

Transition metal-catalyzed polymerization of 1,3,5-trioxane

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Abstract

The molybdenum complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{OTf}]$ (**1a**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$ (**2a–2c**) ($\text{X} = \text{F}_3\text{CSO}_3$ (**a**), F_3CCO_2 (**b**), BF_4 (**c**)), and $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{CH}_3)\text{Mo}(\text{CO})_3\text{OTf}]$ (**3a**) catalyze the cationic ring-opening polymerization (ROP) of 1,3,5-trioxane to polyoxymethylene (POM, **5**). Hitherto unknown **3a** is accessible by treatment of $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{CH}_3)\text{Mo}(\text{CO})_3\text{CH}_3]$ with $\text{CF}_3\text{SO}_3\text{H}$. The precipitation time of the polymerization, which is defined in the following as the time until precipitation starts, is dependent on the Lewis acidity of the transition metal center and the presence of formaldehyde or water. ^{13}C -labeled formaldehyde was copolymerized with 1,3,5-trioxane and randomly incorporated into POM. This observation supports the conception that formaldehyde is reversibly formed during the polymerization. Catalyst **2a** was successfully applied in the ROP of trioxane even in the presence of up to 3.6 mol% of water. Time-dependent ^1H -NMR spectroscopic investigations of the trioxane polymerization revealed the formation of methoxymethyl formate (**4**) as a by-product, an isomer of trioxane. In the presence of **2a** as a catalyst, **4** was degraded to methyl formate (**6**) and POM (**5**) in a ratio of about 2:1. This degradation was monitored by ^1H -NMR spectroscopy. Catalyst **2a** is also able to copolymerize 1,3,5-trioxane with 1,3-dioxepane leading to a thermally stable copolymer after treatment with an aqueous solution of Na_2CO_3 .

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1. Introduction

The cationic ring-opening polymerization (ROP) 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 (POM) consisting mainly of CH_2O units. Polymers of the latter type were investigated for the first time by Kern and Staudinger 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 polymerized in the solid, molten, or dissolved state and even in suspension. In contrast to formaldehyde, 1,3,5-trioxane

is only cationically polymerized [4]. Typical catalysts are Lewis acids like $\text{BF}_3 \cdot \text{OEt}_2$ [5–7], Brønsted 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 acetates (vide infra) have been employed as catalysts for the cationic polymerization of trioxane [10].

Little is known of the trioxane polymerization through direct observation of the individual reactions in the complex process: systems that allow the study of elementary reactions are hardly available. Initial mechanistic studies were carried out in the early 1960s where it was concluded that the presence of formaldehyde is crucial for the polyacetal formation. In the polymerization itself not only free formaldehyde, but also trioxane, and tetraoxane are involved [11].

Although transition metal complexes have been widely tested as catalysts for several kinds of polymerization reactions, like ROMP [12–14], olefin polymerization [15,16], or the copolymerization of carbon

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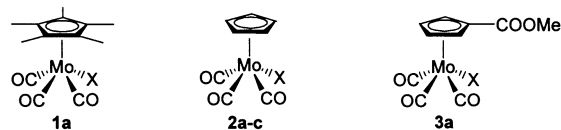
monoxide with olefins [17,18] only very few investigations are known in which such catalysts were employed to initiate the ROP of oxygen-containing heterocycles [19–24]. In particular, acetylacetonato complexes of molybdenum [25], cobalt, and other transition metals have been probed for the polymerization of trioxane and in the case of molybdenum the authors supposed an insertion mechanism which could not be confirmed [26]. 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.

In this investigation, it is demonstrated that η^5 -cyclopentadienylmolybdenum complexes are able to induce the ROP 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 which is still not clear in detail was monitored by NMR 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 only initiation can be controlled through tuning of the metal–ligand entity.

2. Results and discussion

Several years ago, Beck et al. [27–30] reported on the organometallic strong Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^+$ stabilized by weakly coordinating anions like BF_4^- , CF_3SO_3^- , or MF_6^- ($\text{M} = \text{P}, \text{As}, \text{Sb}$). A comparable complex with CF_3CO_2^- as anion was briefly described by Williams and Lalor [31]. The first mentioned authors established that the BF_4^- anion in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{BF}_4$ was easily replaced for cyclic ethers like oxirane, oxetane, tetrahydrofuran or 1,4-dioxane to give cationic complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3 \text{ ether}][\text{BF}_4]$. 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 subject 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 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–2c**) or related complexes (**1a** and **3a**) are suitable systems for studying

the ROP of trioxane (Chart 1). Due to different substitution pattern of the cyclopentadienyl rings, these complexes differ in their Lewis acidity. Also the influence of various weakly coordinating anions was taken into consideration.



a: X = F_3CSO_3^- ; b: X = F_3CCO_2^- ; c: X = BF_4^-

2.1. Synthesis and characterization of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$

The molybdenum complexes were prepared as described in the literature [28,29,31], except for **3a** which has been made accessible by somewhat modified standard methods [50]. It was obtained as a bordeaux red solid, sensitive to aerial oxygen and readily soluble in polar to medium polar organic solvents. Structural information of similar complexes of the type **1a**, **2a–2c**, and **3a** are available [33,34]. To get insight into the molecular motif, **2a** was chosen for an X-ray structural investigation. In Table 1, selected bond distances and bond angles of the piano stool complex **2a** are summarized. The corresponding ORTEP plot with atom labeling is depicted in Fig. 1. Two independent molecules of **2a** 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ (2.012 Å).

