

Ring-Opening Polymerization of Trimethylene Carbonate Catalyzed by Methanesulfonic Acid: Activated Monomer versus Active Chain End Mechanisms

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ABSTRACT: The ring-opening polymerization (ROP) of trimethylene carbonate (TMC) initiated by water or *n*-pentanol and catalyzed by trifluoromethanesulfonic acid (HOTf) or methanesulfonic acid (MSA) has been investigated. In contrast with HOTf, MSA was found to afford poly(trimethylene carbonate) (PTMC) free of ether linkages even under forcing conditions. The comparison of the two acids substantiates further that activity does not simply correlate with acidity. Analysis of the resulting PTMC by Size Exclusion Chromatography (SEC), ¹H NMR spectroscopy and mass spectrometry revealed the absence of molar mass control due to the formation of two polymer populations. This phenomenon was unambiguously attributed to the occurrence of two competitive mechanisms, namely Activated Monomer (AM) and Active Chain End (ACE). Such a situation is frequently encountered in the ROP of cyclic ethers, but is unprecedented for cyclic carbonates. Its deleterious impact on the polymerization control can be significantly reduced by maintaining the monomer concentration low enough so as to minimize the ACE mechanism. Accordingly, multifeed or continuous addition of the carbonate was shown to impart good control of molar mass and end-group fidelity.

Introduction

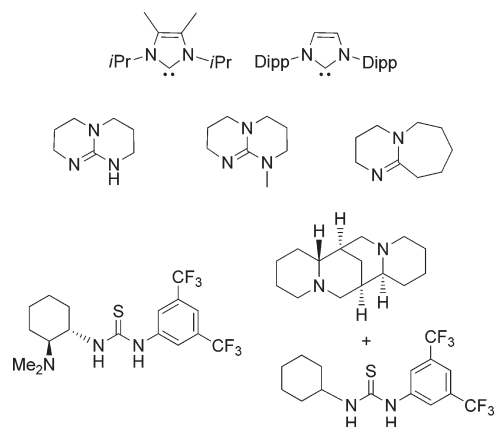
Spectacular advances have been achieved over the past decade in organo-catalytic ring-opening polymerization (ROP).¹ A broad range of organo-catalysts, associated with various activation modes, have been shown to efficiently promote the ROP of oxygen-containing heterocycles (Chart 1):

- Lewis/Brønsted bases allow nucleophilic activation of the monomer and/or basic activation of the initiating/propagating group. Here, the archetypal system is 4-dimethylamino-pyridine (DMAP)² that was the first organo-catalyst to be shown to promote controlled ROP of lactide.³ Later on, this approach was extended to other systems including *N*-heterocyclic carbenes (NHCs)⁴ and bicyclic amidines (such as 1,8-diazabicyclo[5.4.0]undec-7-ene DBU),⁵ for which significantly higher activities were observed.
- Brønsted acids allow electrophilic activation of the monomer, as initially substantiated by Endo with hydrogen chloride.⁶ Recent studies have shown that the polymerization times and catalyst loadings can be significantly reduced using sulfonic acids, and to date, the best acids to promote controlled ROP of lactide and ϵ -caprolactone are trifluoromethanesulfonic acid (HOTf)⁷ and methanesulfonic acid (MSA),⁸ respectively.⁹
- Bifunctional systems combining a Lewis base and a hydrogen-bond donor allow concomitantly basic activation of the initiating/propagating group and electrophilic activation of the monomer. Most representative

of such multicenter catalysts are amine/thiourea combinations^{5,10} and bicyclic guanidine (such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene TBD)¹¹ that provide to date the best compromise in terms of activity, control and robustness.¹²

Initially, the activity and degree of control of all these organo-catalysts have been evaluated toward the polymerization of simple lactones and dilactones. Increasing efforts are currently devoted to extend the scope of such metal-free ROP in order to get access to a wide range of polymer structures. This concerns not only the incorporation of functional groups (within the initiator or the monomer)¹³ but also the ROP of other cyclic monomers. Particularly representative are the recent advances reported for the ROP of cyclic carbonates, including functionalized ones, with Lewis/Brønsted bases and bifunctional systems (Chart 1).¹⁴ Comparatively, Brønsted acids have been essentially used toward ϵ -caprolactone and lactide.^{7–9,15,16} Although Nakano demonstrated as early as in 1999 the ability of sulfonic acids to catalyze the ROP of 4,4-dimethyltrimethylene carbonate, the degree of polymerization control was far from that achieved with the other types of organo-catalysts.¹⁷ Accordingly, two polymer populations were obtained with MSA, something that was ascribed to deleterious backbiting reactions. The better understanding gained over the past few years in sulfonic acid-catalyzed ROP prompted us to reinvestigate this approach toward cyclic carbonates. For this study, trimethylene carbonate (TMC) was chosen as a model monomer, and both HOTf and MSA were evaluated. The main objectives were (i) to evaluate the propensity of sulfonic acids to promote ROP while preventing the undesirable decarboxylation reactions typically encountered with strong Lewis acids and alkylating reagents,¹⁸ (ii) to compare the activity of HOTf and MSA (the results obtained with lactide and

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Chart 1. Lewis/Brønsted Bases and Bifunctional Systems Reported to Efficiently Promote the ROP of Cyclic Carbonates

ϵ -caprolactone^{7,8} suggest that activity does not simply correlate with acidity), and (iii) to shed light into the mechanism of polymerization in order to improve the polymerization control and thereby to get access to poly(trimethylene carbonate) (PTMC) of well-defined structures. The results of this study are reported hereafter.

