Non-steady-state living polymerization: a new route to control cationic ring-opening polymerization (CROP) of oxetane *via* an activation chain end (ACE) mechanism at ambient temperature

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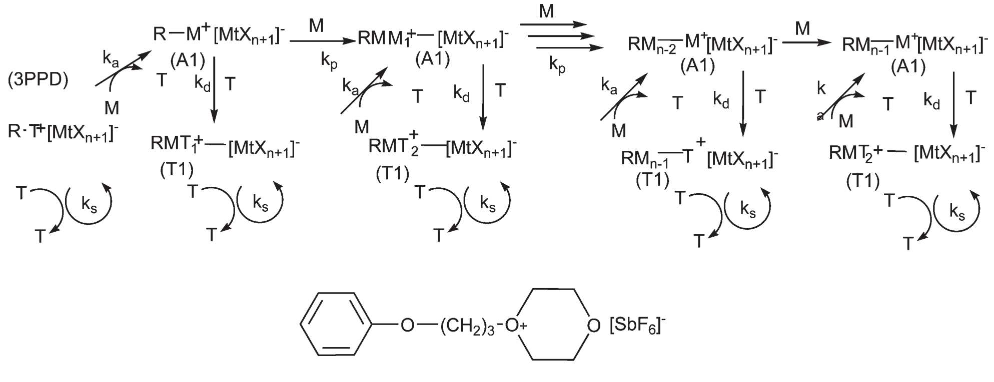
Well-defined polyoxetane with low polydispersivity has been synthesized *via* a novel living polymerisation process using 3-phenoxypropyl 1,4-dioxanium hexafluoroantimonate (3-PPD) as a model of a living "monomeric polyoxetane" initiator, in 1,4-dioxane at 35 °C.†

In the early 1980's, the development of the so-called *quasiliving polymerization QLP* based on a reversible end-capping reaction of the propagating species (*i.e.* terminative QLP) turned out to be a powerful method for controlling, or improving the control of the polymerization of monomers that fail to polymerize in a living manner.[1,2] Originally approached by Kennedy, Tüdős and Faust, for the particular case of the cationic polymerization of vinylic monomers,[1] this concept of polymerization predicts that in a system where a dynamic equilibrium exists between "active" and "dormant" species, control over M_n and M_w/M_n can be achieved throughout the polymerization if the rate constants of interconversion between coexisting species are much larger than the rate of propagation. Under such conditions the effect on the MWDs is negligible and the ratio M_w/M_n is almost identical to a Poisson distribution.[3]

Here we report, for the particular case of the CROP of oxetane by an ACE mechanism, a novel terminative QLP process that allows living polymerization.[4] In this system (see Scheme 1) an ether additive T is used to end-cap irreversibly the ACE propagating species A1 in the form of a strain free tertiary oxonium ion ("dormant" species T1). Unlike conventional QLP based on reversible end-capping reactions,[1,2] the "dormant" species is reactivated by a monomer addition reaction and this occurs without inducing redistribution by chain breaking reactions[5] and without formation of cyclic oligomers[5] or dead polymer chains.[5] In order to prevent transfer reactions[5] from occurring the additive used as solvent has to be more nucleophilic than the oxygen atom of the backbone of the polymer chains but also less nucleophilic than the oxygen atom of the oxetane molecule, to enable the reactivation of "dormant" species T1 by the monomer. Under these conditions, by conducting the polymerization of 1.125 M of oxetane in 1,4-dioxane[6] at 35 °C using 0.00114 M of 3-PPD[7] as a fast initiator (initiator reactive enough to give instantaneous initiation), polyoxetane with low polydispersivity (1.18 < PDI < 1.28) was produced with no cyclic oligomer formation.† The $M_{n\ (GPC)}$ (number average molecular weight distribution determined by GPC against PS standards) increased linearly with the monomer conversion from 31,920 to 120,610 g mol^{-1} and upon addition of further monomer, the existing living polymers were extended quantitatively (Fig. 1).† High molecular weight materials ($M_{n\ (GPC)}$ = 160,000 g mol^{-1} and $M_w/M_{n\ (GPC)}$ = 1.2) were produced successfully.[8]† While, 1,4-dioxane as solvent allows living polymerization of oxetane, there is noticeable incorporation of solvent into the polymer chain after 50% monomer conversion. The ^{13}C NMR spectroscopy analysis of the resulting polymer (Fig. S1, ESI†) showed that each unit of 1,4-dioxane incorporated into the polymer,[9] at the level of 1%, was flanked by two oxetane monomer units. Therefore we