Table 1
Selected bond lengths (Å) and bond angles ($^\circ$) for **2a**

Bond length	
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)
Bond angle	
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)

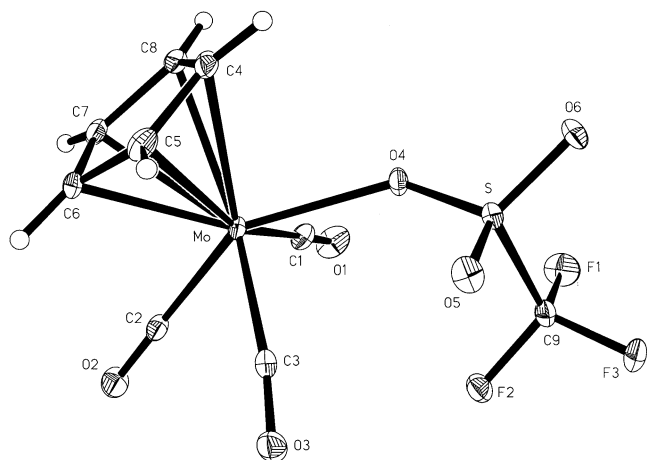


Fig. 1. ORTEP plot of **2a** shown at the 20% probability level.

2.2. Initiation of the polymerization of 1,3,5-trioxane with catalysts **1a**, **2a–2c**, and **3a**

Molten trioxane (6 ml, 76.6 mmol) was treated at 80 °C with 1.2×10^{-2} mmol of the respective catalyst **1a**, **2a–2c**, and **3a** dissolved in 1 ml of dichloromethane (substrate:catalyst, 6380:1). The precipitation time which is the period between the addition of the catalyst and the visible formation of the polymer varied between 7 s and 75 min. Catalysts **2a** and **3a** were most active, the one with the lowest activity was **2b**. Complexes **1a** and **2c** revealed a medium activity. The time until precipitation starts increases in the sequence **3a** ~ **2a** < **1a** < **2c** < **2b** (Fig. 2), which means that the Lewis acidity of the metal center takes influence on the reaction. The decreasing precipitation times are congruent with the increasing electron-withdrawing effect of 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 precipitation 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 forming a contact or solvent separated ion pair

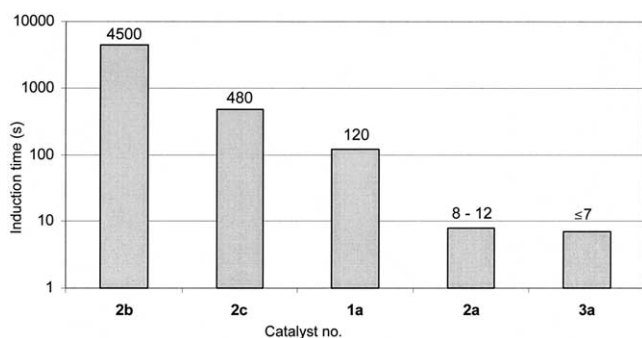


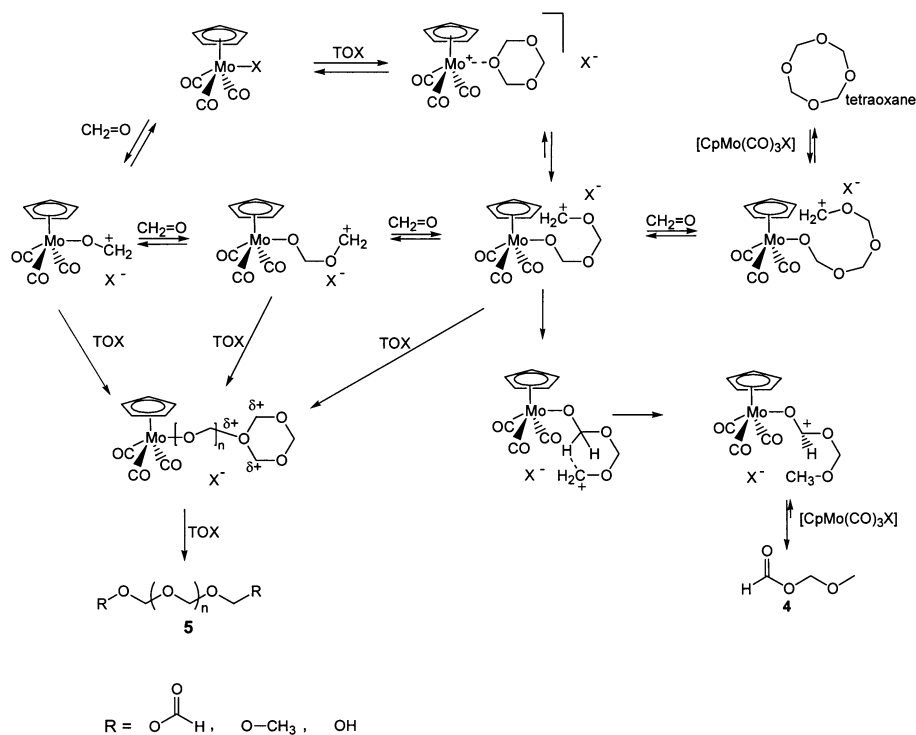
Fig. 2. Different activities of catalysts **1a**, **2a–2c**, and **3a** in the polymerization of 1,3,5-trioxane at 80 °C (no solvent was used).

