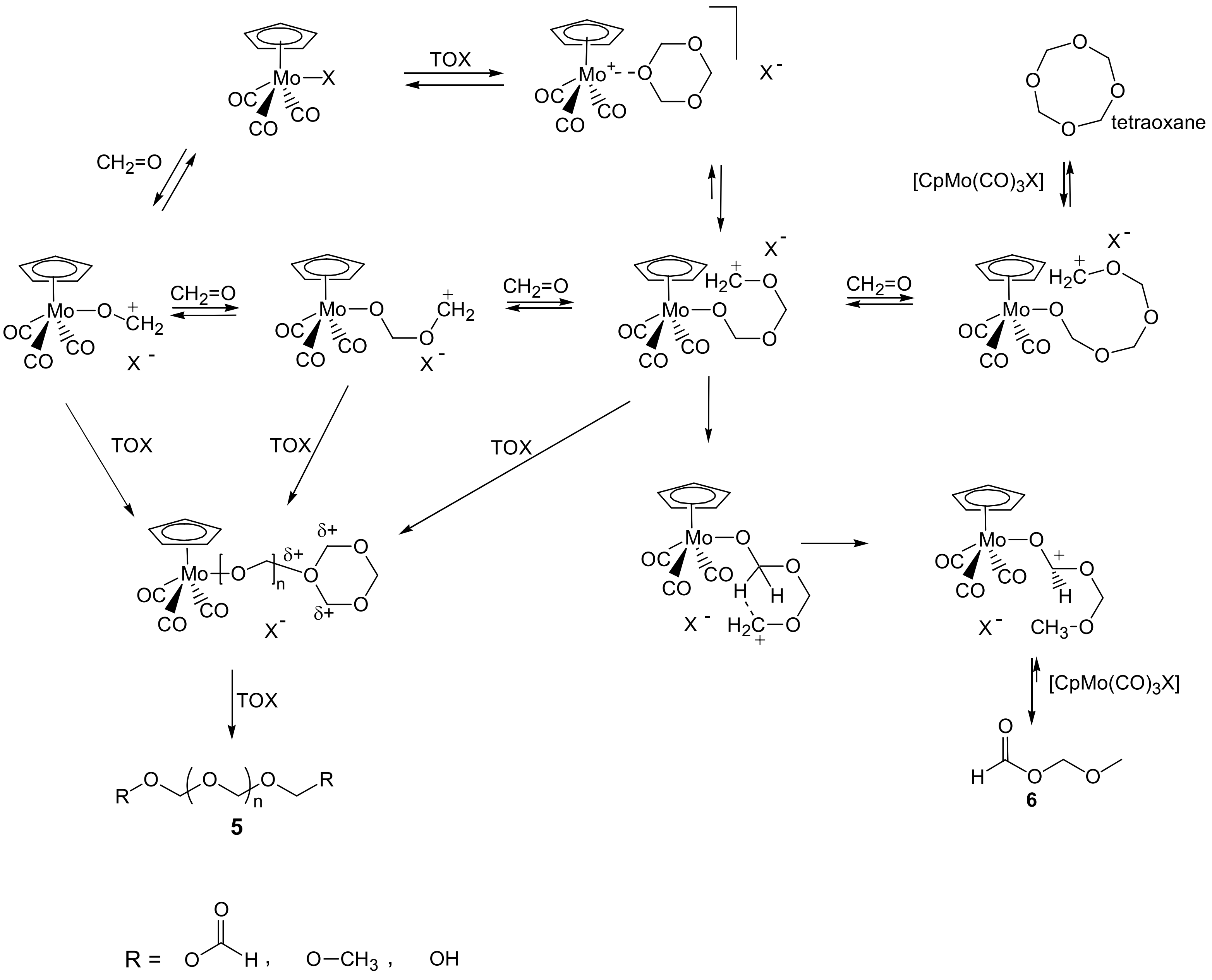


Figure 8. Degradation of 1,3,5-trioxane in the presence of catalyst **2a**, monitored ^{1}H NMR spectroscopically (spectrum 1: top; spectrum 20: bottom).

assigned to methoxymethyl formate (**6**). Its verification succeeded by the measurement of an authentic sample, which was synthesized through reaction of $ClCH_2OCH_3$ with HCO_2Na.[37] After roughly 13 hours trioxane and intermediary formed tetraoxane were consumed and only the signals of methoxymethyl formate, the solvent, HMB, and the catalyst remained (Figure 8, bottom).

Like discussed above, the transition metal catalyzed polymerization of 1,3,5-trioxane is supposed to start as described in Scheme 1. It is proposed, that in a first step trioxane is attacked by complex **2a** with replacement of the triflate anion.[32] A molybdenum-trioxane complex must be very short-lived and can not be isolated or spectroscopically detected (Scheme 1). Subsequently, it is assumed that a carbon-oxygen bond cleavage takes place leading to a carbocationic oxymethylene chain. From this end, formaldehyde may be liberated via a mesomeric oxonium form $CpMo(CO)_3OCH_2OCH_2O^+{=}CH_2$. In a further reaction, this formaldehyde may react with another ring opened cationic trioxane entity to form a cationic formaldehyde tetramer that subsequently may undergo a cyclization to tetraoxane,[7] which is ^1H NMR spectroscopically detected (it is unclear if larger rings are also formed in the process as NMR properties may be very similar).[38] Thus polyoxymethylene (**5**) is formed either from trioxane or tetraoxane (or homologues) in the presence of formaldehyde. The reason that in the course of the ^1H NMR monitoring of the reaction no formaldehyde was observed at 9.6 ppm is easily explained by its high reactivity under the existing reaction conditions. It is immediately consumed in the progressing polymerization (*vide supra*). Also, if the steady state concentration arrived at 0.060 mol/L,[6] NMR observation is not to be expected. Scheme 1 reflects also the formation of methoxymethyl formate (**6**) as a by-product. This side reaction proceeds much slower than the polymerization leading to the thermodynamically more stable redox isomer of trioxane. Of course, this reaction directly finds its equivalence in the polymerization process as described in the introduction, it is a Cannizzaro reaction. The


TOX
tetraoxane
CH2=O
[CpMo(CO)3X]
TOX
5
6
R = O-C(O)H , O−CH3 , OH

Scheme 1.

preferential formation of **6** in the molybdenum-based polymerization is attributed to a metal mediated transformation: a 1,5-hydride shift.[4,12-14,39] The formation of methoxy groups from trioxane was also inferred by other authors.[40] The molybdenum fragment here may stabilize the transition state, lowering the activation energy for this reaction pathway in contrast to the 'free cationic' trioxane polymerization induced by Brœnstedt acids.

2.5. Behavior of Methoxymethyl Formate (6) Toward Catalyst 2a

The monitoring of the trioxane polymerization by ^{1}H NMR spectroscopy over a prolonged period (> 11 hours) showed, that the ^{1}H signal at 5.59 ppm of **6** is losing part of its intensity. This observation led to the question, whether methoxymethyl formate (**6**) is stable under the polymerization reaction conditions. To address this matter a time-dependent ^{1}H NMR spectroscopic investigation of the degradation of **6** was undertaken. For that purpose 14 µL (15.2 mg, $1.69 \cdot 10^{-1}$ mmol) of **6** was dissolved in 0.5 mL of 1,1,2,2-tetrachloroethane to which solutions of 4.5 mg ($2.77 \cdot 10^{-2}$ mmol) of HMB as well as 40 mg ($1.01 \cdot 10^{-1}$ mmol) of catalyst **2a** dissolved in 0.1 mL of 1,1,2,2-tetrachloroethane were added. The reaction was conducted in an NMR tube at 45 °C. The proton signals showed an initial ratio of **6** : **2a** : HMB = 2 : 1 : 1. Beginning with spectrum 1 (Figure 9) two new resonances with increasing intensities occur at 7.95 and 3.62 ppm (see Figure 10, top). These arise at the expense of the signals at δ = 8.02, 5.18 and 3.37 ppm (**6**). The new resonances are ascribed to the protons of the formyl and methoxy groups of methyl formate (**7**) which has been formed. Another new resonance at 4.72 ppm is assigned to polyoxymethylene (**5**). After approximately four hours the degradation of **6** was nearly complete and in Figure 11, bottom, essentially the resonances of methyl formate (**7**), **2a**, and tetraoxane are found. In addition small resonances of the starting material **6** and the polyacetal **5** are visible. To corroborate these findings ^{13}C labeled methoxymethyl formate (**6**), which was synthesized by reaction of $H^{13}C(O)ONa$ with $ClCH_2OCH_3$, was catalytically degraded with **2a**. The $^{13}C{=}O$ group quantitatively reappeared

