Cationic Ring-Opening Polymerization of Oxetane via a Non-Steady-State Controlled Polymerization Process: A Comparison of Initiators Yielding Living and Nonliving Polymers

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ABSTRACT: Our investigations of the cationic ring-opening polymerization of oxetane via active chain end (ACE) mechanism have shown that the use of 1,4-dioxane as solvent can prevent intra- and intermolecular transfer reactions (Scheme 1, part a). Using 3-phenoxypropyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate as a model of an initiator capable of yielding fast initiation, polymers with predictable number-average molecular weight (up to 160 000 g/mol), narrow molecular weight distribution ($1.18 < M_w/M_{n,GPC} < 1.28$) were produced with no cyclic oligomer formation. On the basis of the kinetic data, a mechanism of controlled and living polymerization has been proposed in which the rate of mutual conversion between "*strain ACE species*" (chain terminated by a *tertiary 1-oxoniacyclobutane ion,* A1) and "*strain free ACE species*" (chain terminated by a *tertiary 1-oxonia-4-oxacyclohexane ion,* T1) does not obey a quasi-steady-state assumption but depends on the rate at which the monomer converts the *stable species* T1 into a *living "propagating" center* A1($d[A1]/dt = -d[T1]/dt \neq 0$). With $BF_3{\cdot}CH_3OH$ (i.e., initiator yielding a slow initiation), a drift of the linear dependence $M_{n,GPC}$ vs conversion to lower molecular weight were observed together with the production of cyclic oligomers, ∼10% of the monomer consumed in 1,4-dioxane against ∼ 30% in dichloromethane.

Introduction

The cationic ring-opening polymerization (CROP) of oxolane (tetrahydrofuran)[1] and oxepane[2] by an active chain end (ACE) mechanism is often described as "living". Although studies of the polymerization of these monomers provided indisputable evidence for the absence of termination reactions, complete control over either number-average molecular weight (M_n) or molecular weight distribution (M_w/M_n) is not possible at every temperature below the ceiling temperature when polymerization takes place close to the equilibrium monomer concentration.[3] If narrow molecular weight distributions are required, polymerization in these systems must be limited to low conversions. This is the case of the cationic polymerization of tetrahydrofuran initiated by triflate ester group.[4] The main characteristics of tetrahydrofuran[3,4] polymerization are also found in the cationic polymerization of oxirane[5] and oxetane[6−8] monomers, though intra- and intermolecular transfer reactions (Scheme 1, part a) are more significant, equilibrium monomer concentrations are lower, and conversion is almost quantitative.

Here we report, for the particular case of the CROP of oxetane in 1,4-dioxane, a new synthetic route that allows controlled polymerization.[9] In this system (Scheme 1, part c), the solvent is used to end-cap the strain *tertiary 1-oxoniacyclobutane* ions A1 (rate constant k_d), producing a less reactive terminal *tertiary 1-oxonia-4-oxacyclohexane* group T1. As T1 is less reactive, then there is greater discrimination between the more nucleophilic oxygen atom in oxetane (rate constants $k_{a(exo)}$ and $k_{a(endo)}$) and in 1,4-dioxane (rate constant k_s) than the less nucleophilic polymer chain ether oxygen atoms (see Figure 1),[10,11] suspending backbiting, reversible transfer and intermolecular transfer reactions during the course of the polymerization. The use of 1,4-dioxane as solvent (so that the rate $R_d > R_{tr}$) is necessary to prevent A1 to undergo transfer reactions (rate R_{tr}) as it occurs in normal polymerization in non-nucleophilic dipolar aprotic solvent (Scheme 1, part a). The other effect is that the chains growth in 1,4-dioxane is initially slowed down ($k_{a(endo)} < k_{a(exo)} < k_p$), allowing for a high initiation rate to propagation rate ratio the production of polymer with low PDI. In this article, the living and/or control polymerization of oxetane in 1,4-dioxane (1,4-D) is discussed when $R{-}CH_2(1,4\text{-}D)^+,[SbF_6]^-$ (3-PPOA with $R- = C_6H_5O(CH_2)_3-$ and EMOA with $R- = C_2H_5OCH_2-$)) and $(BF_3{\cdot}CH_3OH)_{1,4-D}$ are used as initiator capable of yielding fast and slow initiation, respectively.

Experimental Section

Materials. Oxetane (Ox) (Lancaster Synthesis, 99%), 1,4-dioxane (1,4-D) (Aldrich, 99.8%) and dichloromethane (DCM) Hi-dry (Romil Chemical Co., >99.9%) were dried over calcium hydride for 48 h and distilled before use. Ox and 1,4-D were further purified by refluxing over sodium/benzophenone radical anion and then distilled before use. Boron trifluoride-methanol complex (Aldrich, 50% w/w in methanol), silver hexafluoroantimonate (Lancaster Synthesis, 97%) were stored in an argon glovebox and were used without any further purification. 3-Phenoxypropyl bromide (3-PPBr) (Aldrich, 96%) and ethoxymethyl chloride (EMCl) (Aldrich, 95%) were dried over molecular sieve and subsequently over calcium hydride and then distilled just before use. 2,6-Di-*tert*-butylpyridine (DtBP) (Aldrich, ≥97.5%) was vacuum distilled at 90 °C to remove any monosubstituted pyridine. Diphenyl ether (DPE) (Aldrich, 99%) was dried by azeotropic distillation of a trace amount of water from its dry toluene solution and stored in the glovebox without further purification. High purity argon was used to provide an inert atmosphere under which all reactions were carried out.

Synthesis of Initiator. The synthesis in situ of 3-phenoxypropyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (3-PPOA), ethoxymethyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (EMOA), and ethyl oxacarbenium hexafluoroantimonate (EOCA) were based on the reported synthesis described by Burgess et al.[12] The structures are shown in Scheme 2.