(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 precipitation time follows the Lewis acidity.

2.3. 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 time only formaldehyde and its oligomers are formed in the polymerization of 1,3,5-trioxane with BF_3 as a catalyst [4,6,11]. Allegedly a “ceiling concentration” of monomeric formaldehyde is necessary to start the polymerization process (vide supra) [6]. This was later supported 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** (1.2×10^{-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 precipitation time to approximately 1.5 min, compared to a precipitation time of 4 min without formaldehyde. The experiments were performed with equal amounts of trioxane and 1,1,2,2-tetrachloroethane as solvent at 80 °C. In contrast to the standard bulk polymerizations without any solvent, the longer precipitation times in the present case result from the added solvent which is necessary to dissolve gaseous formaldehyde. 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 1.2×10^{-2} mmol of catalyst **2a** was analyzed by MALDI (matrix-assisted laser desorption/ionization) and SIMS (secondary ion mass spectro-



Scheme 1.

metry). 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. 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].

To get a further insight into the transition metal-catalyzed polymerization of trioxane, $^1\text{H-NMR}$ spectra of the reaction mixture were recorded 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 $^1\text{H-NMR}$ 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 Fig. 3 ($t = 0$) shows the above-mentioned solution. Immediately after the addition of the catalyst, a weak signal at 5.00 ppm emerges which is attributed to the formation of 1,3,5,7-tetraoxane [5,7,11] (Fig. 4, top). At the same time, the occurrence of another resonance at 4.72 ppm points to the appearance of POM. 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 1 h, three further resonances at 7.99 , 5.59 , and 3.68 ppm appear with steadily increasing intensities. They can unequivocally be assigned to

methoxymethyl formate (**4**). Its verification succeeded by the measurement of an authentic sample, which was synthesized through reaction of $\text{ClCH}_2\text{OCH}_3$ with HCO_2Na [37]. After roughly 13 h, trioxane and intermediary formed tetraoxane were consumed and only the signals of methoxymethyl formate, the solvent, HMB, and the catalyst remained (Fig. 4, 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 cannot be isolated or

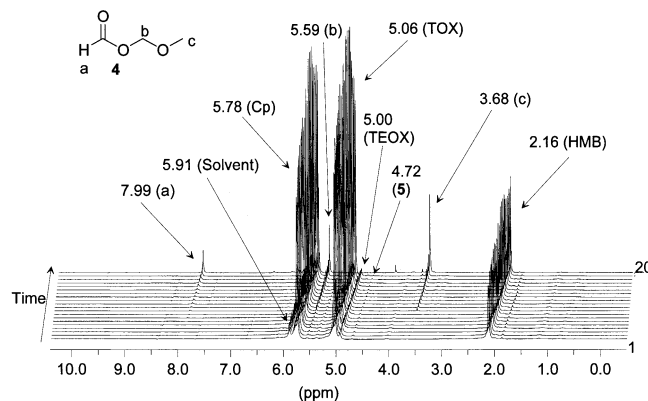


Fig. 3. Degradation of 1,3,5-trioxane in the presence of catalyst **2a** monitored $^1\text{H-NMR}$ spectroscopically. Number of spectra: 1: $t = 0$; 3: $t = 00:01:07$; 6: $t = 00:03:41$; 8: $t = 00:05:08$; 9: $t = 00:59:49$; 12: $t = 01:18:35$; 17: $t = 01:40:32$; 19: $t = 05:52:13$; 20: $t = 12:55:07$.