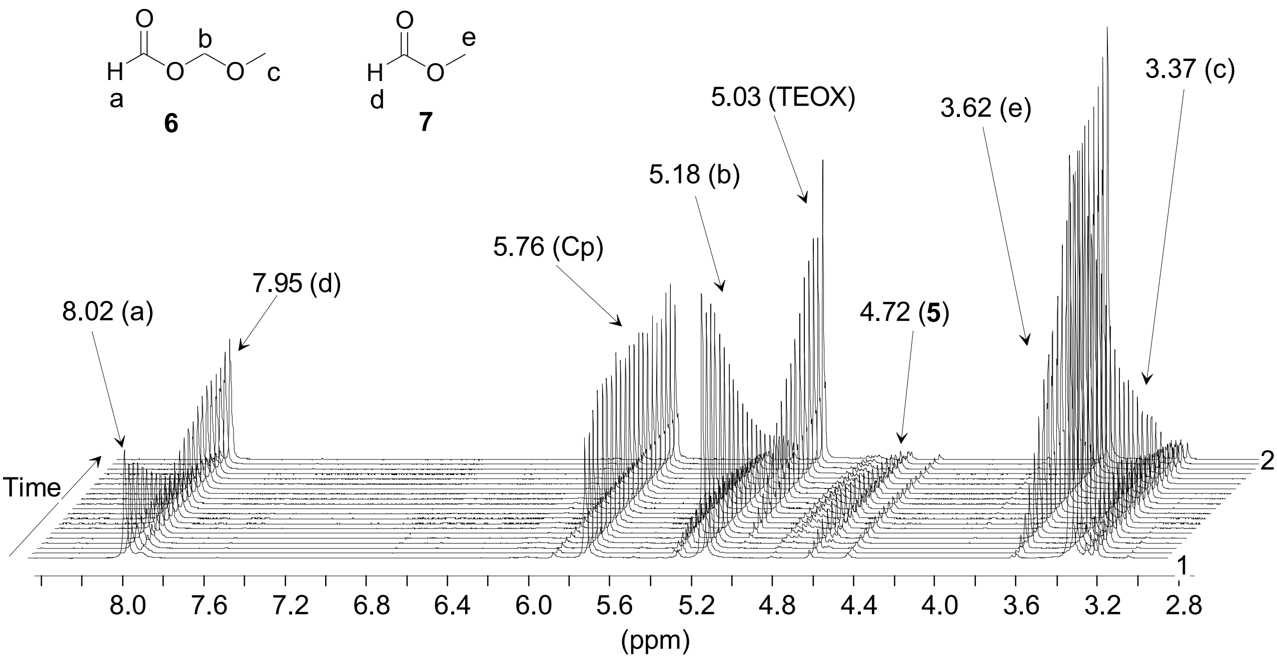


Figure 9. Degradation of methoxymethyl formate (**6**) in the presence of catalyst **2a** monitored ^1H NMR spectroscopically. No. of spectra: 1: t = 0; 2: t = 0:11:36; 4: t = 0:20:48; 6: t = 0:41:34; 8: t = 1:02:22; 10: t = 1:23:09; 12: t = 1:43:57; 14: t = 2:04:44; 16: t = 2:25:31; 18: t = 2:46:18; 20: t = 3:47:06.

in methyl formate (**6**) (Figure 11). In its ^1H NMR spectrum (in 1,1,2,2-$C_2D_2Cl_4$) a doublet at 7.94 ppm is assigned to the HCO function with a coupling constant of $^1J_{CH}$ = 227 Hz. A further doublet at 3.61 ppm with $^3J_{CH}$ = 4.08 Hz is attributed to the protons of the OCH_3 substituent. A retro Cannizzaro reaction does not take place. The low yield of approximately 30 % of polymer **5** obtained from methoxymethyl formate (**6**) is explained by the fact that two thirds of molecule **6** are needed to form **7** (Scheme 2). The decomposition of **6** under the action of catalyst **2a** results from an electrophilic attack at the carboxylate oxygen atom in **6** resulting in the cleavage of the vicinal C-O bond. As a consequence a carbocation and a HC(O)O[M] fragment are formed. Subsequently a CH_3^+ transfer from the carbocation to HC(O)O[Mo] takes place leaving formaldehyde and $[Mo]^+$. On this occasion methyl formate (**7**) is formed.

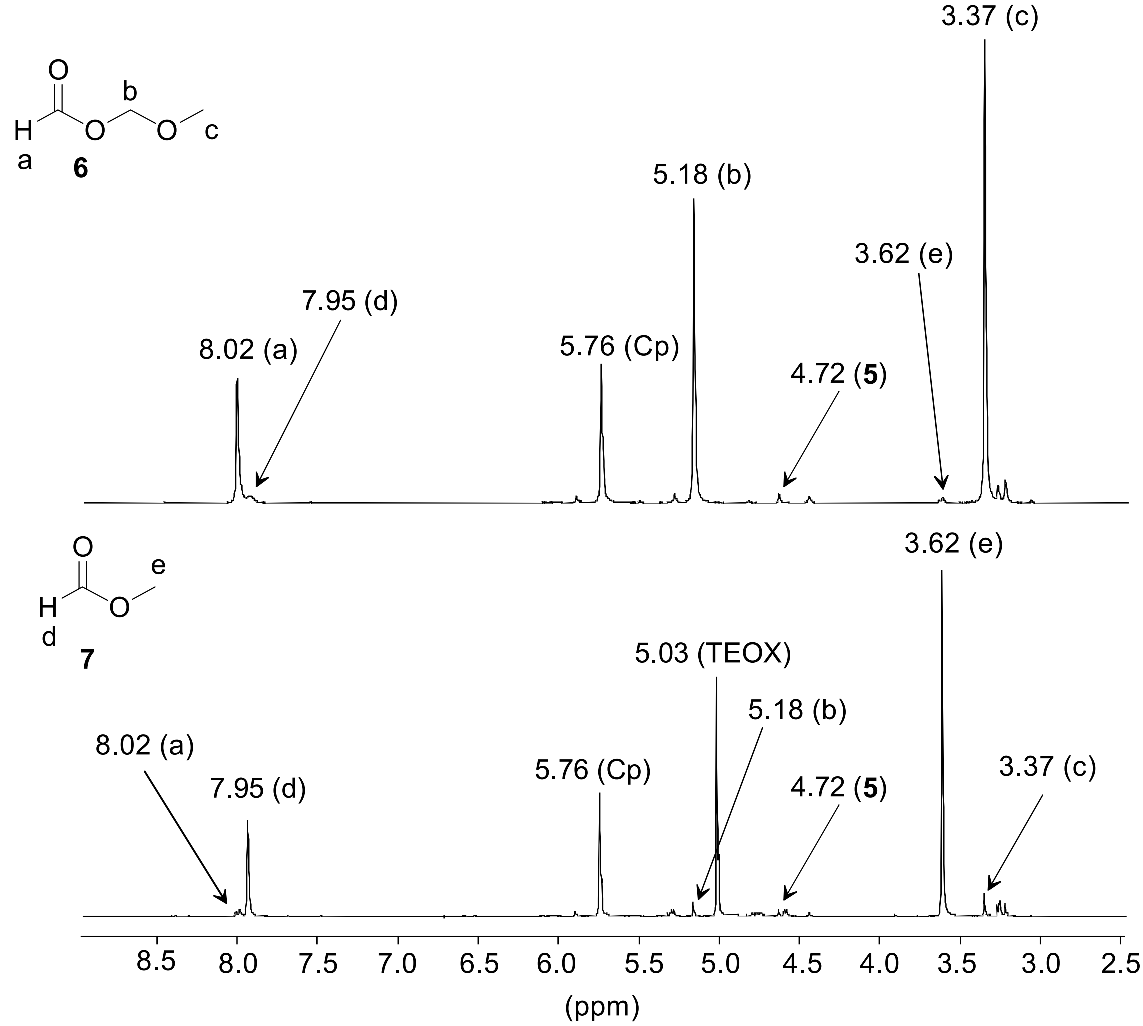


Figure 10. Degradation of methoxymethyl formate (**6**) in the presence of catalyst **2a**, monitored ^1H NMR spectroscopically (spectrum 1: top; spectrum 21: bottom).

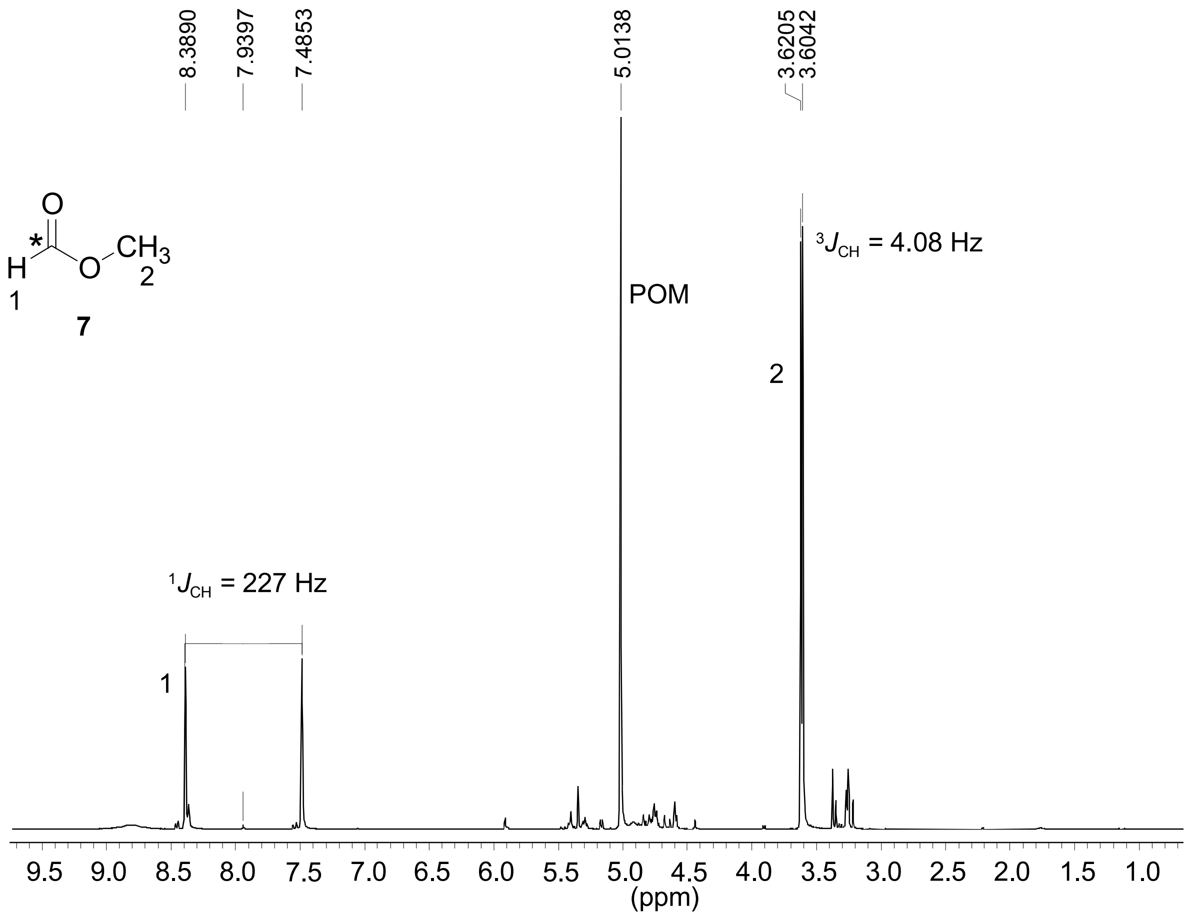
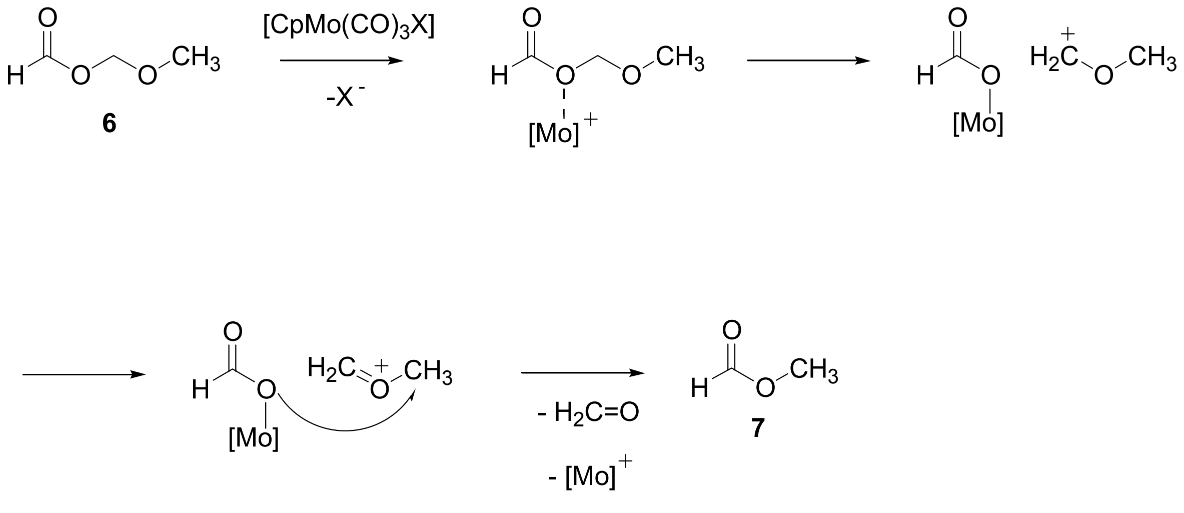