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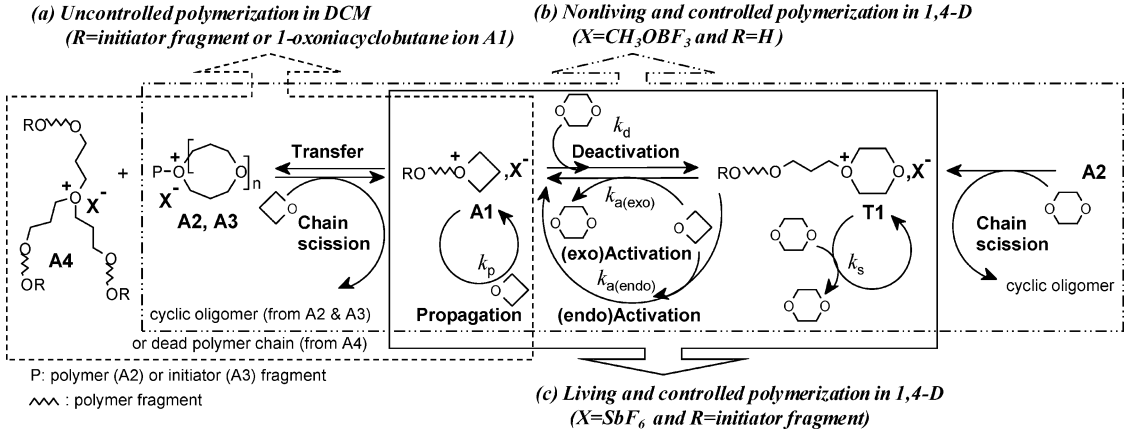
Scheme 1. Mechanism Proposed in Cationic Ring-opening Polymerization of Oxetane via Active Chain End (ACE) Mechanism in Dichloromethane (DCM) and in 1,4-dioxane (1,4-D) at 35 °C



Preparation of 3-PPOA Stock Solution. As an example, 3-PPOA stock solution (28.3 mM) was prepared under argon in the glovebox, the flask protected from the light, by reaction of $AgSbF_6$ (584 mg, 1.7 mmol) with 3-PPBr (332 mg, 1545 μmol) and 60 mL of 1,4-D used as solvent. The colorless mixture was stirred for at least 3 h at room temperature; AgBr precipitated immediately. Because tertiary *1-oxonia-4-oxacyclohexane* salts (or 1,4-dioxonium salts) cannot be prepared under rigorous exclusion of moisture, 1.1 mol equiv of DtBP (380 μL, 1.7 mmol) was used as a non-nucleophilic proton trap in order to neutralize the acid produced during the reaction between cationic species and the traces of water.[13]

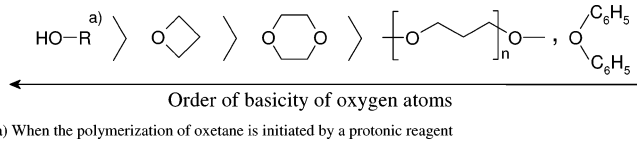
Preparation of EMOA Stock Solution. The preparation in 1,4-D of a 60 mL stock solution of EMOA (16.45 mM) by the reaction of 978 μmol of EMCl (93 mg) with 1085 μmol of $AgSbF_6$ (373 mg) in the presence of 1085 μmol of DtBP (250 μL) was identical to the preparation of 3-PPOA.

Preparation of EOCA Stock Solution. The preparation of a 60 mL stock solution of EOCA (16.4 mM) by the reaction of 968 μmol of EMCl (91.5 mg) and 1065 μmol of $AgSbF_6$ (366 mg) in the presence of 1065 μmol of DtBP (240 μL) was identical to the preparation of 3-PPOA, except that DCM was used as solvent instead of 1,4-D.

Preparation of BF_3·CH_3OH Stock Solution. A 60 mL stock solution of BF_3·CH_3OH (109 mM) in DCM or 1,4-D was prepared in the glovebox.

Polymerization Procedure. A modification of the technique of Biddulph and Plesch[14] was used (Figure S2 in Supporting Information) to monitor the reaction calorimetrically (Figure S1 in Supporting Information). The reactor was flamed under vacuum and cooled down prior to introduction of solvent and monomer through connected storage glass tube. In a typical experiment, 25 mL solution of oxetane in 1,4-D, in 1,4-D/DCM mixed solvent or in DCM were thermostatted at 35 °C under argon. The water from the thermostat bath at 35 °C was continually passed through the outer double jacket. When the system was balanced to 35 °C, 1.9 mL of stock catalyst solution was injected into the calorimeter by means of a bleed valve system. After a proper interval, samples of the polymerizing solution were taken using an anaerobic sampling technique and then quenched by a solution of 10^{-2} M sodium hydroxide in water. The quenched reaction mixture was extracted with DCM and sequentially washed with water to neutralize the pH and to remove the initiator residues and salts. The DCM sample containing the polymer was then dried over $MgSO_4$. The dried polymer solution was filtered and the filtrate washed with dry DCM. The polymer was recovered from the organic layer by removal of the solvent to constant weight. The conversion of oxetane was determined gravimetrically. As an example the results obtained with $[oxetane]_0 = 1.125$ M, $[3\text{-PPOA}]_0 = 1.14$ mM and $[DtBP]_0 = 1.125$ mM in 26.9 mL of 1,4-D for 83% oxetane conversion were as followed: $t = 240$ min, $M_{n,GPC} = 120\,610$ g/mol and $M_w/M_n = 1.23$ (Sample P4.5, Table S2 in Supporting Information).