Experimental Part

Materials. All reactions were performed under an inert atmosphere of argon, using standard Schlenk techniques. Solvents were dried and distilled prior to use: toluene (>99.9%) over sodium and dichloromethane (>99.95%) over phosphorus pentoxide. Trimethylene carbonate (TMC, 1,3-dioxane-2-one, BOEHRINGER) was dissolved in THF at a concentration of 0.7 g/mL and was stirred over CaH_2 for 2 days before being filtered, recrystallized twice from cold THF, finally dried and stored in a glovebox. Trifluoromethanesulfonic acid (HOTf) (99%, Aldrich) was used as received and stored under argon. *n*-Pentanol (99+%) was dried over sodium and distilled before use. Anhydrous methanesulfonic acid (MSA) was kindly furnished by ARKEMA and was used as received.

Characterizations. ^1H NMR measurements were used to determine the monomer conversion and the chain end groups. Spectra were recorded in CDCl_3 on BRUKER Avance 300, 400, and 500 MHz spectrometers at room temperature and ^1H chemical shifts are reported in ppm relative to Me_4Si as an external standard. Monomer conversion was determined from the relative intensities of the OCH_2 signals for the monomer (multiplet at δ 4.45 ppm) and polymer (m at δ 4.20 ppm).

The number-average and weight-average molar masses (M_n and M_w , respectively) and molar mass distribution (M_w/M_n) of the poly(trimethylene carbonate) (PTMC) samples were determined by size exclusion chromatography (SEC) at 35 °C with a Waters 712 WISP high-speed liquid chromatography equipped with a R410 refractometer detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. A SHODEX pre-column (polystyrene AT806M/S $M_w = 50\,000\,000$ g/mol) and a STYRAGEL column (HR 4E, 50–100 000 g/mol) were used. Calibrations were performed using polystyrene standards (400–100 000 g/mol) and raw values of $M_n(\text{SEC raw})$ were thus obtained.

These values were corrected using the correction factors X determined by Guillaume:¹⁹

- $X = 0.57$ for $M_n(\text{SEC raw}) < 5000$ g/mol;
- $X = 0.88$ for $M_n(\text{SEC raw}) > 10\,000$ g/mol;
- within the range $5000 < M_n(\text{SEC raw}) < 10\,000$, a linear relationship between X and M_n is applied, giving $M_n(\text{SEC}) = 7 \times 10^{-5} \times M_n(\text{SEC raw})^2 + 0.18 \times M_n(\text{SEC raw})$ ($X = 7 \times 10^{-5} \times M_n(\text{SEC raw}) + 0.18$).

The exact number-average molar masses were determined by size exclusion chromatography (SEC) at 40 °C with a Waters e2695 liquid chromatograph equipped with a minDAWN light scattering detector instrument (three angles) and using the refractive index increment $dn/dc = 0.041$ mL/g.²⁰ Tetrahydrofuran was used as the eluent and the flow rate was set up at 1.0 mL/min. A SHODEX pre-column (polystyrene AT806M/S $M_w = 50\,000\,000$ g/mol) and two SHODEX columns (KF 802.5, 50–20 000 g/mol and KF 804, 400 000 g/mol) were used.

Electrospray-ionization mass spectra (ESI-MS) were performed on a Perkin-Elmer Sciex API-365 spectrometer operating in positive ion mode. Samples were dissolved in acetonitrile, doped with traces of ammonium hydroxide and infused with a syringe pump at 5 mL/min.

MALDI-TOF-MS analyses were performed on a MALDI Micro MX from Waters equipped with a 337 nm nitrogen laser. An accelerating voltage of 20 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer sample was dissolved in CH_2Cl_2 at a concentration of 1 mg/mL. The cationization agent used was NaI dissolved in MeOH at a concentration of 10 mg/mL. The matrix used was dithranol and was dissolved in CH_2Cl_2 at a concentration of 10 mg/mL. Solutions of matrix, salt, and polymer were mixed in a volume ratio of 3:1:1 respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectrum was recorded in the reflectron mode. Baseline corrections and data analyses were performed using MassLynx version 4.1.

Typical Polymerization Procedure. Trimethylene carbonate (550 mg, 5.4 mmol, 40 equiv) was dissolved in toluene (6 mL, $[\text{TMC}]_0 = 0.9$ mol/L). The initiator, *n*-pentanol (15 μL , 0.13 mmol, 1 equiv), and the catalyst, methanesulfonic acid (9 μL , 0.13 mmol, 1 equiv), were successively added. The reaction mixture was stirred at 30 °C for 5 h (until the complete consumption of TMC as monitored by ^1H NMR spectroscopy). The mixture was then neutralized with an excess of *N,N*-diisopropylethylamine and concentrated under vacuum. The polymer was dissolved in a minimum of dichloromethane and precipitated in cold methanol, then filtered and dried under vacuum. Yield: 90%. ^1H NMR (CDCl_3 , 300 MHz): 4.28 (t, 2H, $J = 6.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 4.21 (t, 4H \times 39, $J = 6.3$ Hz, $n\text{OCH}_2$), 4.11 (t, 2H, $J = 6.7$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.72 (t, 2H, $J = 6.0$ Hz, HOCH_2), 2.03 (pqt, 2H \times 40, $J = 6.3$ Hz, $n\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.90 (pqt, 2H, $J = 6.1$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 1.65 (m, 4H, CH_2), 1.33 (m, 2H, CH_2), 0.89 (t, 3H, $J = 7.2$ Hz, CH_3); SEC (THF, on the reaction crude): $M_n \sim 2900$ g/mol, $M_w/M_n = 1.13$.

General Procedure for the Multi-Feed Experiment. Trimethylene carbonate (140 mg, 1.4 mmol, 10 equiv) was dissolved in toluene (1.5 mL, $[\text{TMC}]_0 = 0.9$ mol/L). The initiator, *n*-pentanol (15 μL , 0.14 mmol, 1 equiv), and the catalyst, methanesulfonic acid (27 μL , 0.42 mmol, 3 equiv), were successively added. The reaction mixture was stirred at 30 °C for 45 min. (until the complete consumption of TMC, as monitored by ^1H NMR spectroscopy). Polymerization was then restarted with 10 equiv of TMC and this operation was repeated two more times, until reaching 40 equiv of TMC. The mixture was then neutralized with an excess of *N,N*-diisopropylethylamine and concentrated under vacuum. ^1H NMR spectroscopy showed complete consumption of TMC and SEC analysis indicated the formation of a PTMC with $M_n = 4100$ g/mol and $M_w/M_n = 1.10$. The polymer was dissolved in a minimum of dichloromethane and precipitated in cold methanol, then filtered and dried under vacuum. Yield: 87%.