Figure 11. ^{1}H NMR Spectrum of the ^{13}C labeled Degradation Product Methylformate (**7**).



Scheme 2.

2.6. Characterization of the Polyacetal

Polymer **5** was obtained as a colorless solid. It is hardly soluble in any common solvents except for 1,1,1,3,3,3-hexafluoro-2-propanol in which GPC measurements were performed. Due to its low solubility, solid state ^{13}C CP/MAS experiments were carried out instead of solution spectroscopy. The spectra revealed a major component with a chemical shift of 88 ppm and a minor component at 161 ppm. On the basis of their isotropic ^{13}C chemical shift, the major component is assigned to methylene groups in the crystalline trigonal phase of POM.[41] This assignment is supported by the ^{13}C spin-lattice relaxation time, T_1 = 25 s,[42] the proton-carbon cross-relaxation time, T_{CH} = 0.23 ms,[43] and the principal components of the carbon chemical shift tensor, δ_{11} = 113(2) ppm, δ_{22} = 85(2) ppm, δ_{33} = 68(2) ppm.[44] The minor component with a chemical shift of 161 ppm has so far not been observed in ^{13}C NMR spectra of POM. A NQS (non-quaternary suppression) ^{13}C NMR experiment indicates that this carbon species is directly bonded to protons, with a longer cross-relaxation time of T_{CH} = 0.40 ms. Given that the carbon chemical shift tensor, $d_{11} = d_{22}$

= 254(2) ppm, d_{33} = 115(2) ppm, is typical of ester groups,[45] it is concluded that this component results from formyl end groups. This is to our knowledge the first time, that such end groups were detected in the polymer itself.

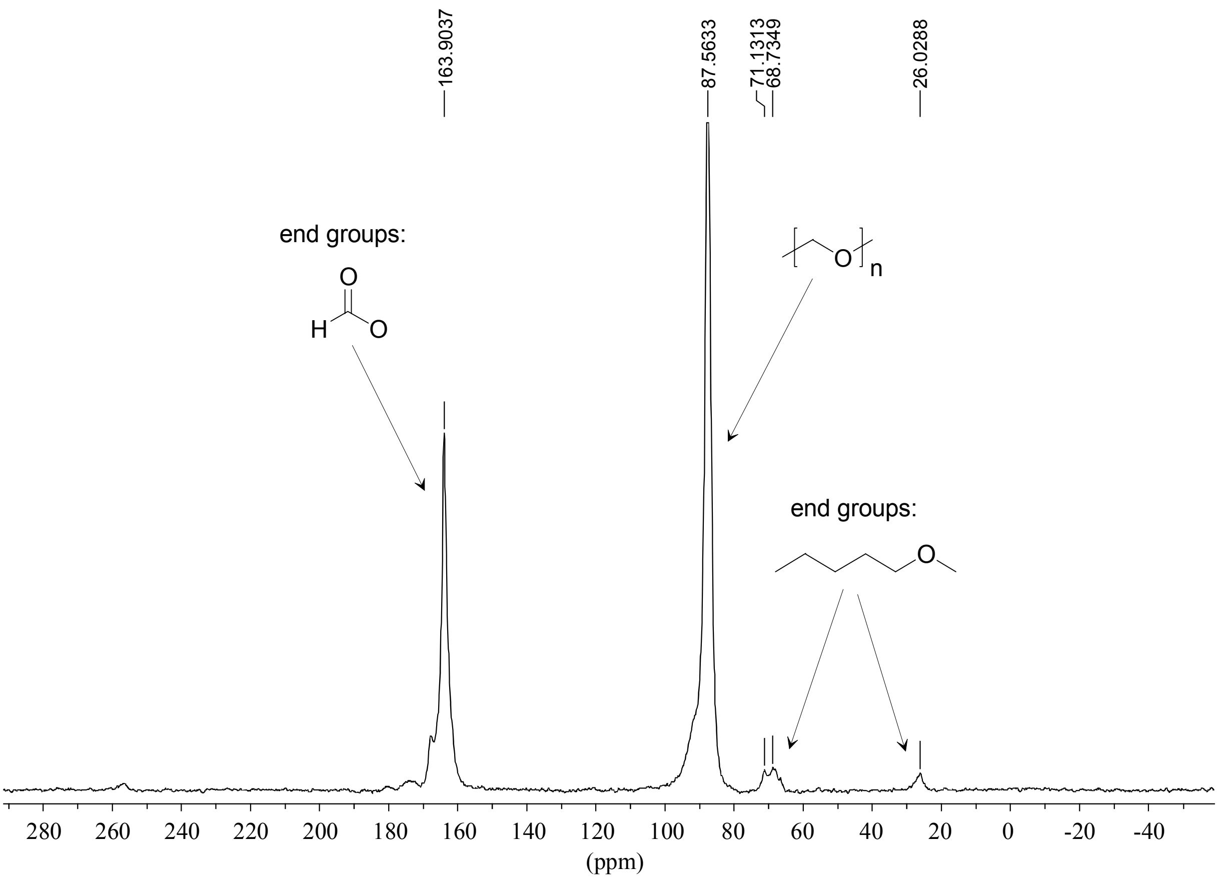


Figure 12. ^{13}C CP/MAS NMR Spectrum of a Trioxane / Dioxepane Copolymer.

To assess the reproducibility of the synthesis of polyoxymethylene (**5**) six runs were performed under the same conditions (see Figure 3; trioxane: 76.6 mmol; catalyst **2a**: $1.2 \cdot 10^{-2}$ mmol; no solvent; t = 80 °C). The induction times varied between 8 and 12 seconds and the turnover numbers were in between 3390 and 4335 (Table 3). After washing with water and acetone and drying at 70 °C polymer yields were found up to 72 %. Molecular masses M_w were in the range between 38200 and 46900 g/mol. To determine the end groups of the polymer chain one of the polymers was subjected to a MALDI investigation. It was found that mainly formyl, hydroxy, and methoxy functions are present. An explanation follows from the consideration of Scheme 1.

Table 3. Selected Data of the Polymerization of 1,3,5-Trioxane with Catalyst 2a.

run	M_w[a] (g/mol)	M_n[a] (g/mol)	M_w/M_n	induction time (s)	yield[b] (g) [%]	TON[c]
1	44400	22800	1.95	11	3.88 [56]	3390
2	38200	20100	1.90	10	4.95 [72]	4335
3	43400	22200	1.95	8	4.00 [58]	3468
4	41800	22400	1.87	12	4.75 [69]	4178
5	46900	23200	2.02	8	4.39 [64]	3862
6	41300	22600	1.83	9	4.69 [68]	4099

[a] Determined by GPC (M_W = weight average molecular weight, M_n = number average molecular weight), [b] Sublimation temperature >175 °C. [c] TON = mol(polymer) / mol(catalyst).

2.7. Influence of Water in 1,3,5-Trioxane on the Polymerization

Since trioxane is prepared from formalin (aqueous formaldehyde) and a rather tedious procedure is applied to arrive at the purity that is necessary for a cationic polymerization, it is of interest to investigate the tolerance of transition metal catalysts in the trioxane (and formalin) polymerization toward water and relate this to that of classical Lewis acids like BF_3. Cationic processes are very sensitive to active proton containing substances. Therefore, experiments were performed to gain insight into the matter whether transition metal complexes of the type $CpMo(CO)_3X$ can polymerize trioxane in the presence of water and thus circumvent a tedious monomer purification procedure. In these investigations, various amounts of water were added to 6 mL of molten trioxane at 80 °C, after which $1.2 \cdot 10^{-2}$ mmol ($1.57 \cdot 10^{-4}$ mol%) of catalyst **2a** was added and the induction time was determined (Figure 13). Up to an amount of 2.18 mol% of water (referred to trioxane) no major change of the