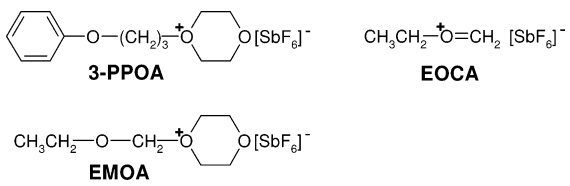
Incremental Monomer Addition Technique. As an example chain extension polymerization in 1,4-D was carried out as described in the polymerization procedure section using 25 mL of oxetane stock solution (4.9 g, 1.21 M) and 1.9 mL of 3-PPOA stock solution (28.3 mM). The initial concentrations were as follows: $[oxetane]_0 = 1.125$ M, $[3\text{-PPOA}]_0 = 2$ mM, and $[DtBP]_0 = 2.2$ mM. After 14 h an aliquot, ~2 mL was taken using anaerobic



a) When the polymerization of oxetane is initiated by a protonic reagent

Figure 1. Order of basicity of oxygen atoms present during the cationic ring-opening polymerization of oxetane.[11]

Scheme 2. Initiators



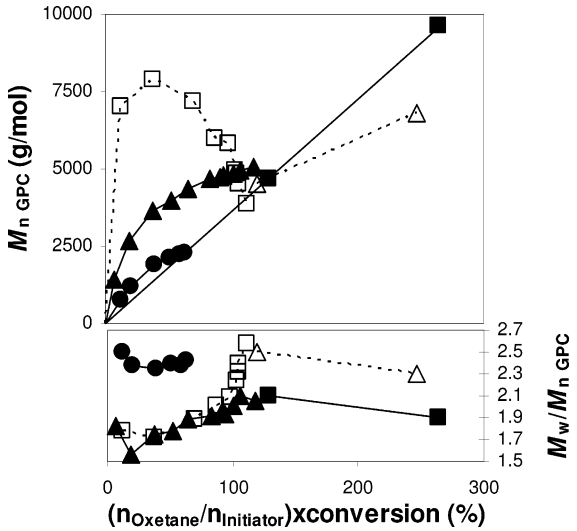


Figure 2. Number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution ($M_w/M_{n,GPC}$) vs ($n_{oxetane}/n_{initiator}$) × conversion for the oxetane (Ox) polymerization in dichloromethane (open symbol) and in 1,4-dioxane (close symbols) at 35 °C with 7.7 mM of BF_3·CH_3OH. Experimental conditions: (□, Δ) $[Ox]_0 = 1$ M; (▲, ■) $[Ox]_0 = 1$ M and $[1,4\text{-D}]_0/[Ox]_0 = 9$; (●) $[Ox]_0 = 0.66$ M and $[1,4\text{-D}]_0/[Ox]_0 = 15.95$. For additional experimental details see Table S1 in Supporting Information.

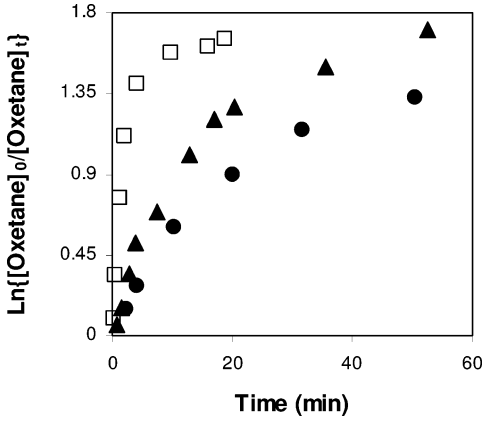


Figure 3. Evolution of $\ln\{[\text{oxetane}]_0/[\text{oxetane}]_t\}$ against time for the oxetane (Ox) polymerization in dichloromethane (open symbol) and in 1,4-dioxane (1,4-D) (close symbols) at 35 °C with 7.7 mM of $BF_3{\cdot}CH_3OH$. Experimental conditions: ([squlo]) $[Ox]_0 = 1$ M; (▲) $[Ox]_0 = 1$ M and $[1,4\text{-D}]_0/[Ox]_0 = 9$; (●) $[Ox]_0 = 0.66$ M and $[1,4\text{-D}]_0/[Ox]_0 = 15.95$. For additional experimental details, see Table S1 in Supporting Information.

sampling technique (conversion = 96% (t = 14 h), M_n = 79 500 g/mol and M_w/M_n = 1.24) followed by the addition of 3 mL of a monomer stock solution (12.9 mL, 9.87 M) containing of DtBP (40 μl, 7.7 mM); conversion = 190% (t = 8 h), M_n = 160 000 g/mol, M_w/M_n = 1.2.

Kinetic Studies by Calorimetric Analysis. Because the cationic ring-opening polymerization of oxetane is an exothermic process ($\Delta H°$ = 80.8 kJ mol^{-1} (19.3 kcal mol^{-1}) at −9 °C in methyl chloride),[6] it was possible to monitor calorimetrically the rate of temperature change (°C s^{-1}) during the polymerization. The deflection was also converted to change in concentration of oxetane (mol L^{-1}) determined gravimetrically. A linear dependence of $((dT/dt)/V)_{t\to 0}$ on $-(d[\text{oxetane}]/dt)_{t\to 0}$ (Figure S1 in Supporting Information) was observed with an intercept close to the origin indicating that the kinetic measurements were performed under adiabatic conditions.

Extraction of Cyclic Oligomers. The extraction of cyclic oligomers (Sample P1.8, Table S1 in the Supporting Information) was carried out using a Soxhlet extractor for 24 h using cyclohexane or *n*-hexane as solvent. The composition of the extracted products was examined by 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectroscopy and mass spectroscopy (Figure S3 in Supporting Information). The ^{1}H and ^{13}C chemical shifts for the various CH_2 groups in poly(oxetane) chains and cyclic oligomers are listed below.

Cyclic Oligomers. ^{1}H NMR ($CDCl_3$, δ ppm): 1.81 (q, 2H, $-OCH_2CH_2CH_2O-$), 3.48 (t, 4H, $-OCH_2CH_2CH_2O-$, $DP_n > 4$), 3.54 (t, 4H, $-OCH_2CH_2CH_2O-$, $DP_n \le 4$). ^{13}C NMR ($CDCl_3$, δ ppm): 30.15 (s, $-OCH_2CH_2CH_2O-$), 67.08 and 67.44 (s, $-OCH_2CH_2CH_2O-$, $DP_n > 4$), 66.07 (s, $-OCH_2CH_2CH_2O-$, $DP_n \le 4$).

Polymer Chains. ^{1}H NMR ($CDCl_3$, δ ppm): 1.82 (q, 2H, $-OCH_2CH_2CH_2O-$), 3.48 (t, 4H, $-OCH_2CH_2CH_2O-$). ^{13}C NMR ($CDCl_3$, δ ppm): 29.76 (s, $-OCH_2CH_2CH_2O-$), 67.49 (s, $-OCH_2CH_2CH_2O-$).