General Procedure for the Continuous-Feed Experiment. Trimethylene carbonate (275 mg, 2.8 mmol, 10 equiv) was dissolved in toluene (3 mL, $[\text{TMC}]_0 = 0.9$ mol/L). The initiator, *n*-pentanol (30 μL , 0.28 mmol, 1 equiv), and the catalyst, methanesulfonic acid (53 μL , 0.84 mmol, 3 equiv), were successively added. The reaction mixture was stirred at 30 °C for 45 min. In a 20 mL syringe, 1.9 g of TMC was dissolved in 20 mL of toluene and

Table 1. ROP of TMC Initiated by Water and Catalyzed by RSO₃H (R = CF₃, CH₃)^a

run	catalyst	<i>T</i> (°C)	[TMC] ₀ /[RSO ₃ H] ₀ /[H ₂ O] ₀	time (h) ^b	<i>M</i> _n ^{c,d}	<i>M</i> _w / <i>M</i> _n ^c	<i>x</i> / <i>y</i> ^e
1	MSA	30	40/1/1	2.5	2400	1.08	100/0
2	HOTf	30	40/1/1	1.5	3500	1.18	99/1
3	MSA	30	40/3/1	1.5	2350	1.09	100/0
4	HOTf	30	40/3/1	1.5	2900	1.21	98/2
5	MSA	30	40/6/1	0.75	2400	1.10	100/0
6	HOTf	30	40/6/1	3.5	1800	1.61	97/3
7	MSA	80	80/1/1	1.5	5800	1.17	100/0
				2.5	5800	1.27	100/0
8	HOTf	80	80/1/1	1	1400	4.39	96/4
				2.5	1100	5.31	91/9

^a Polymerizations of 0.9 mol/L solutions of TMC carried out in toluene. ^b Otherwise stated, polymerization time necessary to achieve monomer conversion >96% according to ¹H NMR spectroscopy. ^c Number-average molar mass (*M*_n) and molar mass distribution (*M*_w/*M*_n) obtained from size exclusion chromatography analysis (in tetrahydrofuran, THF) using polystyrene standards and correction factors.¹⁹ ^d *M*_{n(th)} = 4 036 g/mol, as calculated from the molar mass of TMC (102 g/mol) × the monomer/initiator ratio plus the molar mass of the initiator (18) minus the molar mass of carbon dioxide eliminated at the initiation (44). ^e Carbonates units/ether units determined by ¹H NMR spectroscopy.

added to the reaction mixture at a flow rate of 0.07 mL/min. After the end of the addition, the reaction was stirred 30 more minutes until the complete consumption of TMC, as monitored by ¹H NMR spectroscopy. The mixture was then neutralized with an excess of *N,N*-diisopropylethylamine and concentrated under vacuum. SEC analysis indicated the formation of a PTMC with *M*_n = 8 640 g/mol and *M*_w/*M*_n = 1.12. The polymer was dissolved in a minimum of dichloromethane and precipitated in cold methanol, then filtered and dried under vacuum. Yield: 84%.

Results and Discussion

1. Comparison of HOTf and MSA as Catalysts in the ROP of TMC Initiated by H₂O. The catalytic activities of MSA and HOTf toward the ROP of TMC were first evaluated using water as the protic initiator. 40 equiv of monomer were reacted with 1 equiv of water in toluene solution, [TMC]₀ = 0.9 mol/L, at 30 °C in the presence of 1 equiv of the acid catalyst. In both cases the monomer was completely consumed in less than 3 h [see Table 1, 2.5 h for MSA (run 1) and 1.5 h for HOTf (run 2)] to yield, according to SEC analysis, PTMC of narrow molar mass distribution (*M*_w/*M*_n = 1.08 and 1.18, respectively). These results are in agreement with the ability of MSA to promote the ROP of 4,4-dimethyltrimethylene carbonate under mild conditions, as previously reported by Nakano.¹⁷ In addition, the similar activity of HOTf and MSA, despite their significant difference in acidity (Hammett acidity: MSA = −1; HOTf = −14),²¹ parallels what we observed toward the ROP of ε-caprolactone.⁸ The structure of the obtained polymers was assessed spectroscopically. The ¹H NMR spectra showed the typical signals for PTMC. The sample prepared with HOTf also displays a weak triplet signal at 3.47 ppm associated with ether linkages, indicating that undesirable decarboxylation had occurred (Figure S1). Upon forcing the reaction conditions (increasing the acid to initiator ratio or raising the temperature reaction), the amount of ether linkages slightly increases with HOTf (see runs 2, 4, 6, and 8 in Table 1). Comparatively, no sign of decarboxylation was observed with MSA even when the polymerization temperature was raised up to 80 °C or when 6 equiv of acid catalyst were used (see runs 1, 3, 5, and 7 in Table 1). Similarly to what has been observed for the ROP of ε-caprolactone,⁸ increasing the HOTf to initiator ratio has also a deleterious effect on the polymerization in terms of activity (reaction time increased from 1.5 to 3.5 h when the ratio was increased from 1 to 6, runs 2 and 6) and control (molar mass distribution raised from 1.18 to 1.61). In marked contrast, increasing the MSA/initiator ratio resulted in shorter reaction times (45 min compared to 1.5 h, runs 1 and 5) without broadening of the molar mass distribution

