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# Competitive Processes in Controlled Cationic Ring-Opening Polymerization of Oxetane: a *Lotka-Volterra* Predator-Prey Model of Two Growing Species Competing for the same Resources

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**Summary**: The activation-deactivation pseudo-equilibrium coefficient $Q_t$ and constant $K_o$ ($=Q_t$ x $P_{aT1,t} = ([A1]x[Ox])/([T1]x[T])$) as well as the factor of activation ($P_{aT1,t}$) and rate constants of elementary steps reactions that govern the increase of $M_n$ with conversion in controlled cationic ring-opening polymerization of oxetane (Ox) in 1,4-dioxane (1,4-D) and in tetrahydropyran (THP) (*i.e.* cyclic ethers which have no homopolymerizability (T)) were determined using terminal-model kinetics. We show analytically that the dynamic behavior of the two growing species (A1 and T1) competing for the same resources (Ox and T) follows a *Lotka-Volterra* model of predator-prey interactions.

**Keywords:** kinetics; living; Lotka-Volterra; mechanism; polymerization

## Introduction

The synthetic application of non-(homo)-polymerizable monomer (T) as capping agent for *living ionic polymers* is recognized as one of the most convenient and costless methods to obtained well-controlled block copolymers with high structural integrity. First introduced by Quirk *et* al. in anionic polymerizations,[1] this method has been successfully employed in living carbocationic macromolecular engineering[2–4] (*i.e.* for clean synthesis of blocks (Schemes 1a [2] and 1b[3]) and end-functionalized (co)polymers (Scheme 2a)[4] as well as in reaction clock method (Scheme 2b) evolve in competitions reactions (*i.e.* polymerizations stop short to completion after one cross-propagation step) for the determination of the structure - reactivity scales of vinylic monomers and corresponding living polymers cations.[5] In those systems, this process involved the quantitative capping reaction of the living polymers with a suitable non-(homo)polymerizable monomer[1–4] such 1,1-diphenylethylene or 1,1-ditolylethylene (Scheme 1a) followed, *i.e.* in living cationic sequential block copolymerization by tuning of the Lewis acidity to the reactivity of the second monomer (Scheme 1b).[3] The purpose of the Lewis acidity tuning is to generate stronger nucleophile counterions which ensure a rapid and quantitative initiation (*i.e.* high cross-over efficiency) and a living polymerization of the second monomer.[3]

As an extension of the effort apply on the application of non-(homo)polymerizable, cationic polymerization based on the concept of capping cations by suitable nucleophilic oxygen-base additives, *per se* capable to form dormant *oxonium-like* ions[6b] in true equilibrium with living propagating *oxacarbenium* ions and cationogen non-propagating species (Scheme 2c), has proved to be a successful methodology in yielding good control over $M_n$'s and molecular weight distributions (MWDs) in living cationic polymerization of vinyl

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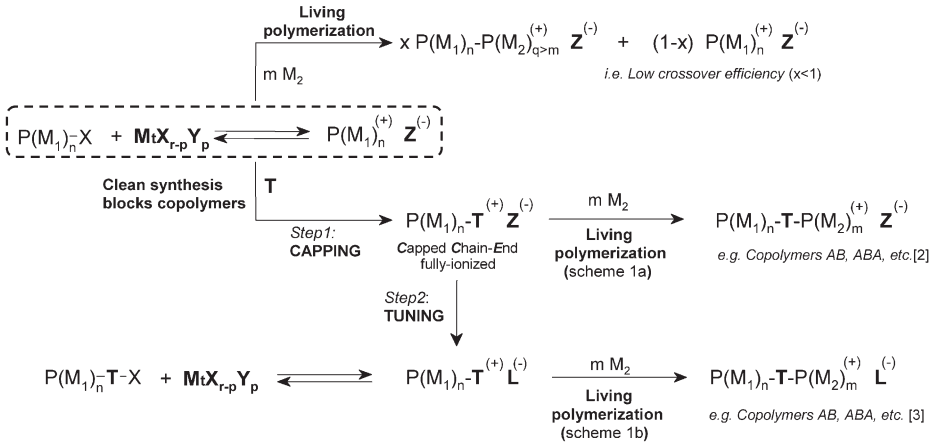
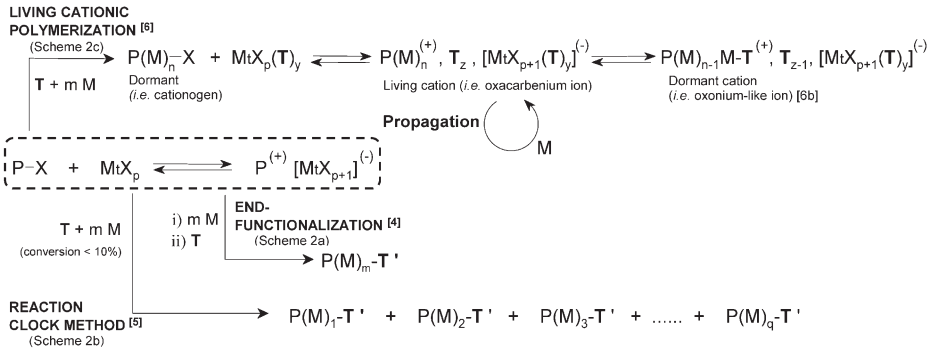
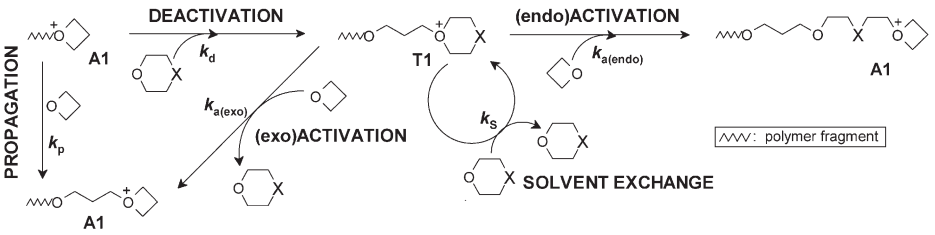