The mass spectroscopy (Figure S3.3 in Supporting Information) showed molecular structures from tetramer to those containing up to 11 oxetane units, the cyclic tetramer being in the greatest abundance.

Measurements. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300.13 MHz for ^{1}H and 75.97 MHz for ^{13}C. $CDCl_3$ was used as the solvent with TMS (δ = 0.00 ppm) and $CDCl_3$ (δ = 77.0 ppm) used as internal reference for ^{1}H and ^{13}C spectra. For ^{13}C NMR analysis the P.E.N.D.A.N.T pulse technique was used, which ensures methyl and methine carbons appear as positive peaks and methylene and quaternary carbon atoms as negative peaks. Gel permeation chromatography (GPC) was performed on a Knauer instrument using a differential refractometer as detector, and two gel columns (supplied by Polymer Laboratories) used in series, 5μ-PL gel columns with exclusion limits of 10^3 Å and a mixed B column. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min at room temperature. The measurements were carried out at ambient temperature. The system was calibrated with polystyrene standards.

Results and Discussions

1. CROP of Oxetane in 1,4-Dioxane Initiated by $BF_3{\cdot}CH_3OH$ at 35 °C. Molecular Weight Control with Cyclic Oligomers Formation. When 7.7 mM of $BF_3{\cdot}CH_3OH$ was used to polymerize 1 M of oxetane in 1,4-D, series P2, the $M_{n,GPC}$ (number-average molecular weight measured by GPC against PS standards) was found to increase but not linearly with $[\text{oxetane}]_0/[BF_3{\cdot}CH_3OH]_0$ × conversion (Figure 2) whereas in DCM, series P1, high $M_{n,GPC}$ are produced at low monomer conversion and then, as soon as one-third of the monomer (∼28.6%) is consumed (i.e., $(n_{Ox}/n_{Initiator})$ × conversion (%) = 3714), the $M_{n,GPC}$ decreases to reach at 80% monomer conversion (i.e., $(n_{Ox}/n_{Initiator})$ × conversion (%) = 10 390) an number-average molecular weight almost identical to that in 1,4-D, decreasing still further at higher conversion. Broad GPC traces ($1.4 < M_w/M_{n,GPC} < 2$) with pronounced tailing were obtained in both solvent (Figures S4 and S5 in Supporting Information), though cyclic oligomers were formed in larger proportion in DCM than in 1,4-D: ∼9% (t = 36 min, conversion = 77.6%) against 28% (t = 10 min, conversion = 79.7%) of the monomer consumed when 1,4-D was used as solvent instead of DCM. The ^{13}C NMR spectra are shown in Figures S3 and S12 in Supporting Information.

The polymerization of 1 M of oxetane with 7.7 mM of $BF_3{\cdot}CH_3OH$ was further studied by chain extension, or incremental monomer addition (Figure 2). In 1,4-D, after withdrawal of 2 mL from polymerizing solution (t = 60 min, conversion = 96%) and addition of 5 mL of oxetane stock solution in 1,4-D (5.8 g, 5 M), $M_{n,GPC}$ increases correspondingly from 4560 to 9200 g/mol after that 80% of the added monomer was consumed (i.e., $(n_{Ox}/n_{Initiator})$ × conversion (%) = 23 920).

In DCM (see Table S1 for experimental conditions), though the redistribution of the MWDs by chains breaking reactions is amplified after each incremental monomer addition (Figure 2 and Table 1), the calorimetric measurement at 35 °C of the initial apparent rate constant of monomer consumption (k_{max}^{app}) showed that the second monomer increment (stage S1.3rd, Table 1) polymerized at nearly the same rate as in the polymerization of the first monomer increment (stage S1.2nd, Table 1). This shows that chain-termination reactions caused by anion-splitting do not proceed to any significant effect. Thus, the curvature of $\ln([\text{oxetane}]_0/[\text{oxetane}]_t)$ vs time (Figure 3) implies that the ACE species coexist in various forms (A1, A2, A3, and A4) and that each has a different reactivity toward the monomer. The mechanism of chain growth, as proposed by Rose,[6] for the CROP of oxetane by ACE mechanism involved competitive reactions between propagation and chain transfer reactions. As depicted in Scheme 1, part a, the possibility that oxetane can regenerate,[8] throughout the polymerization, the growing active centers (A1) by nucleophilic attack of the monomer at one of the three electron deficient α-carbons of the oxonium ion site of the less reactive strain free ACE species (A2, A3, and A4) has to be considered. Here, the fraction of monomer converted into cyclic oligomers (f_{cyclic}) is initiator dependent: ∼30% and 4−6% at ∼85% and 90% monomer conversion with BF_3CH_3OH (9, 7.7 mM, series P1) and EOCA (2 mM in the presence of 2.2 mM of DtBP, series P1), respectively. GPC traces are shown in Figures S4 and S10 in Supporting Information.

The enhancement of the k_{max}^{app} (Table 1) after the first monomer addition in DCM (stage S1.2nd) and in 1,4-D (stage

Table 1. Experimental Results from the Chain Extension Experiments Using BF_3CH_3OH (I) for the Polymerization of Oxetane (Ox) in Dichloromethane (DCM) and in 1,4-dioxane (1,4-D) at 35 °C

stage	$[Ox]_0/[I]_0$, M/mM	$k_{max}^{app}/[I]_0$[b], L mol^{-1} s^{-1} (K L^{-1} s^{-1})	yield, %	$M_{n,th}$, g mol^{-1}	$M_{n,GPC}$, g mol^{-1}	PDI	$f_{1,4;D}$[f], %	f_{cyclic}[g], %
S1.1st [c]	1/7.7	1.25 (11.5)	92 (92[d])	6780	4500	2.4		~33
S1.2nd [c]	1/6.2[a]	1.48 (13.6)	79 (87[d])	14 710	6800	2.3		~32
S1.3rd [c]	1/5.2[a]	1.44 (13.2)	64 (83[d])	21 200	7200	2.4		~28
S2.1st [c]	1/7.7	0.27 (1.39)[e]	96 (96[d])	7800	4560	2.1	~6	~9
S2.2nd [c]	1/6.2[a]	0.29 (1.49)[e]	80 (83[d])	14 440	9200	1.9	~7	~8