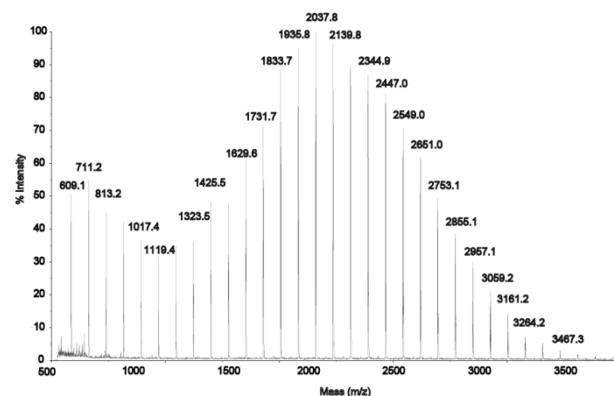
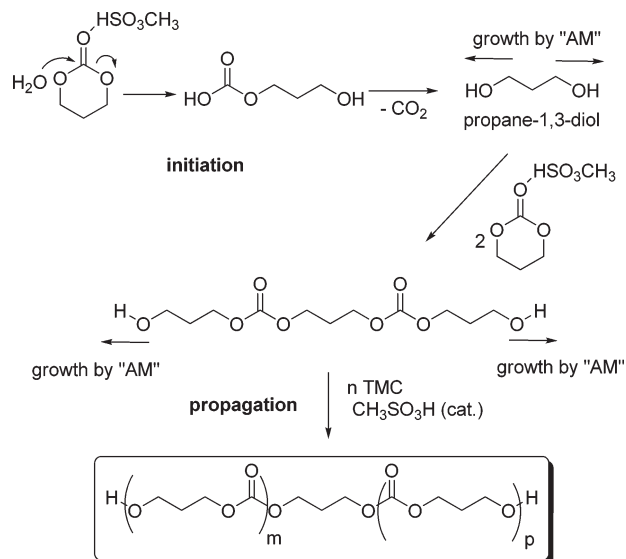


Figure 1. MALDI-TOF MS (region *m/z* 500 to 3800) of a PTMC prepared by polymerization of TMC with H₂O (toluene, 30 °C, [TMC]₀/[H₂O]₀/[MSA] = 40/1/1, [TMC]₀ = 0.9 mol/L). *M* = 18(*M*_{H₂O}) + *n* × 102(*M*_{TMC}) − 44(CO₂) + 23(Na⁺).

(*M*_w/*M*_n < 1.17 in all cases). The different behavior of HOTf and MSA with respect to the catalyst to initiator ratio may result from competition between the activation of the monomer and the deactivation of the initiating/propagating alcohol.⁸

2. Characteristics of the ROP of TMC Catalyzed by MSA.

Taking into account the differences observed between the two sulfonic acids, our attention was then focused on the ROP of TMC catalyzed by MSA. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the polymer obtained by ROP of 40 equiv of TMC with water as initiator and MSA as catalyst showed the exclusive presence of peaks corresponding to polymer chains of molar mass *M*_{PTMC} = *n* × 102(*M*_{TMC}) + 76 (Figure 1). These mass peaks suggest the incorporation of the initiator in the polymer chains (H₂O) but also the loss of one equiv of CO₂ per chain resulting in polymer chains with molar mass *M* = (*n* + 1) × 102(*M*_{TMC}) + 18(*M*_{H₂O}) − 44. This CO₂ loss can be explained by the fact that the addition of water to TMC leads to a carbonic acid, that spontaneously decarboxylates²² to give propan-1,3-diol (*M* = 76 g/mol) (Scheme 1). This diol then acts as a protic initiator in the ROP of the remaining TMC. The resulting polymer is in fact formally initiated by propan-1,3-diol rather than by water itself. This type of initiation had already been described by Endo for the ROP of 1,3-dioxepan-2-one (the parent seven-membered cyclic carbonate) catalyzed by HCl·Et₂O.¹⁵ It leads to well controlled chain ends, but careful analysis of the SEC data of the PTMC obtained by polymerizations with *M*/*I* = 40 and 80 revealed that the observed *M*_n values were much lower than the expected ones (2400 and 4200 g/mol, respectively,

Scheme 1. ROP of TMC Initiated by Water and Catalyzed by MSA: Activated Monomer (AM) Mechanism**Table 2. ROP of TMC Catalyzed by MSA and Initiated by Water or *n*-Pentanol^a**

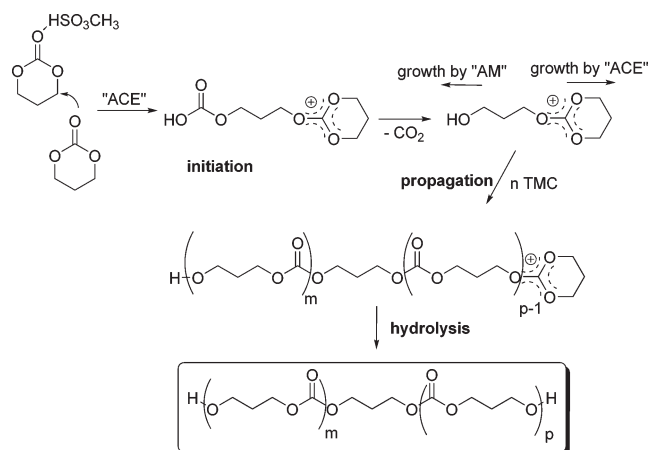
run	initiator	$[\text{M}]_0/[\text{I}]_0$	time (h) ^b	M_n^c	M_w/M_n^c
1	H_2O	40	2.5	2400	1.08
2	H_2O	80	6	4200	1.08
3	PentOH	10	1	850	1.26
4	PentOH	20	1.5	1500	1.28
5	PentOH	40	5	2900	1.13
6	PentOH	80	8	5900	1.17

^a Polymerizations of 0.9 mol/L solutions of TMC carried out in toluene at 30 °C, $[\text{MSA}]_0/[\text{H}_2\text{O}]_0 = 1$ and $[\text{MSA}]_0/[\text{PentOH}]_0 = 1$.
^b Otherwise stated, polymerization time necessary to achieve monomer conversion >96% according to ^1H NMR spectroscopy. ^c Number-average molar mass (M_n) and molar mass distribution (M_w/M_n) obtained from size exclusion chromatography analysis (in tetrahydrofuran, THF) using polystyrene standards and correction factors.¹⁹

instead of 4054 and 8134 g/mol, Table 2), suggesting that more than one polymer chain grows per initiator.