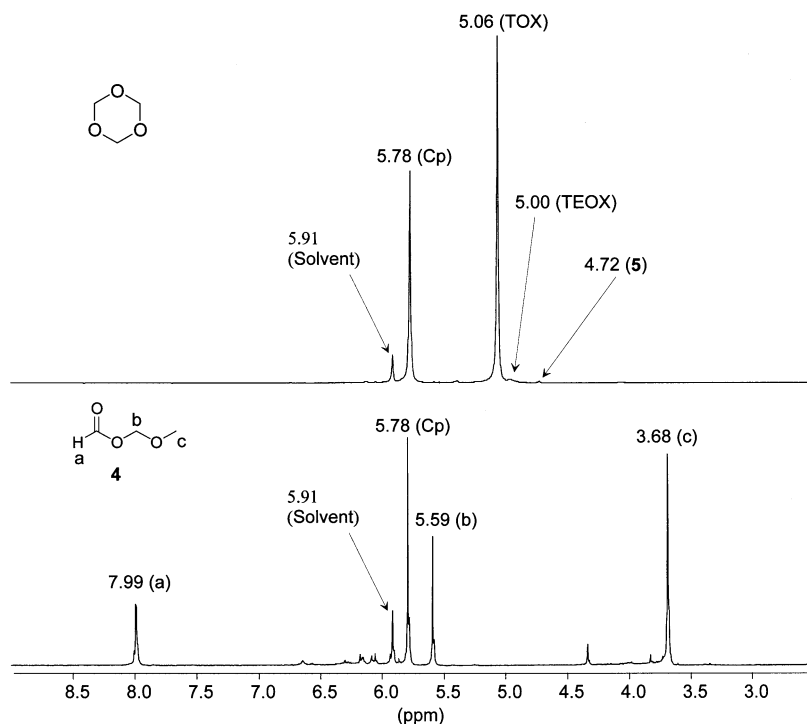


Fig. 4. Degradation of 1,3,5-trioxane in the presence of catalyst **2a**, monitored ^1H -NMR spectroscopically (spectrum 1: top; spectrum 20: bottom).

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 $\text{CpMo}(\text{CO})_3\text{OCH}_2\text{OCH}_2\text{O}^+=\text{CH}_2$. 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 whether larger rings are also formed in the process as NMR properties may be very similar) [38]. Thus POM (**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^{-1} [6], NMR observation is not to be expected. Scheme 1 reflects also the formation of methoxymethyl formate (**4**) 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 preferential formation of **4** in the molybdenum-based polymerization is attributed to a metal-mediated

transformation: a 1,5-hydride shift [4,24,39]. 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 Brønsted acids.

2.4. Behavior of methoxymethyl formate (**4**) toward catalyst **2a**

The monitoring of the trioxane polymerization by ^1H -NMR spectroscopy over a prolonged period ($> 11 \text{ h}$) showed that the ^1H signal at 5.59 ppm of **4** is losing part of its intensity. This observation led to the question, whether methoxymethyl formate (**4**) is stable under the polymerization reaction conditions. To address this matter, a time-dependent ^1H -NMR spectroscopic investigation of the degradation of **4** was undertaken. For that purpose, $14 \mu\text{l}$ (15.2 mg , $1.69 \times 10^{-1} \text{ mmol}$) of **4** was dissolved in 0.5 ml of 1,1,2,2-tetrachloroethane to which solutions of 4.5 mg ($2.77 \times 10^{-2} \text{ mmol}$) of HMB as well as 40 mg ($1.01 \times 10^{-1} \text{ mmol}$) 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 **4**:**2a**:HMB = 2:1:1. Beginning with spectrum 1 (Fig. 5), two new resonances with increasing intensities occur at 7.95 and 3.62 ppm (see Fig. 6, top). These arise at the expense of the signals at $\delta = 8.02$, 5.18, and 3.37 ppm

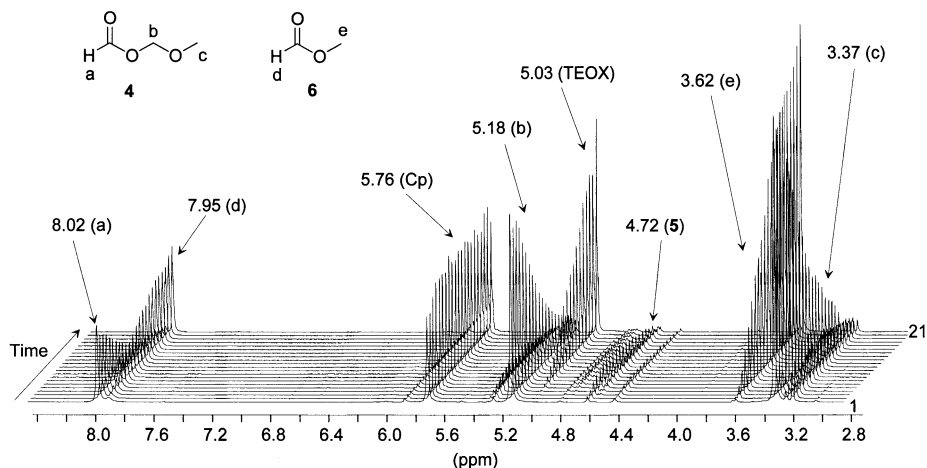


Fig. 5. Degradation of methoxymethyl formate (**4**) in the presence of catalyst **2a** monitored $^1\text{H-NMR}$ spectroscopically. Number of spectra: 1: $t = 0$; 2: $t = 07:15:39$; 4: $t = 07:36:27$; 6: $t = 07:57:13$; 8: $t = 08:18:01$; 10: $t = 08:38:48$; 12: $t = 08:59:36$; 14: $t = 09:20:23$; 16: $t = 09:41:10$; 18: $t = 10:01:57$; 20: $t = 11:02:45$.