[a] Initial concentrations calculated after withdrawn of 2 mL from the polymerizating solution (starting volume 26.9 mL) and addition of 6 mL of monomer solution (5.8 g, 5 M). [b] Calculated calorimetrically (Figure S1.1 and Figure S1.2 in Supporting Information). [c] Time of polymerization of 30 min in DCM and 60 min in 1,4-D. [d] Fraction of monomer consumed after monomer addition. [e] The significant decrease of the heat flow in 1,4-D allowed only an accurate measurement of k_{max}^{app} calorimetrically close to the origin. See Figure S1.2 in Supporting Information. [f] Fraction of 1,4-D fragment into the polymer calculated by NMR (Table S1 in Supporting Information). [g] Fraction of molecule of oxetane converted into cyclic oligomers approximated by NMR (Table S1 in Supporting Information).

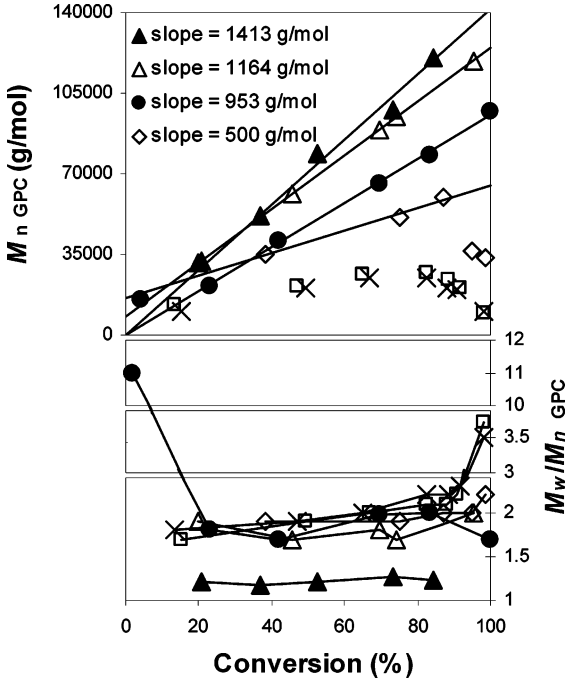


Figure 4. Number-average molecular weight ($M_{n\ GPC}$) and molecular weight distribution ($M_w/M_{n\ GPC}$) vs conversion dependences for the oxetane (Ox) polymerization with (▲, Δ, ◊, □) 3-phenoxypropyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (3-PPOA), (●) ethoxymethyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (EMOA), and (×) ethyl oxacarbenium hexafluoroantimonate (EOCA) as initiators at 35 °C (▲, ●) in 1,4-dioxane (1,4-D); (×) in dichloromethane (DCM); (Δ) in 3/1 v/v 1,4-D/DCM; (◊) in 2/3 v/v 1,4-D/DCM; and (□) in 2/7 v/v 1,4-D/DCM using 2,6-di-*tert*-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: $[Ox]_0 = 1.125$ M, (▲, Δ, ◊, □) $[3\text{-PPOA}]_0 = 1.14$ mM and $[DtBP]_0 = 1.254$ mM; (●) $[EMOA]_0 = 2$ mM and $[DtBP]_0 = 2.2$ mM; and (×) $[EOCA]_0 = 1.14$ mM and $[DtBP]_0 = 1.254$ mM. For additional experimental details, see Table S2 in Supporting Information.

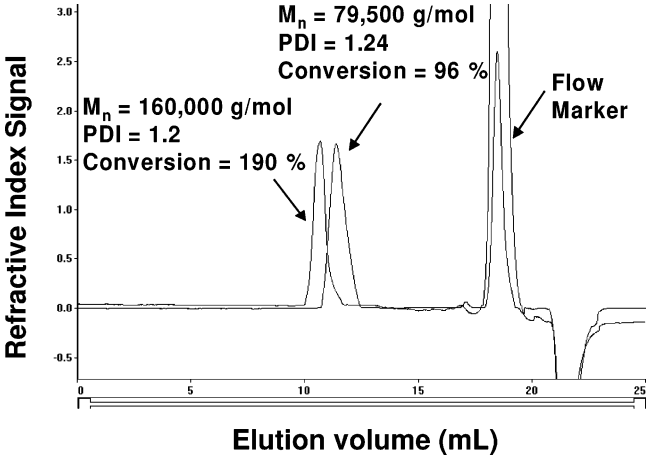
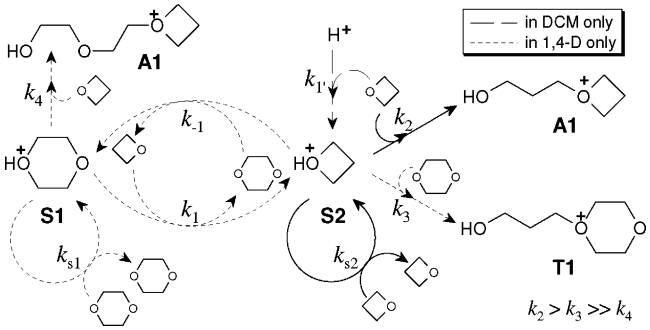


Figure 5. GPC RI traces of the original poly(oxetane) and the poly(oxetane) obtained after the incremental monomer addition experiment in 1,4-dioxane at 35 °C with 3-phenoxypropyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (3-PPOA) as initiating system and 2,6-di-*tert*-butylpyridine (DtBP) as a non-nucleophilic proton trap. For the original poly(oxetane) $t = 14$ h: $[oxetane]_0 = 1.125$ M, $[3\text{-PPOA}]_0 = 2$ mM, and $[DtBP]_0 = 2.2$ mM; and for the extended poly(oxetane) $t = 8$ h: $[oxetane]_0 = 1.1$ M, $[active\ chain\text{-}end]_0 = 1.78$ mM and $[DtBP]_0 = 2.8$ M. For additional experimental details, see Table S3 in Supporting Information.