From a mechanistic viewpoint, an activated monomer (AM) mechanism is conceivable, by analogy with that reported for the ROP of lactones.^{7,8} The monomer, activated by the acid catalyst, would undergo nucleophilic attack at the carbonyl carbon atom by the alcohol initiator. Ring-opening (*O*-acyl cleavage) would then lead to the formal insertion of the monomer unit in the OH bond of the initiator (Scheme 1). The polymer growth would then occur by repetition of the same AM process, the alcohol resulting from the ring-opening of TMC acting as the propagating species. In this particular case, the protic initiator would be the propan-1,3-diol resulting from ring-opening of one monomer by H_2O and subsequent decarboxylation. Propagation would take place from both hydroxyl groups, leading to a dihydroxylated PTMC.

An active chain end mechanism (ACE) can also be envisaged (Scheme 2). Here, the monomer activated by the acid catalyst would ring-open by *O*-alkyl bond cleavage, as the result of nucleophilic attack of another, nonactivated monomer molecule. At this stage, spontaneous decarboxylation would give a difunctional compound featuring hydroxyl and oxonium terminal moieties. These two chain ends would then enable polymer growth via two different propagation mechanisms, AM from the hydroxyl chain end and ACE from the oxonium chain end. This ACE growth mechanism

Scheme 2. ROP of TMC Catalyzed by MSA: Activated Monomer (AM)/Active Chain End (ACE) Bidirectional Propagation

consisting on iterative nucleophilic attack of free monomer on the oxonium chain end, has already been proposed by Kricheldorf and Endo in the case of CH_3OTf -promoted ROP of cyclic carbonates in the absence of protic initiator.^{23,24} Propagation through this bidirectional AM/ACE mechanism would lead, after hydrolysis of the oxonium active chain end, to polymers of similar structures than those deriving from the pure AM mechanism. Hydrolysis/alcoholysis of the oxonium may also occur during the polymerization, inducing a shift from AM/ACE propagation to bidirectional AM propagation. Notwithstanding, the occurrence of the ACE/AM bidirectional propagation simultaneously to the AM one would lead to the growth of more than one polymer chain per initiator, something that is consistent with the low M_n values observed experimentally. However, direct evidence for the coexistence of the two mechanisms is hampered by the identical structure of the obtained polymers.

3. Characteristics of the ROP of TMC Catalyzed by MSA and Initiated with an Alcohol. To shed more light on the possible occurrence of the two mechanisms discussed above, the polymerization of TMC was then investigated using an alcohol as initiator, namely *n*-pentanol. Various PTMC were prepared in toluene at 30 °C in the presence of 1 equiv of MSA with monomer to initiator ratios (M/I) varying from 10 to 80 (Table 2). In all cases the polymerization times required to achieve complete monomer conversion were about twice as long as those observed with H_2O as initiator (when 40 equiv of TMC were reacted with 1 equiv of *n*-pentanol, the monomer was totally consumed in 5 h, compared to 2.5 h. when water was used as the initiator). This is consistent with the mono- versus difunctional character of the initiator (water reacts with TMC to give propan-1,3-diol). SEC analyses revealed that the experimental M_n values are lower than those expected from the M/I ratios (Figure 2), the deviation increasing with the M/I ratio, while the molar mass distribution remain rather narrow. The polymers obtained from M/I ratios superior to 10 displayed SEC traces with bimodal character, with a minor population appearing at shorter elution times. Nakano had made similar observations for the MSA-catalyzed ROP of 4,4'-dimethyl-TMC and concluded that side reactions such as back-biting occurred during the polymerization reaction.¹⁷ Transfer reactions between polymer chains and back-biting reactions might lead to a broadening of the molar mass distribution and/or to the formation of macrocycles.

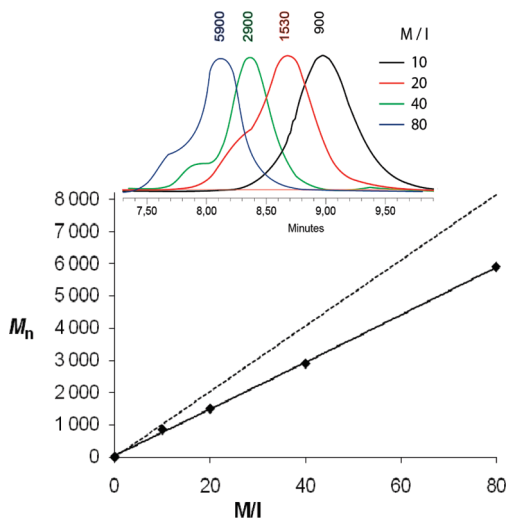


Figure 2. SEC traces and plot of number-average molar mass M_n (◆) (estimated by size exclusion chromatography SEC) versus monomer to initiator ratio. Dotted line: Theoretical number-average molar masses (polymerization conditions: toluene, 30 °C, $[TMC]_0/[n\text{-pentOH}]_0/[MSA] = 40/1/1$, and $[TMC]_0 = 0.9$ mol/L).

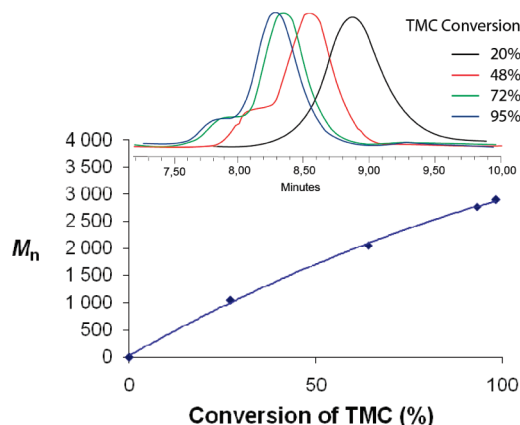


Figure 3. Plot of number-average molar masses M_n (estimated by size exclusion chromatography SEC) versus monomer conversion (toluene, 30 °C) and SEC traces. (Polymerization conditions: $[TMC]_0/[n\text{-pentOH}]_0/[MSA] = 40/1/1$, toluene, 30 °C, $[TMC]_0 = 0.9$ mol/L).