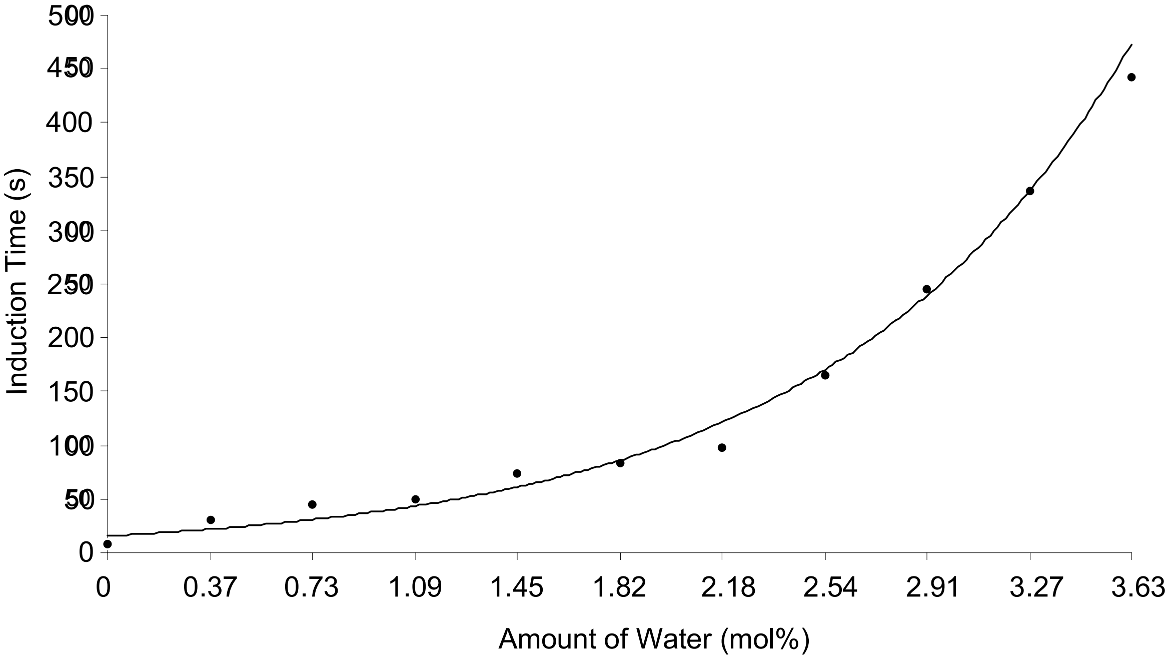


Figure 13. Induction times of the ROP of 1,3,5-trioxane in the presence of different amounts of water using **2a** as catalyst (no solvent was used).

induction time was observed. At higher concentrations of water, a considerable increase of the induction period was found. In the presence of 3.63 mol% of water the induction time rose to a value of approximately 450 seconds. Above this concentration, a partial decomposition of catalyst **2a** occurred. In contrast to these observations, BF_3 (usually applied as an ether adduct) tolerates much less water and the induction period increases from about 3 to 38 minutes if the amount of water is raised from 0.03 to about 0.8 mol%.[5] Selected data of the polymerization of trioxane are summarized in Table 3. It was however found, that the molecular weight of the polyacetal obtained with **2a** in the presence of water is substantially decreased: M_W = 32400 (without water) compared to M_W = 18700 (with 0.1 mL of water).

2.8. Polymerization of 1,3-Dioxepane with Catalyst 2a

Since it is possible to increase the thermal stability of polyoxymethylene by copolymerizing it with 1,3-dioxepane, it is of further interest to investigate the homopolymer of 1,3-dioxepane. For that purpose 6 mL of 1,3-dioxepane were polymerized at 80 °C with catalyst **2a** ($1.2 \cdot 10^{-2}$ mmol), dissolved in 1 mL of dichloromethane. The induction time was considered as the time until the polymer was formed which is realized by a visible increase of the viscosity. No solid was formed during the polymerization process. Afterwards the polymer was examined by GPC without further purification. Obtained polymers provided molecular weights M_W of about 14000 g/mol. Due to its viscosity even at room temperature, the homopolymer of 1,3-dioxepane is not comparable in its properties with the homopolymer of trioxane and in pure form unusable for technical applications.

In the investigation of the polymerization of 1,3-dioxepane also time-dependent ^{1}H NMR studies were performed at 22 °C. For this purpose 38.4 mg ($9.74 \cdot 10^{-2}$ mmol) of catalyst **2a** were dissolved in 450 µL of acetone-d_6. To this solution 50 µL of 1,3-dioxepane ($4.92 \cdot 10^{-2}$ mmol) were added, providing a molar ratio of 2 : 1. The sample was measured ^{1}H NMR spectroscopically for approximately 80 min (Figure 14). In the first spectrum (t = 0) the signals of 1,3-dioxepane are observed at 4.60, 3.60, and at 1.54 ppm. Furthermore the ^{1}H Cp resonance at 6.21 ppm is visible. In the second spectrum (t = 9 min) the beginning polymerization accounts for the emerging of two new signals at 4.55 and 3.5 ppm which are assigned to polydioxepane. Between spectrum 3 (t = 21 min) and spectrum 5 (t = 44 min) the intensities of these new signals increase at the expense of those of the monomeric dioxepane. After 80 min (spectrum 6) a shoulder at 1.3 ppm emerges which is assigned to the $OCH_2C\mathit{H}_2$ group of the polymer.

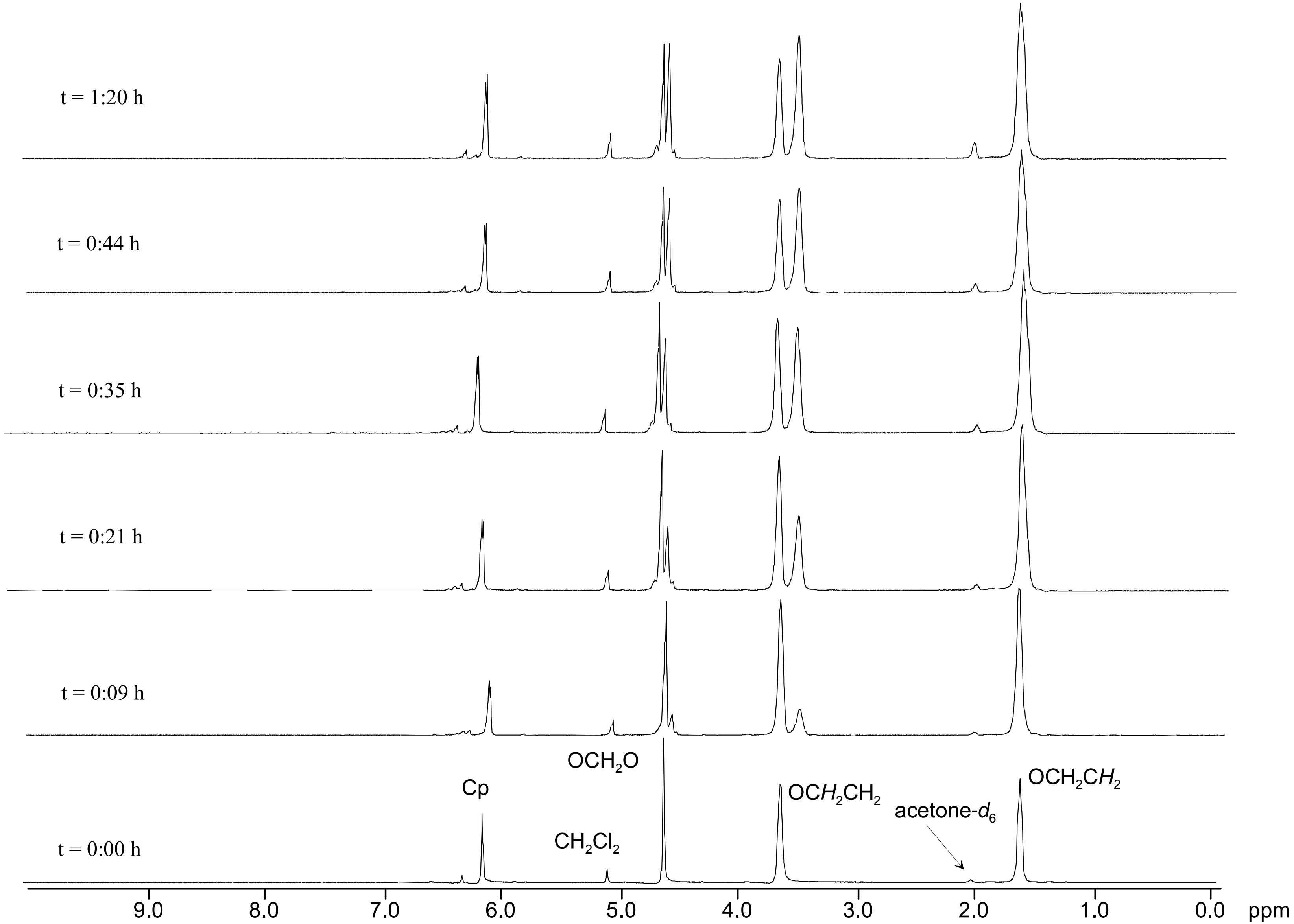


Figure 14. Time-dependent ^{1}H NMR spectroscopic investigation of the polymerization of 1,3-dioxepane with catalyst **2a** at 22 °C.

2.9. Polymerization of 1,3-Dioxepane with Catalyst 2a in the Presence of Water

To probe whether the presence of water takes influence on the polymerization process of 1,3-dioxepane, a time-dependent ^{1}H NMR spectroscopic investigation of the polymerization of water-saturated 1,3-dioxepane with catalyst **2a** was performed. According to the integration of the NMR signals the mixture consisted of 76.6 % of 1,3-dioxepane, 16.6 % of water and 6.8 % of dichloromethane. If this mixture is added to a solution of catalyst **2a** (38.4 mg, $9.74 \cdot 10^{-2}$ mmol) in 50 µL of acetone-d_6 a shift of the water resonance to 3.3 ppm is observed, whereas this signal appears at 2.85 ppm when no catalyst is present. Possibly a water complex with catalyst **2a** is formed. As the reaction proceeds the water resonance is shifted gradually to lower field (Figure 15). It can not be excluded that the change of the pH due to the addition of the strong Lewis acid causes the down-field shift of the H_2O resonance. At the end of the reaction (spectrum 6, t = 10:49 h) the water signal occurs as a peak of very low intensity at 4.3 ppm.