(**4**). The new resonances are ascribed to the protons of the formyl and methoxy groups of methyl formate (**6**) which has been formed. Another new resonance at 4.72 ppm is assigned to POM (**5**). After approximately 4 h, the degradation of **4** was nearly complete and in Fig. 6, bottom, essentially the resonances of methyl formate (**6**), **2a**, and tetraoxane are found. In addition, small resonances of the starting material **4** and the polyacetal **5** are visible. To corroborate these findings, ^{13}C -labeled methoxymethyl formate (**4**), which was synthesized by reaction of $\text{H}^{13}\text{C}(\text{O})\text{ONa}$ with $\text{ClCH}_2\text{OCH}_3$, was catalytically degraded with **2a**. The $^{13}\text{C}=\text{O}$ group quantitatively reappeared in methyl formate (**6**). In its $^1\text{H-NMR}$ spectrum (in 1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$), a doublet at 7.94 ppm is

assigned to the HCO function with a coupling constant of $^1J_{\text{CH}} = 227$ Hz. A further doublet at 3.61 ppm with $^3J_{\text{CH}} = 4.08$ 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 (**4**) is explained by the fact that two-thirds of molecule **4** are needed to form **6** (Scheme 2). The decomposition of **4** under the action of catalyst **2a** results from an electrophilic attack at the carboxylate oxygen atom in **4** resulting in the cleavage of the vicinal C–O bond. As a consequence, a carbocation and a $\text{HC}(\text{O})\text{O}[\text{M}]$ fragment are formed. Subsequently, a CH_3^+ transfer from the carbocation to $\text{HC}(\text{O})\text{O}[\text{Mo}]$ takes place leaving formaldehyde and $[\text{Mo}]^+$. On this occasion, methyl formate (**6**) is formed.

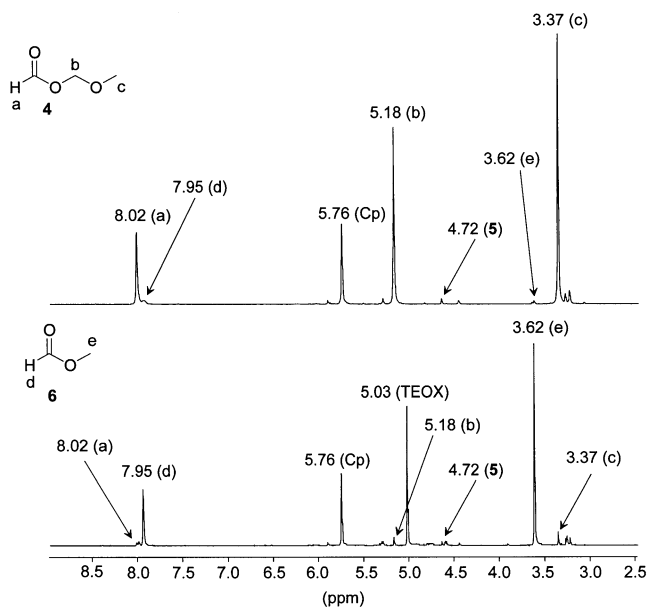
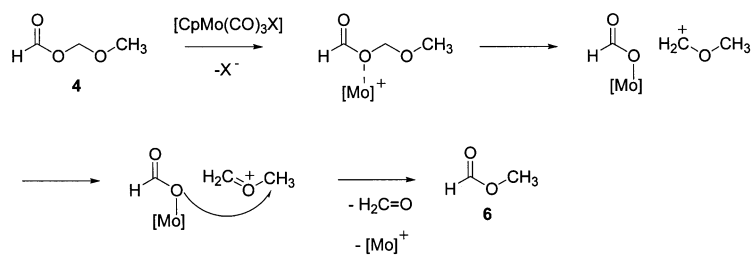


Fig. 6. Degradation of methoxymethyl formate (**4**) in the presence of catalyst **2a**, monitored $^1\text{H-NMR}$ spectroscopically (spectrum 1: top; spectrum 21: bottom).