Furthermore, the plot of M_n versus monomer conversion for a polymerization carried out with a monomer to initiator ratio of 40 revealed that polymer chains grow regularly at low conversions, but a deviation from linearity is observed when the monomer conversion exceeds 30% (Figure 3). This lost of linearity is also observed in the semi-logarithmic plot of monomer conversion versus time (Supporting Information, Figure S3).

The ^1H NMR data of the PTMC prepared with $M/I = 40$ (Figure 4a) confirmed the incorporation of the initiating group to the polymer as an ester chain end, with the characteristic signals of a pentyl ester being observed at 0.95 ppm (CH_3 , a) and 4.05 ppm (OCH_2 , b). However, the integration of these signals relative to the one associated with the CH_2OH chain end (e) deviates significantly from the values expected for exclusive initiation by the alcohol (4.74 for e when the integrals of a and b are calibrated to 3.00 and 2.00, respectively). This deviation is almost negligible for a monomer to initiator ratio of 10 (Supporting Information, Figure S4a), and it becomes more and more significant as the M/I ratio increases. Both SEC analyses and NMR spectroscopy

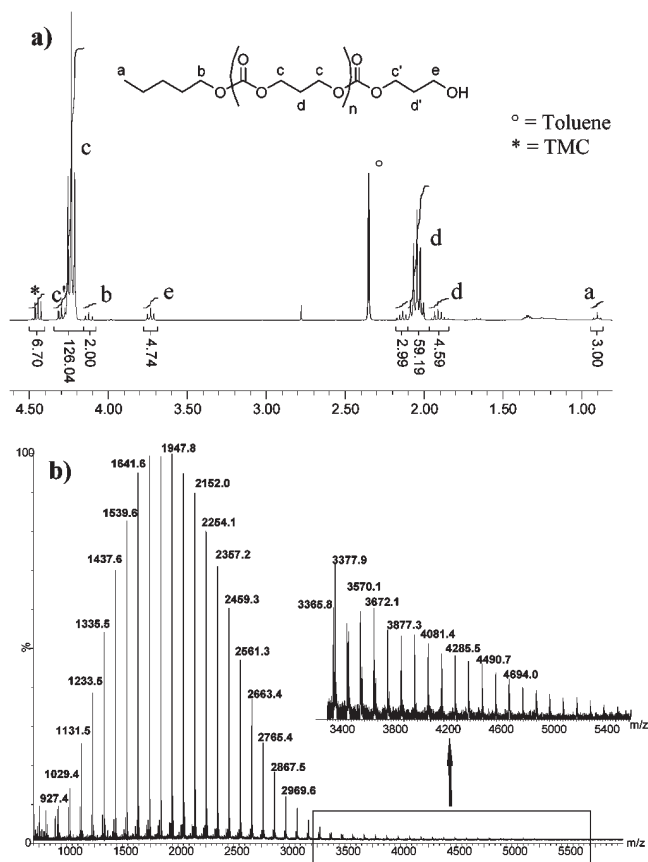
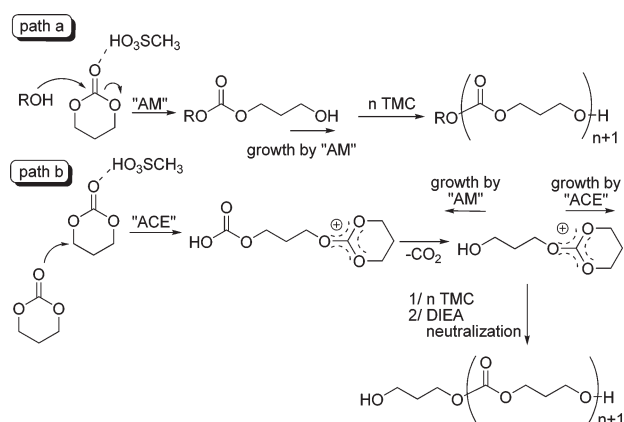


Figure 4. (a) ^1H NMR spectrum (CDCl_3 , 300 MHz) of a PTMC. (b) MALDI-TOF MS (region m/z 1000 to 5500) of a PTMC. $M = 88(M_{n\text{-pentOH}}) + n \times 102(M_{TMC}) + 23(\text{Na}^+)$ and $M = 76(M_{\text{propan-1,3-diol}}) + n \times 102(M_{TMC}) + 23(\text{Na}^+)$ in the region m/z 3300 to 5500 (polymerization conditions: $[TMC]_0/[n\text{-pentOH}]_0/[MSA] = 40/1/1$, toluene, 30 °C, and $[TMC]_0 = 0.9$ mol/L).

thus seem to indicate the presence of a minor population with linear architecture and at least one hydroxyl chain end. This fact was further confirmed by MALDI-TOF-MS analysis. The MALDI-TOF-MS spectrum shows the presence of a main population of polymer chains corresponding to the molar mass $M = 88(M_{n\text{-pentOH}}) + n \times 102(M_{TMC})$, resulting from the “regular” initiation with n -pentanol. No peaks attributable to macrocycles were detected, but a second polymer population was found at higher masses, corresponding to the molar mass $M = n \times 102(M_{TMC}) + 76$ (see Figure 4b). Taking into account the results obtained with water as initiator, this second population can be attributed to the initiation with propan-1,3-diol, suggesting competitive initiation with residual water. However, ESI-MS of a PTMC prepared with a monomer to initiator ratio of 10 (the one presenting a monomodal SEC trace) showed a single population of polymer chains corresponding to the molar mass $M = 88(M_{n\text{-pentOH}}) + n \times 102(M_{TMC})$, denoting exclusive initiation with n -pentanol (Supporting Information, Figure S4b). In order to confirm or discard the competitive initiation with water, three polymerization reactions were carried out under the same conditions with TMC of different degrees of purity (see Supporting Information, Table S1). The three reactions led to the same results in terms of time reaction, molar masses and extent of the second population in the SEC traces, supporting that water content in the monomer is not at the origin of the second population. All these results strongly suggest that a competitive polymerization mechanism occurs for high M/I ratios.