***Scheme 1.***
Application of non-(homo)polymerizable monomer (T) in living carbocationic sequential bloc copolymerization of vinylic monomers ($M_1$ and $M_2$) according to capping (a) [2] and capping/tuning methodologies (b) [3].




***Scheme 2.***
Application of non-(homo)polymerizable monomer (T) in living polymer chain-end functionalization (a) [4], in reaction clock method (b) [5] and in living carbocationic polymerization of vinyl ethers (M) (c) [6].




***Scheme 3.***
Elementary step reactions regulating the pseudo-equilibrium between strain (A1) and non-strain (T1) oxonium tertiary active-chain end species in "living" and controlled CROP of oxetane in THP (X = $-CH_2^-$) and in 1,4-D (X = $-O-$).

ethers in the presence of either ether (diethyl ether, THF, THP, oxepane, 1,4-dioxane, ...) or ester (ethyl acetate, ...) used as additive or (co)solvent.[6] Based on this approach, we recently reported a new synthetic route that allow ''living'' and/or controlled cationic ring-opening polymerization oxetane (Ox) in 1,4-dioxane (1,4-D) and tertahydropyran (THP) (cyclic ethers which have no homopolymerizability) solvent.[7] In those systems (Scheme 1), the solvent is used to end-cap the strain *tertiary 1-oxoniacyclobutane* ions A1 (rate constant $k_d$), producing a less reactive strain free terminal *tertiary 1-oxonium ions* T1. As T1 is less reactive, then there is greater discrimination between the more nucleophilic oxygen atom in Ox (rate constants $k_{a(exo)}$ and $k_{a(endo)}$) and in solvent T (rate constant $k_s$) than the less nucleophilic polymer chain ether oxygen atoms,[6c,7a-d] suspending backbiting and intermolecular transfer reactions as it occurs in normal polymerization of Ox in non-nucleophilic dipolar aprotic solvent.[9] In those systems, the dependence $M_{n(GPC)}$ vs conversion revealed the existence of a state of ''equilibration'' (*i.e.* $T1 + T \rightarrow T1 + T$, $k_s$) from where (*i.e.* $[Ox]_l^{THP} = 0.14\text{-}0.2\,M$ and $[Ox]_l^{1,4-D} < 0.07\,M$), in the apparent absence of reversible transfer (*i.e.* $A1 + Ox \leftrightarrow A1$), no fall of the $M_n$'s were recorded. The coexistence of the growing species in the form of *strain ACE species* (propagating chain terminated by a tertiary 1-oxoniacyclobutane ion, A1) and *strain free ACE species* (''dormant'' chain T1) was demonstrated from the microstructures of the copolymers as each non(hom)polymerizable co-monomer fragment inserted into the polymer ($F_{1,4\text{-}D} = 0{,}02$ and $F_{THP} = 0{,}2\text{-}0{,}3$) are flanked by two trimethylene oxide fragments and thus, deactivation ($A1 + T \rightarrow T1$, $k_d$), activation ($T1 + Ox \rightarrow A1 + T$, $k_{a(exo)}$ ; $T1 + Ox \rightarrow A1$, $k_{a(endo)}$) and solvent exchange reaction ($k_s$) occur throughout the polymerization process.