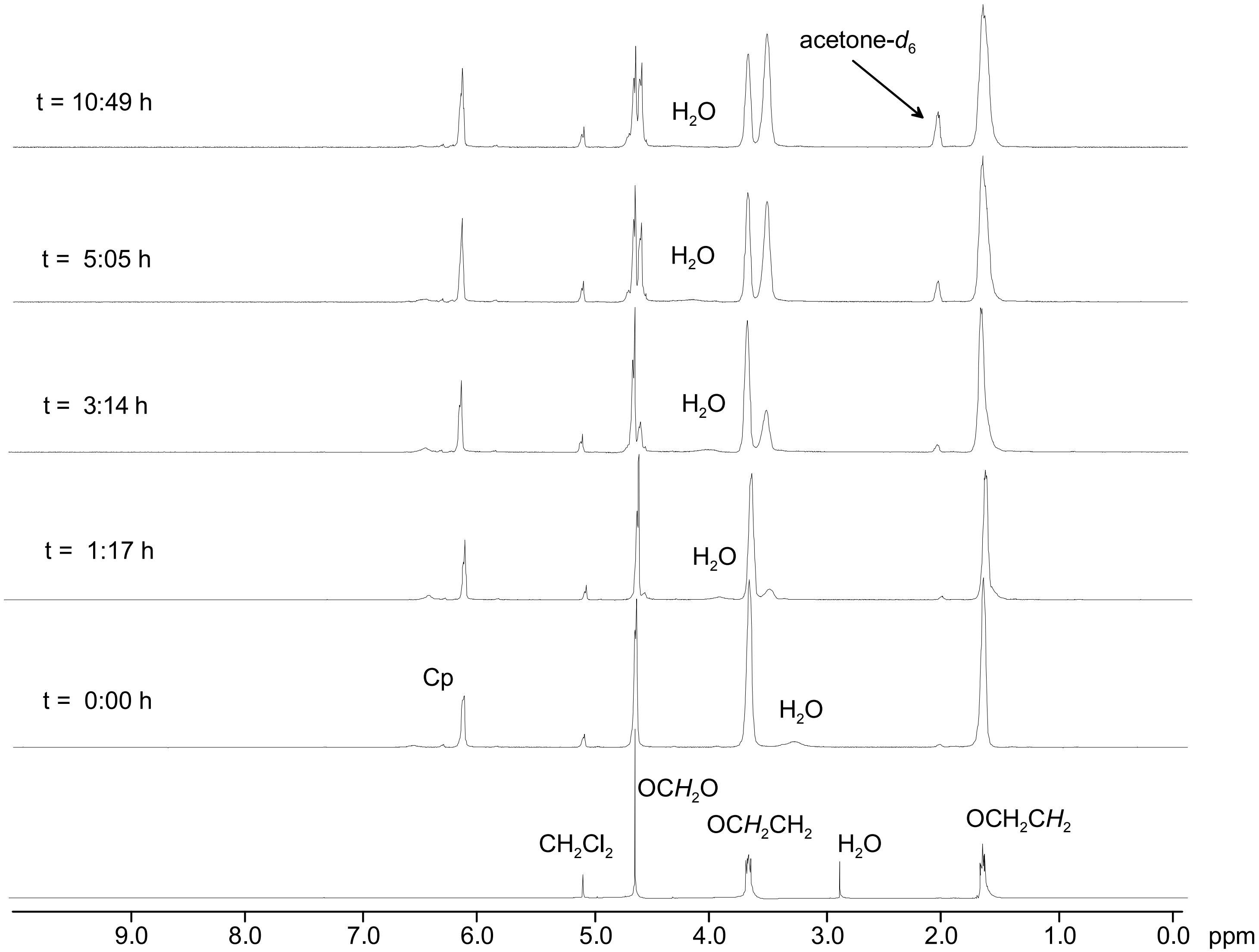


Figure 15. Time-dependent ^{1}H NMR spectroscopic investigation of the polymerization of water-saturated 1,3-dioxepane with **2a** at 22 °C.

2.10. Copolymerization of 1,3,5-Trioxane with 1,3-Dioxepane

Catalyst **2a** is also able to polymerize 1,3-dioxepane.[46] Since the copolymerization of 1,3,5-trioxane with suitable comonomers[47,48] leads to an increased stability of the resulting copolymer compared to pure polyoxymethylene, in a further attempt 1,3,5-trioxane was copolymerized with 1,3-dioxepane. For this purpose, $1.2 \cdot 10^{-2}$ mmol of catalyst **2a** was added to 6 mL (76.6 mmol) of molten trioxane containing 0.180 mL (2.3 mol%) of 1,3-dioxepane at 80 °C. Induction times were measured, which vary between 19 and 24 seconds. The tolerance of **2a** toward water in this copolymerization is comparable to that of the trioxane homopolymerization (*vide supra*) and induction times increase by the same order of magnitude with the water concentration. Samples of the copolymers were subjected to solid state ^{13}C CP/MAS NMR spectroscopic examinations revealing signals at 87 and 160 ppm which are assigned to the carbon atoms of CH_2 functions and HCO end groups, respectively. Other resonances between 71.3 and 66.6 ppm and at 26 ppm with intensities of 3 – 4 % according to contact time variation experiments[45a] point to carbon atoms of the C_4-chain consisting of an internal ethyl moiety and terminal alkoxy entities, respectively. They result from the incorporation of 1,3-dioxepane into the copolymer.

For the post-processing the polymers were heated to approximately 100 °C in 100 mL of an 1 M aqueous Na_2CO_3 solution. Unstable parts of the polymer chain are degraded until at both ends of the chain C_4 units remain resulting from 1,3-dioxepane. Molecular weights measured after treatment with Na_2CO_3 and drying for 1 h at 75 °C are summarized in Table 4. Molecular masses (M_w) of the copolymers were between 21000 and 27000 g/mol. The yields after post-processing of the copolymers with Na_2CO_3 were found up to 64 %. The turnover numbers which are defined as mol (polymer)/mol (catalyst) achieved values of approximately 3900.

Table 4. Selected Data of the Copolymerization of 1,3,5-Trioxane with 1,3-Dioxepane with Catalyst 2a.

run	M_W[a] (g/mol)	M_n[a] (g/mol)	M_w/M_n	induction time (s)	yield[b] (g) [%]	yield[c] (g) [%]	TON[d]
1	21000	9929	2.12	21	6.43 [93]	3.87 [56]	3387
2	21200	10000	2.13	19	6.43 [93]	3.48 [50]	3045
3	23300	15300	1.52	22	6.31 [91]	4.44 [64]	3885
4	27400	17800	1.54	22	6.27 [91]	3.79 [55]	3317
5	23500	15300	1.54	24	6.31 [91]	4.19 [61]	3667

[a] Determined by GPC. [b] Prior to treatment with an aqueous Na_2CO_3 solution. [c] After treatment with an aqueous Na_2CO_3 solution. Melting points: 171 – 172 °C. [d] TON = mol(polymer) / mol(catalyst).

2.11. Polymerization of the Extraction Mixture with Catalysts 2a, 2c, and 4a

A certain amount of the extraction mixture (6 mL) was polymerized with catalysts **2a** (18.7 mg, $4.49 \cdot 10^{-2}$ mmol), **2c** (22.8 mg, $5.48 \cdot 10^{-2}$ mmol), and **4a** (13.0 mg, $3.13 \cdot 10^{-2}$ mmol) at 65 °C. In contrast to the bulk polymerization of trioxane, the polymers obtained from the extraction mixture show an enormous loss of weight of up to 96 % after post-processing with an 1 M aqueous Na_2CO_3 solution. This is not remarkable, because these polymers are not provided with dioxepane-stabilized end groups and can thus be hydrolyzed by aqueous Na_2CO_3. Induction times varied between 30 min and > 4 h. Molecular weights M_W after post-processing were from 8100 to 19200 g/mol.

2.12. Influence of the Temperature on the Polymerization of the Extraction Mixture Using Catalysts 2a and 4a

To get an insight into the dependence of the polymerization of the extraction mixture on the temperature various experiments with catalysts **2a** and **4a** at different temperatures have been performed. Catalyst **2a** is able to polymerize the extraction mixture already at 50 °C however, the induction time was approximately 240 min. The resulting polymer revealed a relatively low loss in weight after post-processing of about 40 % and had a molecular mass of

M_W = 30100 g/mol. Rising the temperature to 65 °C leads to a decrease of the induction period to 30 min. But the loss in weight after post-processing rose to 85 %. Obtained molecular weights M_W were 21000 g/mol. At 80 °C polymerization started after 10 min and at 100 °C even after 5 min. Molecular masses were 10000 (80 °C) and 12700 (100 °C) (Table 5).

Complex **4a** showed a stronger dependence on the temperature. At 50 °C no polymerization takes place, at 65 °C the induction period is more than 4 h, and when the temperature is raised to 80 and 100 °C the polymerization starts after 50 min and 10 min, respectively. The loss in weight of the polymers of approximately 90 % after post-processing is very high, because these polymers are not provided with end-capped chains (*vide supra*).

Table 5. **Selected Data of the Polymerization of the Extraction Mixture with Catalysts 2a and 4a.**

catalyst	T (°C)	catalyst (mmol)	induction time (min)	yield[a] (%)	M_w[b] (g/mol)	M_n[b] (g/mol)	M_w/M_n
2a	50	0.0353	>240	60	30100	11500	2.62
4a	50	0.0313	no polymer	-	-	-	-
2a	65	0.0354	30	15	21700	7000	3.10
4a	65	0.0313	>240	3	19200	7300	2.63
2a	80	0.0353	10	7	10000	3300	2.22
4a	80	0.0313	50	6	9100	2800	3.29
2a	100	0.0353	5	75	12700	6100	2.07
4a	100	0.0313	10	64	19100	7300	2.55

[a] After post-processing. [b] Determined by GPC.

2.13. Influence of the Amount of the Added Solvent on the Polymerization of 1,3,5-Trioxane with Catalyst 2a

To investigate whether the solvent included in the extraction mixture has any influence on the polymerization, various polymerization runs with pure 1,3,5-trioxane were performed to which several amounts of 1,2-dichloroethane (DCE) were added. From Table 6 it can be derived that the induction times even in the presence of 4 mL of solvent are approximately 3 min. This seems to be a normal dilution effect. It is not possible to determine a clear dependency of the molecular weights on the amount of added solvent. Only the yields seem to decrease with increasing amounts of added 1,2-dichloroethane.

Table 6. Selected Data of the Polymerization of Trioxane with Addition of 1,2-Dichloroethane, Using Catalyst 2a.