Scheme 3. Initiation Step in Cationic Ring-opening Polymerization of Oxetane with $BF_3{\cdot}CH_3OH$ in 1,4-dioxane (1,4-D) and in Dichloromethane (DCM)



S2.2nd) was then accounted for by a slow initiation. In 1,4-D, the dependence $M_{n,GPC}$ on conversion (Figure 2) as well as the broad GPC curves with pronouncing tailing (Figure S5 in Supporting Information) can only be explained by the coexistence of secondary oxonium ions in the forms of S1 and S2. As shown in Scheme 3, the mutual conversion between S2 and S1 as well as the solvent protonation reactions of S1 (rate constant k_{S1}) decrease the concentration of initiating species S2 and slow down the rate of conversion of S1 into A1 and T1 via the formation of S2. By increasing the ratio $[1,4\text{-D}]_0/[Ox]_0$ from 9.45 to 15.95 and keeping the concentration of BF_3CH_3OH at 7.7 mM, it was then possible to slow down the rate of initiation and subsequently to monitor a decrease of k_{max}^{app} (Figure 3) together with the observation from the GPC RI traces (Figure S6 in Supporting Information) of the formation of small oligomerics peaks indicating that growing ACE species are formed throughout the polymerization process.

2. Living CROP of Oxetane in 1,4-Dioxane Initiated by a Tertiary 1-Oxonia-4-oxacyclohexane Hexafluoroantimonate Species at 35 °C. Molecular Weight Control Free of Cyclic Oligomers. Because the rate of initiation by protonic initiators is slow compared to propagation and a nucleophilic hydroxyl end group is generated, a *tertiary 1-oxonia-4-oxacyclohexane ions* T1 (structure equivalent to a "dormant" species)[15,16] was synthesized in situ and used as a "fast" initiator (i.e., an initiator

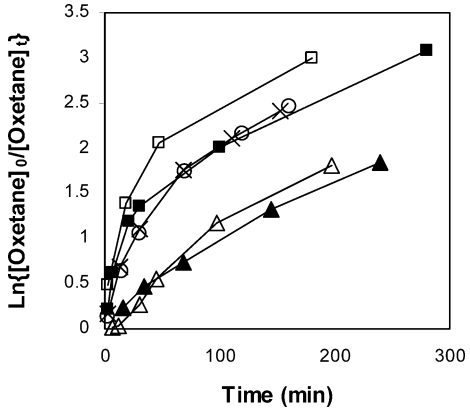


Figure 6. Evolution of $\ln\{[\text{oxetane}]_0/[\text{oxetane}]_t\}$ against time for the oxetane (Ox) polymerization with (▲, ■, □, ○) 3-phenoxypropyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (3-PPOA), (Δ) ethoxymethyl-1-oxonia-4-oxacyclohexane hexafluoroantimonate (EMOA), and (×) ethyl oxacarbenium hexafluoroantimonate (EOCA) as initiators at 35 °C (▲, Δ) in 1,4-dioxane (1,4-D); (×) in dichloromethane (DCM); (■) in 3/1 v/v 1,4-D/DCM; (□) in 2/3 v/v 1,4-D/DCM; and (○) in 2/7 v/v 1,4-D/DCM using 2,6-di-*tert*-butylpyridine (DtBP) as a non-nucleophilic proton trap. Experimental conditions: $[\text{Ox}]_0 = 1.125$ M, (▲, ■, □, ○) $[\text{3-PPOA}]_0 = 1.14$ mM and $[\text{DtBP}]_0 = 1.254$ mM; (Δ) $[\text{EMOA}]_0 = 2$ mM and $[\text{DtBP}]_0 = 2.2$ mM; and (×) $[\text{EOCA}]_0 = 1.14$ mM and $[\text{DtBP}]_0 = 1.254$ mM. For additional experimental details, see Table S2 in Supporting Information.

reactive enough to give instantaneous initiation, $k_i \geq k_{a(exo)}$) for the living polymerization of oxetane. The structure of 3-PPOA (Scheme 2) was used as a model for the propagating center A1 as it was able to form a stable tertiary oxonium T1 in solution. Under these conditions, by conducting the polymerization of 1.125 M of oxetane in 1,4-dioxane at 35 °C using 1.14 mM of 3-PPOA (series P4) as a fast initiator in the presence of 1.25 mM of DtBP, poly(oxetane)s with low polydispersities (1.18 < PDIs < 1.28) were produced with no cyclic oligomer formation. The $M_{n,GPC}$ increased linearly from 31 900 to 120 600 g/mol with the monomer conversion (Figure 4), and upon addition of further monomer, the existing living polymer chains were extended quantitatively (Figure 5). Additionally no tailing appeared in the low molecular weight region (Figure S8 in Supporting Information).[17] High number-average molecular weight polymer ($M_{n,GPC} = 160\,000$ g/mol and $M_w/M_{n,GPC} = 1.2$) was produced successfully with no cyclic oligomer formation.

An attempted living polymerization of 1.125 M of oxetane with 3.4 mM of EMOA (series P8) in the presence of 3.74 mM of DtBP in 1,4-D (Figure 4) did not give the expected control over MWDs (decrease of $M_w/M_{n,GPC}$ from 1.1 to 1.7) due to the lack of solubility of the initiating species in 1,4-D. The slow initiation with EMOA was observed by the formation, at low conversion only, of oligomers peaks of various molecular weights (Figure S9 in Supporting Information) corresponding to different generation of living growing i-mers. An induction period of ~16 min was observed (Figure 6). The data from this study are listed in Table S2, series P4 and P8, in Supporting Information.