In this article, the activation-deactivation pseudo-equilibrium coefficient ($Q_t$) describing the process of ''equilibration'' (*i.e.* $T1 + T \rightarrow T1 + T$, $k_s$) and mutual conversion between A1 and T1 is discussed based on the determination of the rate constants of elementary step reactions (Scheme 1 and Table 2) that governs the increase of $M_n$ with conversions. Here, the dynamic behaviors of the two species (A1 and T1) competing for the same resources (Ox and T) is described by a set of first-order ordinary differential equations in the general form of a *Lotka-Volterra* (LV) systems (Figure 2).[10]

## Experimental Part

For full experimental details on initiator synthesis, polymerization procedure, microstructure and kinetics, the reader is referred elsewhere.[7a-d]

### Kinetics Analysis

The kinetics studies was focused on data obtained in copolymerization of Ox with THP initiated with $C_2H_5OCH_2(THP)^+[SbF_6]^-$ (ethoxymethyl-1-oxoniacyclohexane hexafluoroantimonate, EMOA), conditions under which the process exhibit characteristics of a ''living'' and controlled polymerization process which implies linear dependences $M_{n(GPC)}$ vs $M_{n(th)}$ with no cyclic formation, copolymer (*i.e.* poly-((oxetane)$_x$-co-(tetrahydropyran)$_{1-x}$) with $x < 0.3$) with pseudoperiodic sequences (each pentamethyleme oxide fragment inserted into the polymer is flanked by two trimethylene oxide fragments) and well controlled $DP_n$ ($= \Delta([Ox] + [THP])/[EOMA]_0$) thought MWDs are slightly broader ($1.1 < MWDs < 1.7$) than predicted by Poison distribution ($MWDs > 1 + 1/DP_n$). Under pseudo-first-order conditions; *i.e.* at various monomer feed ratio ($[THP]_0/[Ox]_0 = 9.9/0.472$; 9.6/1; 9.2/1.454; 9/1.81) using 1.115 mM of EMOA ($[AgSbF_6]_0/[EMCl]_0 = 1.1$ in THP) or at various targeted DPn in Ox ($= [Ox]_0/[EMCl]_0 = 630$; 1 265; 2 520) for a feed ratio $[THP]_0/[Ox]_0 = 9.2/1.454$, in the presence of DtBP as non-nucleophilic proton trap ($[DtBP]_0/[EMCl]_0 = 1.1$), Ox and THP were observed to react in first order

dependences on $[Ox]_0$ and $[EOMA]_0$ with an intercept of the X-axis, by the linear dependence–d[Ox]/dt and–d[THP]/dt vs $[Ox]_0$, at approximately the limited monomer-to-polymer conversion ($[Ox]_l = 0.2$ M). Therefore, from the elementary step reactions regulating the rate of mutual conversion between strained tertiary 1-oxoniacyclobutane (A1) and non-strained (T1) tertiary 1-oxoniacyclohexane (Scheme 1), it was possible to express the overall rates of monomer consumption of Ox and THP as given by the equation 1 and 2, respectively.

$$-\frac{d}{dt}[Ox] = k_{Ox}^{app} \times [Ox] = \left(k_p^{app} + k_{a(endo)}^{app} + k_{a(exo)}^{app}\right) \times [Ox] \quad (1)$$

$$-\frac{d}{dt}[THP] = k_{THP}^{app} \times [Ox] = k_{a(endo)}^{app} \times [Ox] \quad (2)$$

where, $k_{Ox}^{app}$ ($s^{-1}$), $k_p^{app}$ ($s^{-1}$), $k_d^{app}$ ($s^{-1}$), $k_{a(endo)}^{app}$ ($= k_{THP}^{app}$) ($s^{-1}$) and $k_{a(exo)}^{app}$ ($s^{-1}$) are the apparent rate constant of Ox consumption of A1 and T1, propagation of A1, deactivation of A1, (endo)activation of T1 (copolymerization of THP) and (exo) activation of T1, respectively. Here the equation 2 predicts that the rate of THP consumption is kinetically controlled by the rate of (endo)activation of T1 (*i.e.* $k_{a(endo)}^{app}$ x [Ox]) rather than by the rate of deactivation of A1 (*i.e.* $k_d^{app}$ x [THP]) as THP can be regenerated from T1 by (exo)activation (*i.e.* $k_{a(exo)}^{app}$ x [Ox]). Because the solvent exchange reactions (*i.e.* $k_s^{app}$ x [THP]) suspend, at the ''equilibration'' (*i.e.* $[Ox]_l = 0.2$-$0.14$ M), the activation of T1 (*i.e.* $k_s^{app}$ x [THP] >> $k_a^{app}$ x $[Ox]_l$) as well as reversible transfer (*i.e.* depropagation), our kinetics consideration predict that the overall apparent rate constant of activation ($k_a^{app}$) is related to the solvent exchange reaction by

$$k_a^{app} = k_{a(endo)}^{app} + k_{a(exo)}^{app} = \left(k_{a(endo)} + k_{a(exo)}\right) \times P_{aT1,t} \times [T1] \quad (3)$$

with

$$P_{aT1,t} = \frac{\left(k_{a(endo)} + k_{a(exo)}\right) \times \left([Ox] - [Ox]_l\right)}{\left(k_{a(endo)} + k_{a(exo)}\right) \times \left([Ox] - [Ox]_l\right) + k_s \times [THP]} \quad (4)$$