DCE[a] (mL)	catalyst (mmol)	induction time (s)	yield[b] (%)	M_w[c] (g/mol)	M_n[c] (g/mol)	M_w/M_n
0.0	0.0254	60	73	32400	12900	2.51
0.2	0.0335	60	65	30700	12700	2.42
0.5	0.0264	150	68	28700	12100	2.38
1.0	0.0310	120	69	30100	12100	2.49
2.0	0.0325	165	60	22900	10500	2.17
4.0	0.0289	180	56	28300	12400	2.28

[a] 1,2 Dichloroethane. [b] After post-processing. [c] Determined by GPC.

3. Conclusion

In this investigation it was highlighted that transition metal complexes can serve as mediators for the cationic ROP of 1,3,5-trioxane. As examples cyclopentadienyl molybdenum complexes of different Lewis acidity were employed tolerating considerable more water than classical Lewis acid catalysts like $BF_3 \cdot OEt_2$ or *t*$BuClO_4$. They are less active than iridium or palladium catalysts,[49] but $[(\eta^5\text{-}C_5H_5)Mo(CO)_3OTf]$ (**2a**) proved to be an excellent example to carry out time-dependent ^1H NMR spectroscopic studies to follow the course of the polymerization process. In the polymerization of trioxane it was impossible to completely avoid induction times by adding gaseous formaldehyde, but they were reduced to one half or one third. In contrast to other authors[25] complexes of the mentioned or similar type do not prefer an insertion mechanism, but a transition metal induced cationic polymerization. The entire process of polymerization seems to be similar to that one of classical Lewis acids. In fact, many of the known aspects of the trioxane polymerization could be found in the 'catalysis', some of which are untypical for metal centered reactions. This observation holds for the intermediary occurrence of formaldehyde and tetroxane during the reaction. Time-dependent ^1H NMR spectroscopic investigations point to the formation of several by-products such as methoxymethyl formate (**6**), which is an isomer of 1,3,5-trioxane. It is the first time, that these Cannizzaro-type redox processes were observed directly, finally resulting in the appearance of methyl formate (**7**). Another product of this degradation is POM (**5**). The existence of these by-products is considered as the main difference between the polymerization of 1,3,5-trioxane with classical Lewis acids as catalysts and the mentioned molybdenum complexes.

Time-dependent ^1H NMR investigations on the polymerization of the comonomer 1,3-dioxepane revealed that complex **2a** functions also in this case as a catalyst. A medium molecular mass of about 14000 g/mol was observed. Even a water-saturated 1,3-dioxepane solution can be polymerized with **2a**. It has been noticed that the water ^1H NMR resonance was shifted to lower field during the ^{1}H NMR spectroscopic measurement. The added water only took influence on the induction time of the polymerization. When the polymerization temperature of the extraction mixture is raised, the catalytic activity is increased. This effect seems to be stronger in the case of the tungsten complex **4a**.

Furthermore the influence of added solvent to pure trioxane has been studied. It was shown that with increasing amounts of solvent the induction period did not significantly rise. The actual retardation arises from the water in the extraction mixture which deactivates the catalyst by formation of a molybdenum aqua complex.

4. Experimental Section

4.1. General Comments

All experiments except polymerizations and copolymerizations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried with appropriate reagents, distilled, degassed and stored under argon. 1,3,5-Trioxane was dried with CaH_2 and distilled in a flask that was heated to 70 °C and afterwards stored at 70 °C to prevent resolidification. 1,3,5-Trioxane and 1,3-dioxepane were BASF products. ^{13}C labeled sodium formate, ^{13}C labeled paraformaldehyde, and 1,1,2,2-tetrachloroethane-d_2 were purchased from Deutero GmbH and were used without further purification. Hexamethylbenzene, 1,1,1,3,3,3-hexafluoro-2-propanol, and chlorodimethyl ether were purchased from Aldrich. Methyl formate was obtained from Merck and used without further purification. Complexes **1a**, **2a**-**c**, and $[C_5H_4CO_2CH_3]Na$ were synthesized according to literature methods.[28,29,31,50]

High resolution NMR spectra were recorded on a Bruker DRX 250 spectrometer (field strength 5.87 T) at 296 K if not otherwise mentioned. Frequencies are as follows: ^1H NMR: 250.13 MHz, $^{13}C\{^1H\}$ NMR: 62.90 MHz. Chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. FD mass spectra were taken on a Finnigan MAT 711 A instrument, modified by AMD and reported as mass/charge (*m/z*). CP/MAS solid state NMR spectra were recorded on a Bruker DSX 200 multinuclear spectrometer equipped with a wide bore magnet (field strengths of 4.7 T). Magic angle spinning was applied up to 10 kHz (4 mm ZrO_2 rotors). Frequencies, standards and acquisition parameters: ^{13}C, 50.288 MHz (4.7 T), [TMS, carbonyl resonance of glycine ($\delta = 176.0$) as secondary standard], 90 ° proton pulse length 3.8 μs (B_1 field 65 kHz), contact time T_c 1 ms, recycle delay 2 s. The non-quaternary suppression ^{13}C NMR experiment[51] was carried out using a dephasing delay of 40 μs. Chemical shift anisotropies were determined from analysis of spinning sideband intensities in slow-MAS spectra or for static samples using the programs HBA and WSolids1.[52] GPC measurements were carried out by dissolving 5 mg of the respective polymer or copolymer in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol at 28 °C on a GPC system equipped with a Knaur Column Air-Ofen, a Bischoff HPLC pump Model 2200, a 8 x 300 mm PFG column, a Viscotek Dual Detector Model 250, and Janus GPC software. MALDI spectra were measured with a Bruker Biflex III MALDI spectrometer, SIMS data were obtained from an ION TOF III spectrometer from ION TOF. IR measurements were obtained from a Bruker IFS 48 FT-IR spectrometer, elemental analyses were carried out on a Vario EL (Elementar Analytische Systeme Hanau).

4.2. Synthesis of $[(\eta^5\text{-}C_5H_4CO_2CH_3)Mo(CO)_3CH_3]$

The reaction of $[C_5H_4CO_2CH_3]Na$ (1.56 g, 10.7 mmol) with $Mo(CO)_3(CH_3CN)_3$ (3.253 g, 10.7 mmol) in 80 mL of boiling THF (2d) affords a dark brown product, which was stirred in 50 mL of diethyl ether until an ochre suspension was formed. After filtration (P3) the yellow powder was dried under vacuum. Subsequently the crude product was dissolved in 50 mL of THF and 2.275 g (16.0 mmol) of methyl iodide was added. The mixture was stirred over night at room temperature. All liquid components were removed under reduced pressure and the brown residue was dissolved in 5 mL of a mixture of cyclohexane/dichloromethane 1 : 1 and purified by column chromatography (elution medium: 150 mL of a 1 : 1 mixture of cyclohexane/dichloromethane; short column filled with 2 cm of silica). Removal of the solvent in vacuo yielded 2.35 g (69 %) of an air sensitive brownish yellow powder. ^1H NMR ($CDCl_3$): δ 5.68, 5.31 (s, 4H, C_5H_4), 3.75 (s, 3H, OCH_3), 0.37 (s, 3H, $MoCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 237.8, 225.1 (s, MoCO), 165.2 (s, CpC=O), 98.2, 94.8, 94.5 (s, C_5H_4) 52.5 (s, CH_3). FD-MS: *m/z* 260.0 [M^+], 232.1 [M^+ – CO]. IR (CH_2Cl_2, cm^{-1}): δ (CO) 2018, 1982, 1929. Anal. Calcd for $C_{11}H_{10}MoO_5$: C, 41.53; H, 3.17. Found: C, 41.75; H, 3.10.

4.3. Synthesis of [(η^5-$C_5H_4CO_2CH_3$)$Mo(CO)_3OSO_2CF_3$] (3a)

[(η^5-$C_5H_4CO_2CH_3$)$Mo(CO)_3CH_3$] (2.35 g, 7.4 mmol) was dissolved in 20 mL of CH_2Cl_2 at room temperature. After addition of trifluoromethanesulfonic acid (1.11 g, 7.4 mmol, 0.65 mL) a vigorous formation of methane was observed. The mixture was stirred for 2 h and the solvent was removed under reduced pressure. The product was purified by sublimation of the educt (50 °C) yielding 2.28 g (68 %) of **3a**. ^{1}H NMR ($CDCl_3$): δ 6.12, 5.92 (m, 4H, C_5H_4), 3.76 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 237.0, 223.4 (s, CO), 163.7 (s, CpC=O), 100.1, 97.6 (s, C_5H_4), 53.0 (s, OCH_3). FD-MS: *m/z* 451 [M^+], 424 [M^+ – CO]. IR ($CHCl_3$, cm^{-1}): ν(CO) 2077, 2007, $\nu(C{=}O_{ester})$ 1734. Anal. Calcd for $C_{11}H_7O_8F_3MoS$: C, 29.22; H, 1.56. Found: C, 28.97; H, 1.69.

4.4. General Procedure for the Polymerization of 1,3,5-Trioxane

To 6 mL (76.6 mmol) of molten trioxane which was stirred at 80 °C, the respective catalyst **1a**, **2a** – **c**, or **3a** ($1.2 \cdot 10^{-2}$ mmol), dissolved in 1 mL of dichloromethane, was added. After 10 min the polymer block was grinded and washed with 50 mL of acetone and 50 mL of water and dried at 75 °C for 1 h. In this way purified polymers were analyzed by GPC (Table 3). ^{13}C CP/MAS NMR: δ 163.9 (s, CHO), 87 (s, CH_2). IR (KBr, cm^{-1}): ν(CH) 2984, 2927. Anal. Calcd for $(CH_2O)_n$: C, 40.00; H, 6.71. Found: C, 39.39;[53] H, 6.40.

To probe the tolerance of the catalytic polymerization of 1,3,5-trioxane with **2a** the same procedure has been applied, however the experiments were performed in the presence of different amounts of water (see Figure 13).