2.5. 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, $T_{\text{CH}} = 0.23$ ms [43], and the principal components of the carbon chemical shift tensor, $\delta_{11} = 113(2)$ ppm, $\delta_{22} = 85(2)$ ppm, $\delta_{33} = 68(2)$ ppm [44]. The minor component with a chemical shift of 161 ppm has so far not been observed in $^{13}\text{C-NMR}$ spectra of POM. A non-quaternary suppression $^{13}\text{C-NMR}$ 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.

To assess the reproducibility of the synthesis of POM (5), six runs were performed under the same conditions (see Fig. 2; trioxane: 76.6 mmol; catalyst 2a: 1.2×10^{-2} mmol; no solvent; $t = 80$ °C). The precipitation times varied between 8 and 12 s and the turnover numbers were in between 3400 and 4400 (Table 2). 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 38 200 and 46 900 g mol^{-1} . To determine the end groups of the polymer chain, one of the polymers was subjected to a MALDI investigation. It was established that mainly formyl, hydroxy, and methoxy functions are found without any negative impact on the properties of the polymers. An explanation follows from the consideration of Scheme 1.

2.6. 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 $\text{CpMo}(\text{CO})_3\text{X}$ 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 1.2×10^{-2} mmol (1.57×10^{-4} mol%) of catalyst 2a was added and the precipitation time determined (Fig. 7). Up to an amount of 2.18 mol% of water (referred to trioxane), no major change of the precipitation time was observed. At higher concentrations of water, a considerable increase of the precipitation time was found. In the presence of 3.63 mol% of water, the precipitation time rose to a value of approximately 450 s. 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 precipitation time increases from about 3 to 38 min if the amount of water is raised from 0.03 to 0.8 mol% [5]. Selected data of the polymerization of trioxane are summarized in Table 2. It was, however, found that the molecular weight of the polyacetal obtained with 2a in the presence of water is substantially decreased: $M_w = 32\,400$ (without water) compared to $M_w = 18\,700$ (with 0.1 ml of water).

Table 2
Selected data of the polymerization of 1,3,5-trioxane with catalyst 2a

Run	M_w^a (g mol^{-1})	M_n^a (g mol^{-1})	M_w/M_n	Induction time (s)	Yield ^b (g) [%]	TON ^c
1	44400	22800	1.95	11	3.88 [56]	3400
2	38200	20100	1.90	10	4.95 [72]	4300
3	43400	22200	1.95	8	4.00 [58]	3500
4	41800	22400	1.87	12	4.75 [69]	4200
5	46900	23200	2.02	8	4.39 [64]	3900
6	41300	22600	1.83	9	4.69 [68]	4100

^a Determined by GPC.

^b Sublimation temperature > 175 °C.

^c TON = mol(polymer)/mol(catalyst).

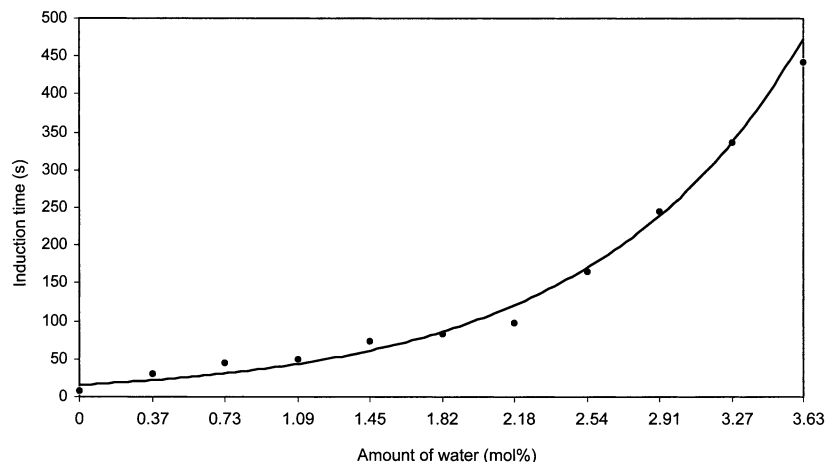


Fig. 7. Induction times of the ROP of 1,3,5-trioxane in the presence of different amounts of water using **2a** as catalyst (no solvent was used).

2.7. 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 POM; in a further attempt, 1,3,5-trioxane was copolymerized with 1,3-dioxepane. For this purpose, 1.2×10^{-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. Precipitation times were measured, which vary between 19 and 24 s. The tolerance of **2a** toward water in this copolymerization is comparable to that of trioxane homopolymerization (vide supra) and precipitation 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 3. Molecular masses (M_w) of the copolymers were between 21 000 and 27 000 g mol^{-1} . 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.

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 $\text{BF}_3 \cdot \text{OEt}_2$ or $t\text{BuClO}_4$. They are less active than iridium or palladium catalysts [49], but $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{OTf}]$ (**2a**) proved to be an excellent example to carry out time-dependent $^1\text{H-NMR}$ 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. The entire process of the 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 tetraoxane during the reaction. Time-dependent $^1\text{H-NMR}$ spectroscopic investigations point to the formation of several by-products such as methoxymethyl formate (**4**), 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 (**6**). 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.