and

$$P_S = \frac{k_s}{k_{a(endo)} + k_{a(exo)}} \quad (5)$$

Here $P_{aT1}$ ($0 \le P_{aT1,t} < 1$) is the probability of activation of T1 in the consideration of the existence of the solvent exchange reaction ($P_S \neq 0$). On the other hand, 1-$P_{aT1}$ can be read as the average number of solvent exchange step ($T1 + THP \rightarrow T1 + THP$, $k_S$) that chain T1 can takes during a transient lifetime (*i.e.* $T1 + Ox \rightarrow A1 + THP$, $k_{a(exo)}$ ; $T1 + Ox \rightarrow A1$, $k_{a(endo)}$). Therefore $P_S$ can be view as the factor determining the inherent state of ''equilibration''. At the ''equilibration'' ($[Ox]_l^{THP} = 0.2$-$0.14$ M), equation 4 reads $P_{aT1,l} \sim 0$. Since the process of chains growth involve strain A1 and strain-free T1 ACE species in mutual conversion, the first-order plot Ln[Ox]/[Ox] *vs.* time gave, at all concentrations of EMOA and Ox, a quasi-straight line during the major part of the polymerization run (as long as $[Ox]_t > 0.3$ M), indicating that the stationary state concentrations of A1 and T1 are reached at the fairly early stages of the polymerization, *i.e.*

$$-\frac{d[A1]}{dt} = \frac{d[T1]}{dt} = k_d \times [A1] \times [THP] - \left(k_{a(endo)} + k_{a(exo)}\right) \times P_{aT1} \times [T1] \times [Ox] = 0 \quad (6)$$

After rearrangement of the equation 6, the activation–deactivation pseudo-equilibrium coefficient ($Q_t$) which does not formally follow microreversibility is given

by the equation 7.

$$Q_t = \frac{K_0}{P_{aT1}} \quad (7)$$

with

$$K_0 = \frac{k_d}{k_{a(endo)} + k_{a(exo)}} = \frac{[T1] \times [Ox]}{[A1] \times [THP]} \quad (8)$$

Here, $K_0$ is read as the activation-deactivation pseudo-equilibrium constant in the consideration of $k_s = 0$ (*i.e.* $P_S = 0$ and $P_{aT1,t} = 1$). The equation 8 shows that chains growth ($k_{Ox}^{app}$) is determined by relative abundance of A1 and T1 species within the framework [Ox]/[THP], [A1] (*i.e.* $[T1] = [EOMA]_0$–[A1]) decreases with decreasing of [Ox]. At the later stages of the polymerization, decreases for both $k_{a(endo)}^{app}$ and $k_{Ox}^{app}$ ($=k_P^{app} + k_{a(endo)}^{app} + k_{a(exo)}^{app}$) are generally observed, namely, close to the "equilibration" (0.14 - 0.18 M < [Ox] < 0.3 M) indicating the inadequacy of the steady state assumption (equation 6) on which the equation 7 is based at [Ox] < 0.3-0.4 M.[7d] From a mathematical point of view, the dynamic behaviors of the two competing-species towards the chains growth can be described by a set of three ordinary differential equations in the general form of a *Lotka-Volterra* (LV) system[10]

$$(LV)\begin{cases} \dot{x} = -x(\beta_1 + \beta_2 z) & (1) \\ \dot{y} = -x(\gamma_1 + \gamma_2 z) & (2) \\ \dot{z} = -z(\alpha_1 y + \alpha_2 x) + \alpha_3 x & (6) \end{cases}$$

where $z$, is the relative abundance of one of the two species, *e.g.* [A1] (*i.e.* $[T1] = [EOMA]_0 - z$), $x$ and $y$ the concentration of Ox and THP, respectively, and $\dot{x}$ ($dx/dt$), $\dot{y}$ ($dy/dt$) and $\dot{z}$ ($dz/dt$) the change concentrations computed with $\alpha_1 = k_d$, $\alpha 2 = k_a P_{aT1}$, $\alpha 3 = \beta_1 = k_a [EOMA]_0 P_{aT1}$, $\beta_2 = k_p - k_a P_{aT1}$, $\beta_1 = k_p$ , $\gamma_1 = k_{a(endo)} [EOMA]_0 P_{aT1}$, $\gamma_2 = k_{a(endo)} P_{aT1}$.