Effect of the Ratio [1,4-Dioxane]/[Dichloromethane]. The use of DCM as cosolvent was found not to be beneficial for the control of the polymerization over M_n and M_w/M_n since using DCM up to a ratio of DCM/1,4-D of 2/5 v/v gradually increased the rate of monomer consumption (Figure 6), leading to a loss of the control of the polymerization (Figure 4) and the formation of cyclic oligomers, (~6% of cyclic oligomers at 98% conversion, series P7, Table S2 in Supporting Information), when the polymerization was performed in 7/2 v/v DCM/1,4-D solvent mixture or in DCM when EOCA was used as initiator. The loss of the control of polymerization over M_n and MWD with decrease of the ratio $[\text{1,4-D}]_0/[\text{Ox}]_0$ is the demonstration that 1,4-D end-cap readily the propagating species A1. The initial concentrations were the following: $[\text{oxetane}]_0 = 1.125$ M, $[\text{3-PPOA}]_0 = [\text{EOCA}]_0 = 1.14$ mM, and $[\text{DtBP}]_0 = 1.254$ mM. The data from this study are listed in Table S2, series P4−P7 and P8−P9, in Supporting Information.

3. Copolymerization of 1,4-Dioxane with Oxetane. While 1,4-D as solvent allows living and/or controlled polymerization of oxetane, there is noticeable incorporation of 1,4-D into the polymer: at the level of 1% after 70% monomer conversion with 3-PPOA (sample P4.4) and EMOA (sample P8.4) and at the level of 3 and 6% at 6 and 94% monomer conversion with $(BF_3{\cdot}CH_3OH)_{1,4-D}$ (series P2). The ^{13}C NMR spectroscopic analysis of the resulting polymer obtained (Figures S11 and S12 in Supporting Information) showed that each unit of 1,4-dioxane incorporated into the polymer is flanked by two oxetane monomer units indicating that ring-opening of the tertiary *1-oxonia-4-oxacylohexane site* **T1** by the monomer (rate constant $k_{a(endo)}$ in Scheme 1) occur. The results are shown as follows: ^{13}C NMR (in $CDCl_3$): $\delta = 67.49$ ppm (s, $-OCH_2-$ in Ox), $\delta = 29.76$ ppm (s, $-CH_2-$ in Ox), $\delta = 68$ ppm (s, $-CH_2OCH_2CH_2OCH_2CH_2OCH_2-$ in Ox), $\delta = 70.23$ ppm (s, $-OCH_2CH_2OCH_2CH_2O-$ in 1,4-Dox); $\delta = 69.85$ ppm (s, $-OCH_2CH_2OCH_2CH_2O-$ in 1,4-Dox). Similar results were reported by Furukawa for the copolymerization of 1,4-D with 3,3-bischloromethyloxetane.[18]

Living and Controlled CROP of Oxetane in 1,4-Dioxane. Therefore, if $k_{a(endo)}$ and $k_{a(exo)}$ represent the rate constants at which the oxygen atom of the oxetane molecule attacks the endo-cyclic and exo-cyclic electron deficient carbon atoms, respectively, of the *tertiary 1-oxonia-4-oxacylohexane site* T1, an "apparent" pseudo-first-order rate constant of monomer consumption k^{app} (L mol^{-1} s^{-1}) can then be expressed from the full differential equation of the rate monomer consumption (eq 1).

$$k^{app} = -\mathrm{d}(\ln[\text{Ox}])/\mathrm{d}t = k_p \times [\text{A1}] + (k_{a(endo)} + k_{a(exo)}) \times [\text{T1}] = f(t) \quad (1)$$

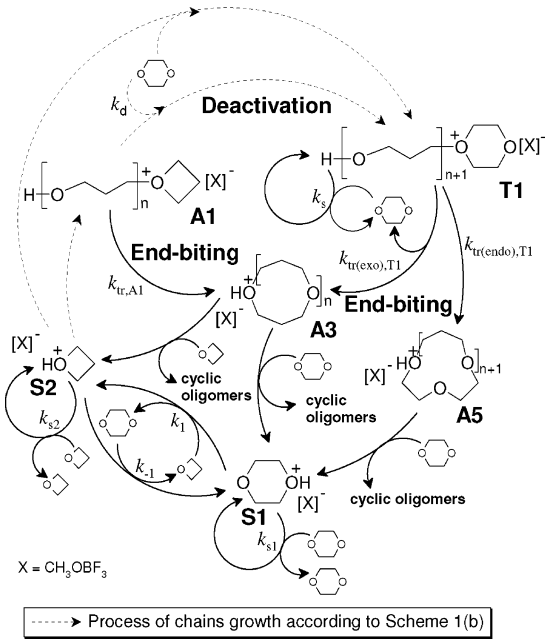
Considering the above equations as well as the linear dependence $M_{n,GPC}$ on conversion (i.e., $c_0 = [\text{A1}] + [\text{T1}]$ remains constant during the polymerization process), the curved nature of the slope of $\ln([\text{Ox}]_0/[\text{Ox}]_t)$ against time (Figure 6) is in agreement with the fact that k_p (L mol^{-1} s^{-1}) is larger than $k_{a(exo)}$ (L mol^{-1} s^{-1}) and that the change in concentration between A1 and T1 species (eq 2) does not obey a quasi-steady state assumption; [A1] decreases with decreasing of [Ox].

$$-\frac{\mathrm{d}[\text{T1}]}{\mathrm{d}t} = \frac{\mathrm{d}[\text{A1}]}{\mathrm{d}t} = (k_{a(endo)} + k_{a(exo)}) \times [\text{T1}] \times [\text{Ox}] - k_d \times [\text{A1}] \times [\text{1,4-D}]_0 \neq 0 \quad (2)$$

We believe such factors are responsible throughout the polymerization process for the narrowness and constancy of the polydipersity ($M_w/M_{n,GPC} \approx 1.2$). This polydispersity is slightly broader than predicted by Poisson behavior,[19] which we believe is attributed to the competition between solvent exchange reactions of the stable species T1 (rate constant k_s) and reversible transfer (i.e., depropagation).[1−3] The living and controlled polymerization of oxetane initiated by 3-PPOA and EMOA can then be depicted as shown in Scheme 1, part c.