Table 3
Selected data of the copolymerization of 1,3,5-trioxane with 1,3-dioxepane with catalyst **2a**

Run	M_w^a (g mol ⁻¹)	M_n^a (g mol ⁻¹)	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]	3400
2	21200	10000	2.13	19	6.43 [93]	3.48 [50]	3000
3	23300	15300	1.52	22	6.31 [91]	4.44 [64]	3900
4	27400	17800	1.54	22	6.27 [91]	3.79 [55]	3300
5	23500	15300	1.54	24	6.31 [91]	4.19 [61]	3700

^a Determined by GPC.

^b Prior to treatment with an aqueous Na₂CO₃ solution.

^c After treatment with an aqueous Na₂CO₃ solution. Melting points: 171–172 °C.

^d TON = mol(polymer)/mol(catalyst).

4. Experimental

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 CaH₂ 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. ¹³C-labeled sodium formate, ¹³C-labeled paraformaldehyde, and 1,1,2,2-tetrachloroethane-d₂ were purchased from Deutero GmbH and were used without further purification. Hexamethylbenzene, 1,1,1,3,3,3-hexafluoro-2-propanol, chlorodimethyl ether were purchased from Aldrich. Methyl formate was obtained from Merck and used without further purification. Complexes **1a**, **2a–2c**, and [C₅H₄CO₂CH₃]Na were synthesized according to the literature methods [28,29,31,50].

High-resolution nuclear magnetic resonance 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, ¹³C{¹H}-NMR: 62.90 MHz. Chemical shifts in the ¹H- and ¹³C{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 ZrO₂ rotors). Frequencies, standards, and acquisition parameters: ¹³C, 50.288 MHz (4.7 T) [TMS, carbonyl resonance of glycine ($\delta = 176.0$) as secondary standard], 90° proton pulse length of 3.8 μ s (B₁ field 65 kHz), contact time *T_c* of 1 ms, recycle delay 2 s. The non-quaternary suppression ¹³C-NMR experiment [51] was carried out using a

dephasing delay of 40 μ s. Chemical shift anisotropies were determined from analysis of spinning side-band intensities in slow-MAS spectra or for static samples using the programs HBA and WSolid1 [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 Knauer Column Air-Ofen, a Bischoff HPLC pump Model 2200, a 8 mm × 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 [(η^5 -C₅H₄CO₂CH₃)Mo(CO)₃CH₃]

The reaction of [C₅H₄CO₂CH₃]Na (1.56 g, 10.7 mmol) with Mo(CO)₃(CH₃CN)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 overnight 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 (CDCl₃): δ 5.68, 5.31 (s, 4H, C₅H₄), 3.75 (s, 3H, OCH₃), 0.37 (s, 3H, MoCH₃). ¹³C{¹H}-NMR (CDCl₃): δ 237.8 (s, MoCO), 225.1 (s, MoCO), 165.2 (s, CpC=O), 98.2, 94.8, 94.5 (s, C₅H₄), 52.5 (s, CH₃). FD-MS: *m/z* 260.0 [M⁺], 232.1 [M⁺–CO]. IR (CH₂Cl₂,

cm^{-1}): $\nu(\text{CO})$ 2018, 1982, 1929. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{MoO}_5$: C, 41.53; H, 3.17. Found: C, 41.75; H, 3.10%.

4.3. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{CH}_3)\text{Mo}(\text{CO})_3\text{OSO}_2\text{CF}_3]$ (**3a**)

$[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{CH}_3)\text{Mo}(\text{CO})_3\text{CH}_3]$ (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**. $^1\text{H-NMR}$ (CDCl_3): δ 6.12, 5.92 (m, 4H, C_5H_4), 3.76 (s, 3H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ -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^+], 426 [$\text{M}^+ - \text{CO}$]. IR (CHCl_3 , cm^{-1}): $\nu(\text{CO})$ 2077, 2007, $\nu(\text{C=O}_{\text{ester}})$ 1734. Anal. Calcd for $\text{C}_{11}\text{H}_7\text{O}_8\text{F}_3\text{MoS}$: 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 [53], the respective catalyst **1a**, **2a–2c**, or **3a** (1.2×10^{-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}): $\nu(\text{CH})$ 2984, 2927. Anal. Calcd for $(\text{CH}_2\text{O})_n$: C, 40.00; H, 6.71. Found: C, 39.39 [54]; H, 6.40%.

To probe the tolerance of the catalytic polymerization of 1,3,5-trioxane with **2a** toward water, the same procedure has been applied; however, the experiments were performed in the presence of different amounts of water (see Fig. 7).