### Determination of the Reactivity Ratio $k_s/k_{a(endo)}$ and $k_s/k_{a(exo)}$

Since solvent exchange reaction (*i.e.* $T1 + S \rightarrow T1 + S$, $k_s$) proceeds throughout the polymerization, after combination of the equation 2, 3 and 4 and rearrangement of the resulting equations, one obtain the equation 9

$$\frac{[Ox]_0}{-d[THP]/dt} = \frac{1}{k_{a(endo),t\rightarrow 0}^{app}} + \frac{P_S}{k_{a(endo),t\rightarrow 0}^{app}} \times \frac{[THP]}{([Ox] - [Ox]_l)} \quad (9)$$

from where it was possible to calculate the factor determining the inherent state of "equilibration" $P_S$ as well as the factor determining the average number of solvent exchange step that chain T1 can takes before a single (endo)- or (exo)-activation step, *i.e.* $k_s/k_{a(endo)}$ and $k_s/k_{a(exo)}$, respectively. Here $k_{a(endo),t\rightarrow 0}^{app}$ represents the value extrapolated to zero time, *i.e.* $k_{a(endo)} \times [EOMA]_0$. The data are listed in the Table 1.

***Table 1.***
Calculated value for the rate constant of solvent exchange reaction ($k_s$), probability factor of solvent exchange reaction ($P_s$) and the probability factor of Activation of T1 at t = 0 ($P_{a,T1,t\rightarrow 0}$) for the bulk CROP of oxetane (Ox) with tetrahydropyran (THP) at 35 °C.

| [THP]0/[Ox]0 | $[I]_0$ | $[Ox]_l$ | | | $k_S$ (L Mol$^{-1}$ s$^{-1}$) | |
|---|---|---|---|---|---|---|
| (Mol L$^{-1}$ / Mol L$^{-1}$) | mMol L$^{-1}$ | Mol L-1 | PS | $P_{a,T1,t\rightarrow 0}$ | from equation 9 | from equation 10 |
| 9 / 1.81 | 1.115 | 0.167 | 0.00532 | 0.971 | 0.0254 | 0.0255 |
| 9.2 / 1.454 | 1.115 | 0.193 | 0.00766 | 0.947 | 0.0366 | 0.0367 |
| 9.2 / 1.454 | 2.3 | 0.159 | 0.00637 | 0.956 | 0.0305 | 0.0306 |
| 9.2 / 1.454 | 0.5 | 0.166 | 0.00643 | 0.966 | 0.0307 | 0.0308 |
| 9.9 / 0.5 | 1.115 | 0.172 | 0.00536 | 0.849 | 0.0256 | 0.0257 |
| 9.6 / 1 | 7.7 | 0.187 | 0.00744 | 0.919 | 0.0356 | 0.0357 |
| | | | | $\langle k_s \rangle =$ | 0.0307 | 0.0308 |

***Table 2.***
Kinetic parameters for the bulk CROP of oxetane (Ox) with tetrahydropyran (THP) at 35 °C.

| Parameters | | Value (from equation 10) | Value (from equation 11) |
|---|---|---|---|
| $r_{Ox}$ (= $k_p/k_d$) | monomer reactivity ratio for oxetane | 6.6 | 5.5 |
| $P_{a(endo)}$ (= $k_{a(endo)}/(k_{a(endo)} + k_{a(exo)})$ | probability factor of endo-activation of T1 | 0.4 | 0.37 |
| $k_p$ (L $Mol^{-1}$ $s^{-1}$) | rate constant of propagation of A1 | 45.4 | 54.5 |
| $k_d$ (L $Mol^{-1}$ $s^{-1}$) | rate constant of deactivation of A1 | 6.9 | 9.9 |
| $k_{a(endo)}$ (L $Mol^{-1}$ $s^{-1}$) | rate constant of (endo)activation of T1 | 1.9 | 1.8 |
| $k_{a(exo)}$ (L $Mol^{-1}$ $s^{-1}$) | rate constant of (exo)activation of T1 | 2.9 | 3 |
| $K_o$ (= $k_d/(k_{a(endo)} + k_{a(exo)})$ | ideal pseudo-equilibrium constant ($P_S = 0$) | 1.44 | 2.07 |
| $<k_s>$ | rate constant of solvent exchange reaction | 0.0307 | 0.0308 |

### Determination of Reactivity Ratio $k_p/k_d$ and $k_{a(endo)}/k_{a(exo)}$

By dividing the equation 1 by the equation 2 and combining the resulting equation with equation 6 and 7, after rearrangement one obtains the equation 10 and 11 from where $k_p/k_d$ (= $r_{Ox}$) and $k_{a(endo)}/k_{a(exo)}$ (= $P_{a(endo)}/(1 - P_{a(endo)})$) were calculated

$$\frac{-d[Ox]/dt}{-d[THP]/dt} = \frac{r_{Ox}}{P_{a(endo)}} \times \frac{[Ox]}{[THP]} + \frac{1}{P_{a(endo)}} \tag{10}$$

$$\frac{(F_{Ox})_{x^{Ox}<10\%}}{(F_{THP})_{x^{Ox}<10\%}} = \frac{r_{Ox}}{P_{a(endo)}} \times \frac{f_{Ox}}{f_{THP}} + \frac{1}{P_{a(endo)}} \tag{11}$$

Comparing the $k_p/k_d$ and $k_{a(endo)}/k_{a(exo)}$ values (Table 2) determined from kinetic data using the equation 10 and from the copolymer composition obtained using equation 11 at various feed composition, the agreement is quite reasonable. This shows that as long as $k_{THP}^{app}$ is constant; *i.e.* far from the ''equilibration'', there is no variation of the reactivity ratio with the change of the co-monomer composition, indicating that the insertion of THP proceeds exclusively by (endo)activation.