Controlled Polymerization in 1,4-D with $(BF_3{\cdot}CH_3OH)_{1,4-D}$. Because protonic initiators generate nucleophilic hydroxyl end

Scheme 4. Cyclic Oligomers Formation in Cationic Ring-opening Polymerization of Oxetane with BF_3·CH_3OH in 1,4-dioxane



groups, the apparent control of the polymerization in 1,4-D (Figure 2) together with the production of cyclic oligomers can only be explain if, in parallel with the control process of chain growth described in Scheme 1, part b), a process of cyclic oligomer formation by end-biting reactions (rate constants $k_{tr,A1}$, $k_{tr(endo),T1}$, and $k_{tr(exo),T1}$ in Scheme 4) proceed for ACE species that do not reach a sufficiently high chain length to entropically disfavor end to end polymer chains reactions.[20] Such happening was also observed when diphenyl ether (DPE) was used as acyclic ether additive for the polymerization of 1 M of oxetane by 8 mM of BF_3·CH_3OH in DCM at 35 °C. For a ratio of $[DPE]_0/[Ox]_0/[BF_3$·$CH_3OH]_0$ of 180/130/1, the cyclic oligomer formation was enhanced (48.3% of the 35.1% of monomer consumed ($t = 300$ s)) most probably because of the low basicity of the DPE oxygen atom which failed to compete efficiently with those of polymer chains ether oxygen atoms. For a $[DPE]_0/[BF_3$·$CH_3OH]_0$ ratio of 135, 80 and 40, approximately 32.9% of the 35.1%, 24.3% of the 41.3%, and 17.1% of 46.8% of the polymerized oxetane were converted into cyclic oligomers, respectively. In all experiments the M_n(s) of the resulting polymers were almost unchanged ~10 000 g/mol. ^{13}C NMR spectra are shown in Figure S13 in Supporting Information.

Similarly, the ring-opening expansion of the tertiary *1-oxonia-4-oxacylohexane site* **T1** by end-biting reactions (rate constant $k_{tr(endo),A3}$ in Scheme 4) also proceeds with BF_3·CH_3OH at low concentration in monomer. Indeed, additional peaks of similar intensity appeared at high monomer conversion (Figure S12 in Supporting Information) in the region of resonance of the peak assigned to $-OCH_2CH_2CH_2-$ fragment of small cyclic oligomers (66.06 ppm). The peaks at 66.56 and 65.78 ppm were assigned to the oxetane fragment shifted from 66.06 ppm due to the presence of 1,4-D fragment in the cyclic oligomers. The two others signals at 67.85 and 67.77 ppm found also in the region of resonance of poly(ethylene oxide) and of poly(oxetane) were assigned to the resonance of 1,4-D fragment in cyclic oligomers. The controlled polymerization of oxetane initiated by BF_3·CH_3OH can then be described according to Scheme 1, part b, together with the cyclic oligomers formation process shown in Scheme 4.

Conclusions

In summary, the CROP of oxetane in 1,4-dioxane is the first recorded living/controlled polymerization process[16,17] in which the concentrations of "propagating" A1 and "nonpropagating" T1 species depend on the remaining concentration of monomer and vary inversely to one another. This is also the first cationic polymerization systems that enables, provide a fast and instant initiation (i.e., 3-PPOA), the preparation of ACE "living" polyether(s) with predictable molecular weights and narrow molecular weight distributions. The use of initiator that does not generate hydroxyl end group is also necessary since a subsystem of cyclic oligomers formation by end-biting reactions also take place with the BF_3·CH_3OH initiating system. We believe this system represents a significant advance in term of synthesis of oxetane-based materials and will soon lead to the preparation of more structured complex copolymers.

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Supporting Information Available: Dependence of $((dT/dt)/V)_{t\to 0}$ on $-(d[Ox]/dt)_{t\to 0}$ (Figure S1) for the homopolymerization of oxetane (Ox) initiated by different sources of initiators at 35 °C in dichloromethane (DCM) and in 1,4-dioxane (1,4-D); 300 MHz ^1H and 75 MHz ^{13}C NMR spectrum (Figures S3.1 and S3.2), GPC RI chromatogram (Figure S3.3), and MS spectrum (Figure S3.3) of cyclic oligomers extracted with cyclohexane from poly(oxetane) obtained in DCM with $[Ox]_0 = 1$ M, $[BF_3$·$CH_3OH]_0 = 0.008$ M and conversion = 80.8% (Sample P1.8, Table S1); 300 MHz ^1H and 75 MHz ^{13}C chemical shift in $CDCl_3$ of $-CH_2-$ groups in poly(oxetane) and poly(oxetane-co-1,4-dioxane) (Table S4); tables, GPC RI traces and 75 MHz ^{13}C NMR spectra of poly(oxetane) obtained at 35 °C; at different times using BF_3·CH_3OH in DCM (series P1, Table S1, Figures S3 and S4) and in 1,4-dioxane (1,4-D) (series P2 and P3, Table S1, Figures S5, S6, and S12) with $[Ox]_0 = 0.66-1$ M and $[BF_3$·$CH_3OH]_0 = 7.7$ mM; at different times in DCM with $C_2H_5[OCH_2]^+,[SbF_6]^-$ (EOCA) (series P9 Table S2, Figures S10 and S11) as initiator with $[Ox]_0 = 1.125$ M, $[EOCA]_0 = 1.14$ mM and $[DtBP]_0 = 1.254$ mM; at different time using $C_5H_6O(CH_2)_3$-(1,4-D)$^+,[SbF_6]^-$ (3-PPOA) as initiator in 1,4-D (series P4, Table S2, Figures S8 and S11), in 3/1 v/v 1,4-D/ DCM (series P5, Table S2), in 2/3 v/v 1,4-D/DCM (series P6, Table S2) with $[Ox]_0 = 1.125$ M, $[3\text{-PPOA}]_0 = 1.14$ mM, and $[DtBP]_0 = 1.254$ mM; at different time in 1,4-D using $C_2H_5OCH_2$-(1,4-D)$^+$,-$[SbF_6]^-$ (EMOA) as initiator in 1,4-D (series P6, Table S2, Figure S9) with $[Ox]_0 = 1.125$ M, $[EMOA]_0 = 3.4$ mM and $[DtBP]_0 = 3.74$ mM; in incremental monomer addition experiments in 1,4-D using 3-PPOA (Table S4) and BF_3·CH_3OH (Table S4, Figure S7) as initiator; diagram of the calorimeter (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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