4.5. General Procedure for the ^{1}H NMR Spectroscopic Monitoring of the Polymerization of 1,3,5-Trioxane

To a solution of 40 mg (0.101 mmol) **2a** in 0.6 mL of 1,1,2,2-tetrachloroethane 4.5 mg (0.028 mmol) of HMB and 15.2 mg (0.169 mmol) of 1,3,5-trioxane were added. The reaction was followed in a 5 mm NMR tube at 45 °C. Subsequently in certain time intervals ^{1}H NMR spectra were recorded until the reaction was finished after approximately 13 h (Figure 7). ^{1}H NMR data for **6** (1,1,2,2-$C_2D_2Cl_4$): δ 7.99 (s, 1H, HCO), 5.59 (s, 2H, CH_2), 3.68 (s, 3H, CH_3). ^{1}H NMR data for **5** (1,1,2,2-$C_2D_2Cl_4$): δ 4.72 (s, OCH_2O).

4.6. Synthesis of Methoxymethyl Formate (6)

To compare NMR spectroscopic data of methoxymethyl formate (**6**) which was formed during the polymerization of trioxane, an authentic sample of **6** was synthesized by treatment of chlorodimethyl ether (5.3 g, 65.8 mmol) with sodium formate and ^{13}C=O labeled sodium formate, respectively (4.92 g, 72.38 mmol). The mixture was stirred under reflux for 16 h. Methoxymethyl formate was purified by distillation of the mixture (102 °C), yielding 5.21 g (88 %) of **6**. ^{1}H NMR ($CDCl_3$): δ 8.09 (s, 1H, HCO), 5.27 (s, 2H, CH_2), 3.45 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.0 (s, HCO), 90.1 (s, OCH_2O), 57.0 (s, OCH_3). FD-MS: *m/z* 89.1 [M^+]. Anal. Calcd for $C_3H_6O_3$: C, 40.00; H, 6.71. Found: C, 39.23;[53] H, 5.99.

4.7. General Procedure for the ^{1}H NMR Spectroscopic Monitoring of the Degradation of Methoxymethyl Formate (6)

To a mixture of 14 µL (15.2 mg, $1.69 \cdot 10^{-1}$ mmol) of **6** and 40 mg ($1.01 \cdot 10^{-1}$ mmol) of catalyst **2a** in 0.6 mL of 1,1,2,2-tetrachloroethane, 4.5 mg ($2.77 \cdot 10^{-2}$ mmol) of HMB was added. The reaction was followed in a 5 mm NMR tube at 45 °C. Subsequently in certain time intervals ^{1}H NMR spectra were recorded until the reaction was finished after approximately 4 h (Figure 10). ^{1}H NMR data for **5** (1,1,2,2-$C_2D_2Cl_4$): 4.72 (m, CH_2O). ^{1}H NMR data for **7** (1,1,2,2-$C_2D_2Cl_4$): δ 7.95 (s, 1H, HCO), 3.62 (s, 3H, CH_3). ^{1}H NMR data for TEOX (1,1,2,2-$C_2D_2Cl_4$): δ 5.03 (s, 8H, OCH_2O).

4.8. Degradation of Methoxymethyl Formate (6) with Catalyst 2a

To 10.29 g (114.2 mmol) of **6** 5.0 mg ($1.2 \cdot 10^{-2}$ mmol) of **2a** dissolved in 1 mL of dichloromethane was added. The mixture was heated at 80 °C for 4 h. After 1 h the formation of polyoxymethylene (**5**) was observed and the mixture begun to reflux. After cooling to room temperature the suspension was filtered (P3) yielding 91.2 mmol **7** (80 %, referred to **6**) and 24.6 mmol **5** (65 %, referred to **6**). ^{13}C CP/MAS NMR data for **5**: δ 87.8 (s, CH_2). ^{1}H NMR data for **6** (1,1,2,2-$C_2D_2Cl_4$): δ 7.94 (s, 1H, HCO), 3.61 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR data for **7** (1,1,2,2-$C_2D_2Cl_4$): δ 161.9 (s, HCO), 51.3 (s, OCH_3).[54]

4.9. General Procedure for the Copolymerization of 1,3,5-Trioxane with 1,3-Dioxepane

To 6 mL (76.6 mmol) of molten trioxane, which was stirred at 80 °C, 180 µL (2.3 mol%) of 1,3-dioxepane (179 mg, 1.75 mmol) was added. Then catalyst **2a** (5.0 mg, $1.2 \cdot 10^{-2}$ mmol), dissolved in 1 mL of dichloromethane, was added to the mixture. After 10 min the polymer block was grinded and washed with 50 mL of water and acetone each. The obtained powders were suspended in 100 mL of an 1 M aqueous Na_2CO_3 solution and heated under reflux for 16 h. Subsequently the suspensions were filtered (P3) and the residues were washed with 50 mL of water and 50 mL of acetone and dried at 75 °C for 1 h. In this way purified copolymers were analyzed by GPC (Table 4). ^{13}C CP/MAS NMR: δ 163.9 (s, CHO), 87.7 (s, CH_2), 66.6 – 71.3 (m, CH_2), 26.0 (s, CH_3). Anal. Calcd for $[C_{1.01}H_{2.61}O_{0.95}]_n$, (97.7 % of

1,3,5-trioxane, and 2.3 of % 1,3-dioxepane, referred to initial weights): C, 40.40; H, 8.74. Found: C, 40.03; H, 7.18.

4.10. General Procedure for the Polymerization of 1,3-Dioxepane with Catalyst 2a

To stirred 1,3-dioxepane (6 mL, 58.3 mmol) at 80 °C was added catalyst **2a** (5 mg, $1.2 \cdot 10^{-2}$ mmol), dissolved in 1 mL dichloromethane, and the induction time was recorded. Subsequently the viscous polymer was subjected to GPC measurements without further purification providing molecular masses of about 14000 g/mol.

4.11. General Procedure for the Time-Dependent Monitoring of the Polymerization of 1,3-Dioxepane by ^{1}H NMR Spectroscopy with Catalyst 2a

To a solution of 38.4 mg ($9.74 \cdot 10^{-2}$ mmol) of **2a** in 0.450 mL of acetone-d_6, at 45 °C in an NMR tube, 50 µL of 1,3-dioxepane ($4.92 \cdot 10^{-1}$ mmol) was added. Subsequently the mixture was subjected to ^{1}H NMR measurement for approximately 80 min.

4.12. General Procedure for the Time-Dependent Monitoring of the Polymerization of Water-Saturated 1,3-Dioxepane with Catalyst 2a

To 2 mL (19.4 mmol) of 1,3-dioxepane 0.10 mL (5.6 mmol) of water was added and the mixture was stirred at room temperature for 10 min. After the organic phase separated from water, 50 µL ($4.92 \cdot 10^{-1}$ mmol) of wet 1,3-dioxepane was added to a mixture of 38.4 mg ($9.74 \cdot 10^{-2}$ mmol) of **2a** in 0.450 mL of acetone-d_6. Subsequently the mixture was subjected to ^{1}H NMR measurement for roughly 11 h.

4.13. General Procedure for Investigating the Influence of Temperature on the Copolymerization of the Extraction Mixture with 1,3-Dioxepane using Catalysts 2a and 4a

To 6 mL of the extraction mixture (30.6 mmol trioxane), which was stirred at the respective temperature, 200 µL (7.2 mol%) of 1,3-dioxepane (199 mg, 1.94 mmol) was added. Then catalyst **2a** ($3.53 \cdot 10^{-2}$ mmol) or **4a** ($3.13 \cdot 10^{-2}$ mmol), dissolved in 1 mL of dichloromethane, was added to the mixture and the induction time was recorded.

4.14. General Procedure for Investigating the Influence of Added Solvent on the Copolymerization of Trioxane with 1,3-Dioxepane using Catalyst 2a

To 6 mL (76.6 mmol) of molten trioxane, which was stirred at 80 °C, 180 µL (2.3 mol%) of 1,3-dioxepane (179 mg, 1.75 mmol) was added. Then catalyst **2a** ($2.54 \cdot 10^{-2}$ mmol – $3.25 \cdot 10^{-2}$ mmol) and the respective amount of 1,2-dichloroethane was added and the induction time was recorded (Table 6).

4.15. X-ray structural Analysis for Complexes 2a and 4

Crystals of **2a** and **4** were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the respective compound. A single crystal was mounted on a P4 Siemens diffractometer by using perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used for the measurement of intensity data in the ω-scan mode. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction via ψ-scans was applied. The structures were solved by direct methods with SHELXS-86.[55] Refinement was carried out with full matrix least-squares methods based on F^2 in SHELXL-97[56] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model.

Crystal data and a summary of data collection and refinement details are given in Table 7. In Tables 8 and 9 the atomic coordinates and isotropic parameters of **2a** and **4** are summarized.

Table 7. Crystal Data and Summary of Data Collection and Refinement of 2a and 4.

	2a	**4**
formula	$C_9H_5F_3MoO_6S$	$C_{12}H_9IO_7W$
formula weight	394.13	575.94
temperature (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	6.7424(10)	15.8169(19)
b, Å	7.8701(14)	7.4701(10)
c, Å	12.548(4)	13.096(3)
α, deg	103.00(2)	90
β, deg	97.85(2)	94.095(16)
γ, deg	96.508(13)	90
V, Å^3	635.5(2)	1543.4(4)
Z	2	4
d_{calcd}, g/cm^3	2.060	2.479
μ(Mo Kα), mm^{-1}	1.255	9.512
F(000)	384	1056
crystal size (mm)	0.1 x 0.45 x 0.25	0.08 x 0.6 x 0.2
θ range, deg	2.69 to 27.49	2.58 to 27.50
limiting indices, *hkl*	-8 to 8, -9 to 9, -16 to 16	-20 to 20, -9 to 9, -17 to 12
reflections collected / unique	5766 / 2883 [R(int) = 0.0315]	12771 / 3558 [R(int) = 0.1032]
completeness to theta = 27.49°	99.0 %	100.0 %
absorption correction	Empirical	Empirical
max. and min. transmission	0.3901 and 0.2694	1.0000 and 0.1425
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data / restraints / parameters	2883 / 0 / 182	3558 / 0 / 193
GOF on F^2	1.083	1.135
R indices [I>2σ(I)]	R1 = 0.0309, wR2 = 0.0791	R1 = 0.0542, wR2 = 0.1477
R indices (all data)	R1 = 0.0349, wR2 = 0.0815	R1 = 0.0559, wR2 = 0.1494
extinction coefficient	0.0126(16)	0.0015(4)
largest diff. peak and hole (e/Å^{-3})	0.800 and -1.133	4.270 and -4.535

$R_1 = \Sigma(||F_o|-|F_c||) / \Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$; $w = [\exp(5\ \sin\theta)^2)]/[\sigma^2(F_o^2) + 0.3472P + (0.0455P)^2]$; $P = [F_o^2 + 2F_c^2]/3$.