Scheme 3. ROP of TMC Catalyzed by MSA and Initiated with *n*-Pentanol: Activated Monomer (AM) and Active Chain End (ACE) Mechanisms and the Resulting Polymers



In agreement with that previously discussed for water initiation, the typical AM mechanism can explain the main population (path a, AM, Scheme 3). The minor population can be explained by the occurrence of the ACE mechanism, an hydroxyl–oxonium species allowing bidirectional growth of the polymer via a combination of AM and ACE (path b, ACE–AM, Scheme 3). After neutralization with *N,N*-diisopropylethylamine and hydrolysis, the AM–ACE polymer can be formally considered as being initiated by propan-1,3-diol. In contrast to that observed in the polymerization reactions initiated with water, these two competitive propagation pathways lead here to two different polymer structures that can be differentiated analytically. MALDI–TOF–MS spectrometry allows direct observation of the two PTMC populations. The coexistence of the two mechanisms is consistent with all the observations discussed above: (i) the obtained M_n values are lower than those expected from the monomer feed, and (ii) the integration of the ^1H NMR signal associated with the hydroxyl chain end CH_2OH exceeds that associated with the CH_2OCO moiety of the pentyl ester chain end.

Such a competition between AM and ACE mechanisms has already been reported by Penczek and Kubisa for the ROP of cyclic ethers (such as ethylene oxide, epichlorhydrin, or glycidol) catalyzed by Brønsted acids in the presence of alcohols as initiators.²⁵ Here, the incidence of the ACE mechanism is all the more important that the nucleophilicity of the cyclic ethers (monomers) approaches that of the alcohols (initiating/propagating species). In contrast, the possible occurrence of the ACE mechanism has been recently discarded in the HOTf-catalyzed ROP of lactide,^{7d} and to the best of our knowledge, there is no experimental evidence for significant contribution of this ACE mechanism in the Brønsted acid-catalyzed ROP of lactones and dilactones.^{7,8} The higher nucleophilicity of cyclic carbonates is likely at the origin of the occurrence of the ACE mechanism evidenced in this work for the MSA-catalyzed ROP of TMC.

From a practical viewpoint, the coexistence of the AM and ACE mechanisms prevents from good control of the polymerization and leads to several polymer populations.²⁵ Efforts have thus been devoted to reduce as much as possible the incidence of the ACE mechanism. In particular, it was found that the AM mechanism can be favored by slow addition of the monomer, so as to decrease its proportion relative to the propagating alcohols.^{25b} For example, slow continuous addition of propylene oxide (PO) was found to efficiently minimize the ACE mechanism and improve the control of

Table 3. ROP of TMC Catalyzed by MSA and Initiated by *n*-pentanol^a

$[\text{M}]_0/[\text{I}]_0$	time (h) ^b	$M_{n(\text{th})}$ ^c	M_n ^d	M_w/M_n
40	3	4080	2900	1.13
40 ^e	3	4080	4100	1.10
80	5	8248	6200	1.17
80 ^f	6	8248	8640	1.12

^a Polymerizations of 0.9 mol/L solutions of TMC carried out in toluene at 30 °C, $[\text{MSA}]_0/[\text{I}]_0 = 3$. ^b Polymerization time necessary to achieve monomer conversion > 95% according to ^1H NMR spectroscopy.

^c Calculated from $[M_{n-\text{pentOH}} + ([\text{M}]_0/[\text{I}]_0 \times M_{\text{TMC}})] \times \text{conversion}$.

^d Number-average molar mass (M_n) and molar mass distribution (M_w/M_n) obtained from Size Exclusion Chromatography analysis (in tetrahydrofuran, THF) using polystyrene standards and correction factors.¹⁹

^e 4-fold addition of TMC. ^f Continuous feed of TMC.

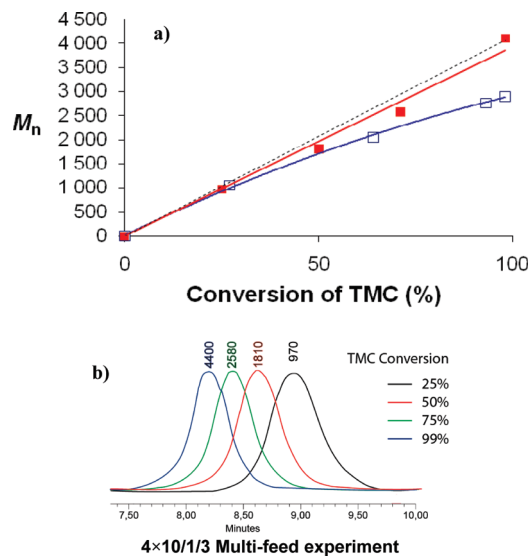


Figure 5. (a) Plot of number-average molar mass M_n (estimated by size exclusion chromatography SEC) versus monomer conversion (toluene, 30 °C) for a one feed experience ($[\text{TMC}]_0/[\text{n-pentOH}]_0/[\text{MSA}]$ 40/1/3, $[\text{TMC}]_0 = 0.9$ mol/L) (\square) and a multiple feed experience ($4 \times [\text{TMC}]_0/[\text{n-pentOH}]_0/[\text{MSA}]$ 10/1/3, $[\text{TMC}]_0 = 0.9$ mol/L) (\blacksquare) (dotted line: theoretical values calculated from $[M_{n-\text{pentOH}} + ([\text{M}]_0/[\text{I}]_0 \times M_{\text{TMC}})] \times \text{conversion}$). (b) SEC traces for the multiple feed experience.

the polymerization, as long as the $[\text{PO}]:[\text{alcohol}]$ ratio is low enough (< 0.1 – 0.2).²⁶ It was thus tempting to evaluate if a similar approach could be applied to the polymerization of TMC catalyzed by MSA in order to obtain well-controlled PTMC with end-group fidelity.