4.5. General procedure for the $^1\text{H-NMR}$ 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 $^1\text{H-NMR}$ spectra were recorded until the reaction was finished after approximately 13 h (Fig. 3). $^1\text{H-NMR}$ data for **4** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 7.99 (s, 1H, HCO), 5.59 (s, 2H, CH_2), 3.68 (s, 3H, CH_3). $^1\text{H-NMR}$ data for **5** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 4.72 (s, OCH_2O).

4.6. Synthesis of methoxymethyl formate (**4**)

To compare NMR spectroscopic data of methoxymethyl formate (**4**) which was formed during the polymerization of trioxane, an authentic sample of **4** was synthesized by treatment of chlorodimethyl ether (5.3 g, 65.8 mmol) with sodium formate and $^{13}\text{C}=\text{O}$ -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 **4**. $^1\text{H-NMR}$ (CDCl_3): δ 8.09 (s, 1H, HCO), 5.27 (s, 2H, CH_2), 3.45 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -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 $\text{C}_3\text{H}_6\text{O}_3$: C, 40.00; H, 6.71. Found: C, 39.23; H, 5.99%.

4.7. General procedure for the $^1\text{H-NMR}$ spectroscopic monitoring of the degradation of methoxymethyl formate (**4**)

To a mixture of 14 μl (15.2 mg, 1.69×10^{-1} mmol) of **4** and 40 mg (1.01×10^{-1} mmol) of catalyst **2a** in 0.6 ml of 1,1,2,2-tetrachloroethane, 4.5 mg (2.77×10^{-2} mmol) of HMB was added. The reaction was followed in a 5-mm NMR tube at 45 °C. Subsequently, in certain time intervals $^1\text{H-NMR}$ spectra were recorded until the reaction was finished after approximately 11 h (Fig. 5). $^1\text{H-NMR}$ data for **5** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 4.72 (m, CH_2O). $^1\text{H-NMR}$ data for **6** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 7.95 (s, 1H, HCO), 3.62 (s, 3H, CH_3). $^1\text{H-NMR}$ data for TEOX (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 5.03 (s, 8H, OCH_2O).

4.8. Degradation of methoxymethyl formate (**4**) with catalyst **2a**

To 10.29 g (114.2 mmol) of **4**, 5.0 mg (1.2×10^{-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 POM (**5**) was observed and the mixture begun to reflux. After cooling to room temperature, the suspension was filtered (P3) yielding 91.2 mmol of **6** (80%, referred to **4**) and 24.6 mmol of **5** (65%, referred to **4**). ^{13}C CP/MAS NMR data for **5**: δ 87.8 (s, CH_2). $^1\text{H-NMR}$ data for **6** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 7.94 (s, 1H, HCO), 3.61 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR data for **6** (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 161.9 (s, HCO), 51.3 (s, OCH_3) [55].

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, 1.2×10^{-2} mmol), dissolved in 1 ml of dichloro-

methane, 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 Na₂CO₃ 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 3). ¹³C CP/MAS NMR: δ 163.9 (s, CHO), 87.7 (s, CH₂), 66.6–71.3 (m, CH₂), 26.0 (s, CH₃). 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. X-ray structural analysis for complex 2a

Crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **2a**. A single crystal was mounted on a P4 Siemens diffractometer by using perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo–K_α radiation (λ = 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 [56]. Refinement was carried out with full-matrix least-squares methods based on *F*² in SHELXL-97 [57] 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 4.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 208875. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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Table 4
Crystal data and summary of data collection and refinement of **2a**

Formula	C ₉ H ₃ F ₃ MoO ₆ S
Formula weight	394.13
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	6.7424(10)
<i>b</i> (Å)	7.8701(14)
<i>c</i> (Å)	12.548(4)
α (°)	103.00(2)
β (°)	97.85(2)
γ (°)	96.508(13)
<i>V</i> (Å ³)	635.5(2)
<i>Z</i>	2
<i>d</i> _{calcd} (g cm ⁻³)	2.060
μ(Mo–K _α) (mm ⁻¹)	1.255
<i>F</i> (0 0 0)	384
Crystal size (mm ³)	0.1 × 0.45 × 0.25
θ range (°)	2.69–27.49
limiting indices, <i>h k l</i>	–8 to 8, –9 to 9, –16 to 16
Reflections collected/unique	5766/2883 [<i>R</i> _{int} = 0.0315]
Completeness to θ = 27.49°	99.0%
Absorption correction	empirical
Max. and min. transmission	0.3901 and 0.2694
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2883/0/182
GOF on <i>F</i> ²	1.083
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0791
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0349, <i>wR</i> ₂ = 0.0815
Extinction coefficient	0.0126(16)
Largest diff. Peak and hole (e Å ⁻³)	0.800 and –1.133

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; wR_2 = \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)]^{0.5}}; w = \frac{1}{[\exp(5 \sin^2 \theta)] / [\sigma^2(F_o^2) + 0.3472P + (0.0455P)^2]}; P = [F_o^2 + 2F_c^2]/3.$$

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