### Determination of $k_p$, $k_d$, $k_s$, $k_{a(endo)}$, $k_{a(exo)}$

Since the initial rate of living chains end growth is first-order dependence on $[Ox]_0$ and $[EMCl]_0$ (=$[EMOA]_0$). Considering the terminal model for the chains growth, the expression of the average binary copolymerization rate constant $\langle k_M \rangle$ is given by the general equation 12.

$$\langle k_M \rangle = \frac{\langle k_M{}^{app} \rangle}{[EMOA]_0} = \frac{-d[Ox]/dt - d[THP]/dt}{[Ox] \times ([A1] + [T1])} \tag{12}$$

Here $\langle k_M \rangle$, which is experimentally accessible (*i.e.* $[EMOA]_0 = [A1] + [T1]$), can then be express as simple function of co-monomer feed ratio instead of concentration of A1 and T1 by combining the equation 1, 2, 7, 8 and 12, and rearranging the resulting equation as given by the equation 13.

$$\left(r_{Ox} + (1 + P_{a(endo)}) \times \frac{f_{THP}}{f_{Ox}}\right) \times \frac{[EMOA]_0}{\langle k_M{}^{app} \rangle} = \frac{1}{k_d} + \frac{Q_t}{k_d} \times \frac{f_{THP}}{f_{Ox}} \tag{13}$$

The values of $k_d$ and $Q_t$ calculated from the intercept and the slope, respectively, of the plot of left side of the equation 13 vs. $f_{THP}/f_{Ox}$ were used, by mean of the reactivity ratio $r_{Ox}$, $P_{a(endo)}$ and $P_S$ (equation 5), to calculate the rate constant of reactions involved in the living cationic ring-opening copolymerization of Ox with THP (see Scheme 1). In this study, the two series of values obtained for $k_p$, $k_d$, $k_s$, $k_{a(endo)}$, $k_{a(exo)}$ are based on either $k_p/k_d$ and $k_s$ were determined from the kinetic data obtained using equation 10 (method (i)) or from the copolymer composition obtained

using equation 11 (method (ii)). The data are listed in the Table 2.

### Copolymerization Model Fitting and Mechanistic Interpretation

Using concentrations of [THP] = 9.2 M and [Ox] = 1.452 M, the following time intervals ($\tau$) between two consecutive events have been calculated at the early stages of the polymerization process.

$$11\,\text{ms(i)} < \tau_d = 1/(k_d \times [\text{THP}]0) < 15.7\,\text{ms(ii)}$$

$$\tau_{a(exo)} = 1/(P_{aT1,t=0} \times k_{a(exo)} \times [\text{Ox}]_0) = 0.24\text{s}$$

$$\tau_{a(endo)} = 1/(P_{aT1,t=0} \times k_{a(endo)} \times [\text{Ox}]_0) = 0.41\text{s}$$

$$12.6\,\text{ms (i)} < \tau_p = 1/(k_p \times [\text{THP}]_0) < 15.3\,\text{ms (ii)}$$

$$\tau_s = 1/(k_s \times [\text{THP}]_0) = 3\text{s}\ (\tau_s = 1/((1 - P_{aT1,t=0}) \times k_s \times [\text{THP}]_0) = 57\,\text{s})$$

with

$$P_{aT1,t=0} = 0.947$$

Thus, the time interval between two activations is relatively long, 0.41 s by (endo)activation and 0.24 s by (exo)activation. At this stage, solvent exchange reactions does not suspend the process of activation as the time interval between two reactions is 3 s (57 s) >> 0.41 s. The tertiary 1-oxoniacyclobutane A1 stay active for a very short time; only 15.7 ms, before deactivation takes place, and the polymer end goes back to a kind of ''dormant'' state. At the early stages of the polymerization, 6.7% of the living ACE species bear the terminal group A1. Propagation is 0.87 times slower than deactivation, however (monomer incorporates on average every 12.6 ms), and 9 monomer units are added after 10 active cycle. Similarly the