4. Influence of the Polymerization Conditions on the Incidence of the AM/ACE Mechanisms. As discussed above, a monomodal distribution was observed in SEC and a unique polymer population was detected by MALDI–TOF–MS when the initial monomer to initiator ratio was set to 10 (see section 3). With this in mind, we decided to investigate the influence of the instantaneous monomer concentration by comparing two polymerization experiments differing in the way the monomer was added (Table 3): (i) a unique feed of 40 equiv of TMC relative to PentOH (that is to say $[\text{M}]_0/[\text{I}]_0 = 40$), and (ii) taking advantage of the living character of the polymerization, a quadruple-feed of 10 equiv of TMC, so that the $[\text{M}]/[\text{ROH}]$ ratio is maintained below 10.

In contrast with the bimodal distribution observed for the one feed experiment (Figure 3), monomodal SEC traces were obtained at all stages of the polymerization for the multi-feed experiment (Figure 5). The molar mass of the polymer chains increases linearly with monomer conversion, and the final M_n matches that expected from the initial monomer to

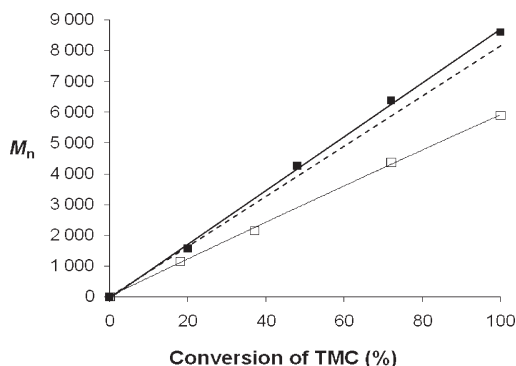


Figure 6. Plot of number-average molar mass M_n (estimated by size exclusion chromatography SEC) versus monomer conversion (toluene, 30 °C) (□) ($[TMC]_0/[n\text{-pentOH}]_0/[MSA] = 80/1/3$, $[TMC]_0 = 0.9$ mol/L) and a continuous feed experience (■) ($[TMC]_0/[n\text{-pentOH}]_0/[MSA] = 10 + 70/1/3$, $[TMC]_0 = 0.9$ mol/L).

initiator ratio ($M_{n(\text{exp})}$ 4100 and $M_{n(\text{th})}$ 4080). Moreover, the ^1H NMR spectrum showed integration values close to those expected for exclusive initiation by the exogenous alcohol and a unique polymer population resulting from AM propagation was detected by MALDI-TOF-MS (Supporting Information, Figure S5). All these features are consistent with the propagation proceeding predominantly via the AM mechanism and negligible contribution of the ACE mechanism.

Encouraged by these results, we studied the preparation of a PTMC of higher molar mass ($[M]_0/[I]_0 = 80$) via continuous addition of the monomer rather than multiple feed. Accordingly, a toluene solution of TMC (70 equiv, 0.9 mol/L) was slowly added on a toluene solution containing 10 equiv of TMC, 1 equiv of *n*-pentanol, and 3 equiv of MSA. The TMC feed was performed over 5 h at a flow rate of 0.07 mL/min so that the monomer to alcohol ratio was maintained below 8. SEC analysis of the obtained PTMC showed a monomodal but slightly dissymmetric trace, and consistently, MALDI-TOF-MS indicated the presence of only a very small amount of the polymer population resulting from the ACE mechanism (Figure S6). The molar mass of the polymer chains increases linearly with monomer conversion (Figure 6), and the final molar mass ($M_n = 8640$) matches the targeted one ($M_{n(\text{th})} = 8248$), in marked contrast with that observed for the one feed experience ($M_n = 6200$). From these data as a whole, it appears that the incidence of the undesirable ACE mechanism can be significantly reduced by decreasing the instantaneous monomer concentration, so that well-controlled polymerization of TMC can be achieved with MSA as catalyst.

Conclusion

Methanesulfonic acid was found to be a better organocatalyst than trifluoromethanesulfonic acid for the ROP of trimethylene carbonate. In the presence of a stoichiometric amount of initiator, similar polymerization kinetics were observed for the two acids despite the fact that MSA is less acidic than HOTf by more than 10 units in pK_a . Therefore, activity does not simply correlate with acidity, similarly to what was observed toward ϵ -caprolactone. In contrast with HOTf, MSA does not induce undesirable decarboxylation reactions even under forcing conditions and thus affords poly(trimethylene carbonate) free of ether linkages. Detailed investigation of the water and alcohol-initiated polymerizations by size exclusion chromatography, ^1H NMR spectroscopy and mass spectrometry revealed the coexistence of two polymerization pathways. The activated-monomer mechanism

typically encountered in Brønsted acid-catalyzed ROP of lactones and dilactones is accompanied in the case of TMC by some active chain end propagation. Such a competition between AM and ACE mechanisms had been reported for the ROP of cyclic ethers, but was unprecedented for cyclic carbonates. The ACE mechanism has a detrimental effect over the polymerization control, but its incidence can be significantly limited by lowering the instantaneous monomer concentration via multifeed or continuous addition. This study affords better understanding of the sulfonic acid-catalyzed ROP of cyclic carbonates and provides an efficient access to PTMC of controlled molar mass with high end-group fidelity.

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Supporting Information Available: Table S1, giving ROP data for TMC, and Figures S1–S5, showing ^1H NMR spectra, overlapping of SEC RI and viscosimetric/MALS traces, and a semi-logarithmic plot of monomer conversion versus time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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