Table 8. Atomic Coordinates ($\cdot 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \cdot 10^3$) for 2a. U(eq) is Defined as one Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x	y	z	U(eq)
Mo	5567(1)	6897(1)	7650(1)	19(1)
S	8968(1)	10695(1)	8125(1)	23(1)
F(1)	7239(4)	11880(3)	6512(2)	51(1)
F(2)	8465(3)	9480(3)	5965(2)	38(1)
F(3)	10457(4)	11940(3)	6596(2)	51(1)
O(1)	2743(4)	8564(4)	6053(2)	48(1)
O(2)	3810(4)	3715(3)	5614(2)	43(1)
O(3)	9352(4)	5828(3)	6583(2)	39(1)
O(4)	6960(3)	9700(3)	8094(2)	27(1)
O(5)	10609(3)	9706(3)	8242(2)	36(1)
O(6)	9189(4)	12456(3)	8806(2)	35(1)
C(1)	3740(5)	8000(4)	6622(3)	30(1)
C(2)	4435(5)	4873(4)	6362(3)	28(1)
C(3)	8015(4)	6320(4)	6953(3)	27(1)
C(4)	5828(5)	7563(4)	9616(3)	32(1)
C(5)	6751(5)	6066(5)	9269(3)	33(1)
C(6)	5255(5)	4741(4)	8579(3)	29(1)
C(7)	3382(5)	5437(4)	8487(2)	28(1)
C(8)	3759(5)	7200(4)	9133(3)	29(1)
C(9)	8774(5)	11014(4)	6719(3)	30(1)

Table 9. Atomic Coordinates (· 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 · 10^3) for 4. U(eq) is Defined as one Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x	y	z	U(eq)
W(1)	8174(1)	1737(1)	1714(1)	20(1)
I(2)	6950(1)	4348(1)	1088(1)	47(1)
O(1)	9208(5)	4446(12)	469(5)	55(2)
O(2)	9328(5)	-907(12)	614(5)	54(2)
O(3)	6892(4)	-445(11)	240(5)	47(2)
O(4)	9251(4)	-2546(8)	3011(6)	41(1)
O(5)	7932(4)	-3024(8)	3327(6)	44(2)
O(6)	6551(4)	-1153(9)	3303(6)	41(2)
O(7)	6237(4)	1763(7)	3412(6)	36(2)
C(1)	8832(6)	3454(13)	864(7)	36(2)
C(2)	8921(5)	77(12)	995(6)	31(2)
C(3)	7348(4)	355(11)	751(6)	30(2)
C(4)	8405(4)	13(9)	3134(5)	22(1)
C(5)	7638(4)	1047(9)	3267(5)	20(1)
C(6)	7886(4)	2881(10)	3364(5)	22(1)
C(7)	8763(5)	3027(9)	3271(6)	24(1)
C(8)	9088(4)	1249(11)	3133(6)	25(1)
C(9)	8565(5)	-1956(9)	3135(7)	28(2)
C(10)	6755(4)	402(12)	3326(6)	27(2)
C(11)	5351(6)	1364(17)	3558(11)	55(3)
C(12)	4970(7)	2944(17)	4048(12)	62(3)

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6. Summary

Polyoxymethylenes (POM) are materials mainly consisting of OCH_2 units and afford a variety of applications e.g. in the automobile industry. Modified polyoxymethylenes offer a highly thermal and mechanical stability and are therefore used as precision components. Generally they are made accessible by a cationic ring opening polymerization (ROP) of 1,3,5-trioxane or 1,3,5,7-tetraoxane, and cationic or anionic polymerization of gaseous formaldehyde, respectively. Typical catalysts are classical Lewis acids such as $BF_3 \cdot OEt_2$, Brœnsted acids, or *tert*-butyl perchlorate, which is used by the BASF Aktiengesellschaft.

The intention of this thesis was to find robust transition metal catalysts which are able to polymerize raw or even wet trioxane. Furthermore it was an objective to elucidate whether the catalytic trioxane polymerization is cationically induced or a metal centered reaction. As catalysts served the η^5-cyclopentadienylmolybdenum and -tungsten complexes $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3OTf]$, $[(\eta^5\text{-}C_5H_5)M(CO)_3X]$ (M = Mo, W; X = CF_3SO_3, BF_4, F_3CCO_2), and $[(\eta^5\text{-}C_5H_4(CO_2Me))Mo(CO)_3OTf]$, which has been produced by a modified standard method. The structure of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3OTf]$ was investigated by an X-ray structural analysis.

It was demonstrated that the above-mentioned η^5-cyclopentadienylmolybdenum and -tungsten complexes are able to induce a ring opening polymerization of trioxane even in the presence of some water. Expectedly the tungsten complexes were somewhat lower active than the molybdenum catalysts. Bulk polymerizations were conducted in molten 1,3,5-trioxane under addition of the respective catalyst, dissolved in dichloromethane. All obtained polymers were grinded, purified, dried, and subjected to GPC measurements; the dioxepane polymers were measured without purification. Due to the fact that in various publications the release of monomeric formaldehyde during the polymerization of trioxane was claimed and that the concentration of monomeric formaldehyde in the reaction mixture takes influence on the induction time, an essential part of this thesis was devoted to this issue. Various bulk polymerizations of trioxane were carried out, in the course of which gaseous formaldehyde was added to the mixture prior to the addition of the catalyst. It was demonstrated that indeed the induction times depend on the concentration of formaldehyde, and decreased by feeding gaseous formaldehyde into the reaction mixture. However, in contrast to statements in the literature the induction periods could not be avoided.

Furthermore it was investigated whether gaseous formaldehyde forms a polymer independent from trioxane, or a copolymerization takes place. Therefore a polymerization with trioxane in 1,2-dichloroethane solution saturated with ^{13}C labeled gaseous formaldehyde was performed. MALDI and SIMS experiments of these polymers revealed fragments with 30 and 31 Da. Clearly this is an indication that indeed a copolymerization happened.

To get a further insight into the transition metal catalyzed polymerization of trioxane, ^{1}H NMR spectra of the reaction mixture were recorded at different time intervals at 45 °C. In the course of the reaction new NMR resonances appeared, showing that not only polyoxymethylene, but also by-products such as 1,3,5,7-tetraoxane and methoxymethyl formate were produced. The latter product was formed by a redox Cannizzaro reaction. Due to its high reactivity evolving formaldehyde could not be detected during the polymerization process. Methoxymethyl formate was also subjected to a transition metal catalyzed polymerization. However, the yield of polyoxymethylene was only approximately 30 %. The reason for this low yield was probed by another time-dependent ^{1}H NMR spectroscopic investigation of the transition metal catalyzed polymerization of methoxymethyl formate. During the polymerization process methyl formate occurred as another by-product. Obviously two thirds of methoxymethyl formate are necessary to form methyl formate and only one third is responsible for polyoxymethylene.

All polymers were obtained as colorless solids, hardly soluble in any organic solvent except 1,1,1,3,3,3-hexafluoro-2-propanole, in which GPC measurements were carried out. Solid state ^{13}C CP/MAS NMR experiments of the polymers showed two resonances, one major peak at 88 ppm and a minor one at 161 ppm. The latter signal is assigned to formyl end groups and that one at 88 ppm is attributed to CH_2 units of the polymer. End groups were also detected by MALDI measurements, which showed that mainly formyl, hydroxy, and methoxy functions are present.

The objective to elucidate the water tolerance of the polymerization was clarified by several bulk polymerizations at 80 °C to which a specified amount of water was added prior to the addition of the catalyst. It was established that transition metal catalysts like $[(\eta^5\text{-}C_5H_5)Mo(CO)_3OTf]$ tolerate much more water than classical Lewis acids like BF_3.

Also 1,3-dioxepane was polymerized with the mentioned transition metal catalysts. Experiments were carried out in the same way as the trioxane bulk polymerizations by adding the catalyst to stirred and heated 1,3-dioxepane. The obtained polymers represent viscous liquids and hence are not useful as homopolymers. The dioxepane polymerization was also studied by time-dependent ^1H NMR spectroscopy at 22 °C. New resonances assigned to the polymer are slightly down field shifted.

Another ^1H NMR experiment was devoted to the transition metal induced polymerization of dioxepane which was saturated with water. Polymerizations have taken place even in the presence of water giving rise to the expectance that the copolymerization of technical (wet) trioxane with 1,3-dioxepane could be successful. Indeed this was proved and the water peak shifted from 2.85 to 4.3 ppm. It is suspected that this shift is traced back to the formation of molybdenum aqua complexes and the change of the pH after addition of the strong Lewis acid.

It was further possible to copolymerize 1,3,5-trioxane with 1,3-dioxepane to attain to copolymers providing a higher thermal and hydrolytic stability than homopolymers, because C_4 units resulting from the comonomer dioxepane can not be hydrolyzed or thermally degraded. After post-processing the copolymer ideally is provided with two C_4 end groups up to which the polymer can be hydrolyzed.

A further test to probe the activity of the molybdenum catalysts was the polymerization of the extraction mixture which is technical trioxane contaminated with about 1 % of water and 60 % of solvent. The polymers yielded from the extraction mixture showed a somewhat lower molecular weight, resulting from a chain termination caused by the water.

Another experiment to probe the influence of the reaction temperature was carried out by polymerizing the extraction mixture at different temperatures. The applied molybdenum catalyst was able to polymerize the extraction mixture already at 50 °C, whereas the tungsten catalyst induced the polymerization only at 65 °C. No dependence between the reaction temperature and the molecular weights was observed. Furthermore a normal increase in the activity of both catalysts with rising temperature was obvious.

To study the influence of the solvent on the polymerization, a series of polymerizations of 1,3,5-trioxane was conducted to which different amounts of 1,2-dichloroethane was added prior to the addition of the catalyst. Water takes a much greater influence on the induction times and the properties of the resulting polymers than the solvent dichloroethane.

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