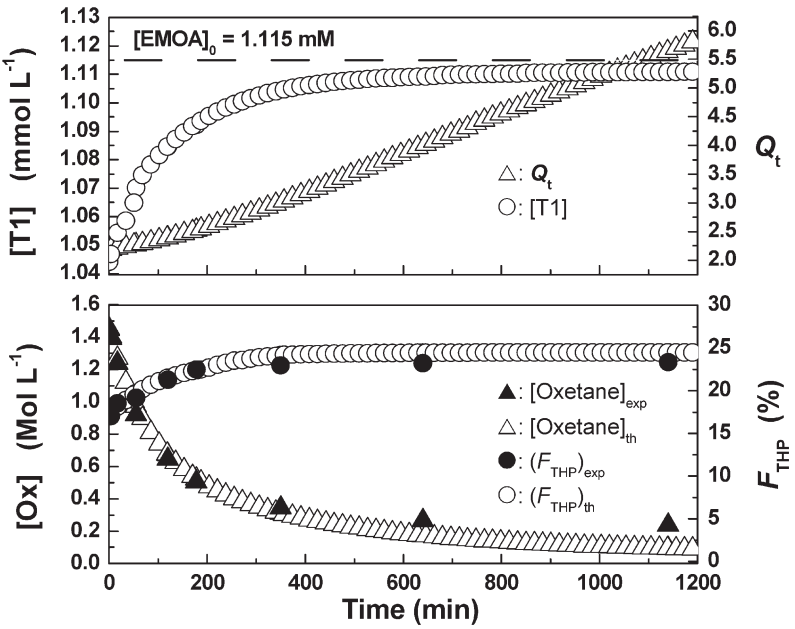



***Figure 1.***

Predicted values of the copolymer composition in tetrahydropyran $F_{THP}$, and of the activation-deactivation pseudo-equilibrium coefficient $Q_t$ together with the variation in concentrations of monomer [Ox] and of dormant species [T1] as function of time in the bulk living copolymerization of oxetane (Ox) with tetrahydropyran (THP) initiated by EMCl/$AgSbF_6$ in the presence of 2,6-di-tert-butylpyridine (DtBP) ([EMCl]/[$AgSbF_6$]/[DtBP] = 1/1.1/1.1) at 35 °C. The open symbol represents the theoretical dependences based on the terminal model and the closed symbol represents the experimental data. $[Ox]_o$ = 1.452 M, $[THP]_o$ = 9.2 M, $[EMCl]_o$ = 1.115 mM, $[DtBP]_o$ = 1.12 mM, $[AgSbF_6]_o$ = 1.2 mM.

(exo)activation is 1.7 times faster than (endo)activation (copolymerization) and 10 Ox units and 4 THP units are added after 10 actives cycles. The number of monomer molecules added during first 10 active cycles is 18 Ox units and 4 THP units. Since the deactivation reaction is time-independent in the considered system ($[THP] \sim [THP]_0$ throughout the polymerization process), the number of monomer units added by cycle decrease with conversion.

The Figure 1 shows that the kinetics parameter obtained in this study provide a reasonable fit with the $\langle k_M^{app} \rangle$ and composition ($F_{Ox}$) data. The Figure 2 gives the calculated values for the activation-deactivation pseudo-equilibrium coefficient ($Q_t$) change together with the variation of the molar fraction of A1 ($f_{A1,t}$) as a function of the fraction of oxetane consumed (*i.e.* $[Ox]_t/[Ox]_0$ and *xtOx*), modeled as competing-species in Lokta-Volterra prey-predator relations (equation (1) and (6)) within the competitive framework $[THP]_0/[Ox]_0$ (= 9.9/0.472; 9.2/1.454; 9/1.81), when the controlled cationic copolymerization of Ox with THP is initiated by 1,115 mM of EOMA.

## Conclusion

The living and controlled CROP of Ox in THP (with has no homopolymerizability) led readily to a copolymer chains with

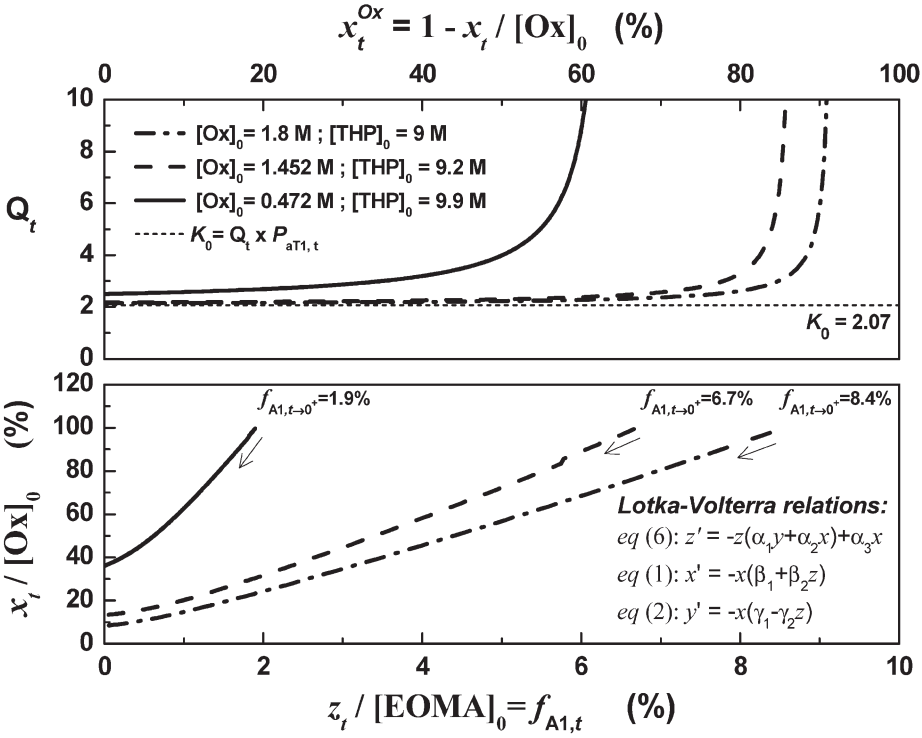



***Figure 2.***
Predicted values for the activation-deactivation pseudo-equilibrium coefficient ($Q_t$) change together with the variation of the molar fraction of A1 ($f_{A1,t} = z_t/[EOMA]_o$ with $z_t = [A1]_t$) as a function of the fraction of oxetane consumed ($x_t^{Ox} = 1 - x_t/[Ox]_o$ with $x_t = [Ox]_t$) for various monomer feed ratio ($[THP]_o/[Ox]_o$ = 9.9/0.472; 9.2/1.454; 9/1.81) when the living cationic copolymerization of Ox (*x*) with THP (*y*) is initiated by 1.115 mM of EMCl/$AgSbF_6$ in the presence of 2,6-di-tert-butylpyridine (DtBP) ($[EMCl]/[AgSbF_6]/[DtBP] = 1/1.1/1.1$) at 35 °C. Functions $z_t$ (equation 6) and $x_t$ (equation 1) are interpreted in Lotka-Volterra predator-prey mechanism with $\alpha_1 = k_d$, $\alpha 2 = k_a P_{aT1}$, $\alpha 3 = \beta_1 = k_a[EOMA]_o P_{aT1}$, $\beta_2 = k_p - k_a P_{aT1}$, $\beta_1 = k_p$ , $\gamma_1 = k_{a(endo)}[EOMA]_o P_{aT1}$, $\gamma_2 = k_{a(endo)} P_{aT1}$.

pseudoperiodic sequences and controlled molecular weight. The coexistence of the growing species in the form of *strain ACE species* (propagating chain terminated by a tertiary 1-oxoniacyclobutane ion, A1) and *strain free ACE species* (''dormant'' chain T1) was demonstrated from the microstructures of the copolymers as each comonomer T (*i.e.* 1,4-D or THP) fragment inserted into the polymer ($F_{1,4\text{-D}} = 0{,}02$ and $F_{\text{THP}} = 0{,}2\text{-}0{,}3$) are flanked by two trimethylene oxide fragments and thus, deactivation ($\text{A1} + \text{T} \rightarrow \text{T1}$, $k_{\text{d}}$), activation ($\text{T1} + \text{Ox} \rightarrow \text{A1} + \text{T}$, $k_{\text{a(exo)}}$ ; $\text{T1} + \text{Ox} \rightarrow \text{A1}$, $k_{\text{a(endo)}}$) and solvent exchange reaction ($k_{\text{s}}$) occur throughout the polymerization process. The activation-deactivation pseudo-equilibrium coefficient $Q_t$ and constant $K_0$ ($= Q_t$ x $P_{\text{aT1,t}}$) were determined in a pure theoretical basis, using terminal-model kinetics. Although there is appreciable uncertainty concerning the estimations of the $k_{\text{s}}$ ($1/P_{\text{aT1,t}} = 1 + k_{\text{s}}/k_{\text{a}}\text{x}[\text{T}]/([\text{Ox}]\text{-}[\text{Ox}]_l)$) for the *strain free ACE* species T1, the kinetics parameters calculated in this study provide a reasonable fit with the measured apparent rate constant of monomers consumption ($k_{\text{Ox}}^{\text{app}}$ and $k_{\text{solvent}}^{\text{app}}$) and with the copolymer composition data. The form of the pseudo-equilibrium equation shows that $Q_t$ is strictly dependent on $P_{\text{aT1,t}}$ and stay, even if it increases during the course of the copolymerization with [T1]/[A1], close to the lowest value $K_0$ (pseudo-equilibrium constant in the consideration of $k_{\text{s}} = 0$), a state of mutual conversion in which macro tertiary oxonium ions are predominantly ($\sim$94%) in the ''dormant'' form T1. Although the occurrence of some extent of transfer cannot be excluded with appreciable uncertainty, the formation of polymer with large PDI ($\sim$1.2-1.8) is more likely to be the result of slow mutual conversion between of A1 and T1 in respect with chains growth (e.g. $k_{\text{p}}/k_{\text{d}} \sim 5.4$ and $k_{\text{p}}/k_{\text{a}} \sim 11.3$ in THP) than the cause of chain scissions reactions. Mathematical treatment of the molecular weight distribution as a function of chain length with will be published elsewhere.

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