3PPD

Scheme 1

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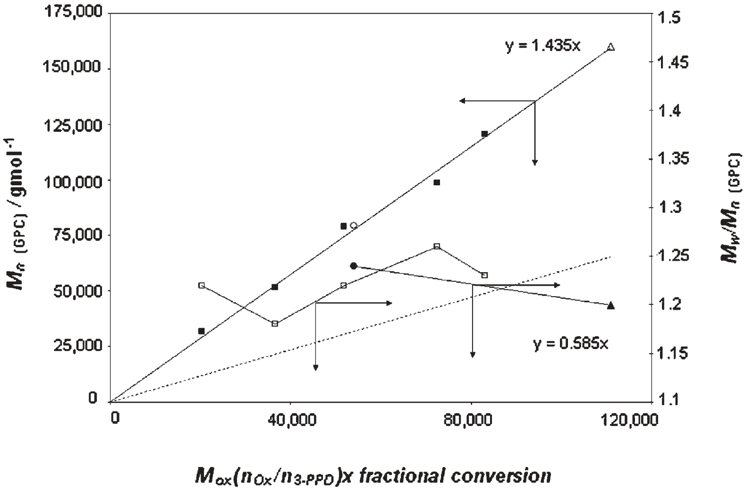


Fig. 1 Dependence of $M_{n\ (GPC)}$ (■,○,△) and $M_w/M_{n\ (GPC)}$ (□,•,▲) on conversion for the polymerization of 1.125 M of oxetane initiated by 0.00114 M of 3-PPD in 1,4-dioxane at 35 °C (■,□) and after chain expansion polymerization of polyoxetane (▲,△) obtained by addition of monomer solution onto active polymer solution (●,○), almost free of monomer issue from the polymerization of 1.125 M of oxetane by 0.002 M of 3-PPD in 1,4-dioxane at 35 °C. (—) is the theoretical dependence of $M_{n\ (GPC)}$ *vs.* conversion computed for M_w/M_n = 1.0.[8]†.

concluded that if $p_{a(endo)}$ and $p_{a(exo)}$ represent respectively the probability that the oxygen atom of the oxetane molecule attacks the endo-cyclic and exo-cyclic electron deficient carbon atoms of the *1,4-dioxanium site* T1, the rate constant of activation can be expressed as follows:

$$k_a = k_{a(exo)}{\cdot}p_{a(exp)} + k_{a(endo)}{\cdot}p_{a(endo)} \tag{1}$$

The postulated mechanism, described now in Scheme 2, was demonstrated by the non-linear first order kinetic-plot (Fig. 2). Indeed, the activation of the "dormant" species by monomer addition reaction implies that the rate of interconversion between "active" A1 and "dormant" T1 species (Eqn. (2)) does not obey the quasi-steady state assumption.

$$-\frac{d[T1]}{dt} = \frac{d[A1]}{dt} = k_a{\cdot}[T1]{\cdot}[Ox] - k_{d(endo)}{\cdot}[A1]{\cdot}[T]_0 \neq 0 \tag{2}$$

This leads to a system in which the concentration of "active" A1 and "dormant" T1 species are dependent on the [Ox], the [A1] decreases with the increase of [Ox]. Therefore, if c_0 (c_0 = [A1] + [T1]) is the total concentration of growing living centres and if α_t (α_t = [A1]/c_0) denotes the instantaneous mole fraction of living A.C.E growing species in the form A1 at a given time *t*, 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 (Eqn. (3)).

$$-\frac{d[Ox]}{dt} = k_p{\cdot}[A1]{\cdot}[Ox] + k_a{\cdot}[T1]{\cdot}[Ox] = k_{app}{\cdot}[Ox] \tag{3}$$

$$k_{app} = -d\ \ln[Ox]/dt = (k_a + (k_p - k_a)\ \alpha_t)\ c_0 \tag{4}$$

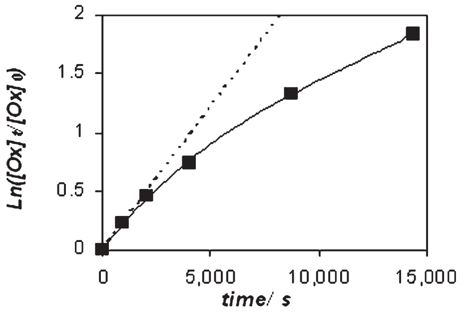
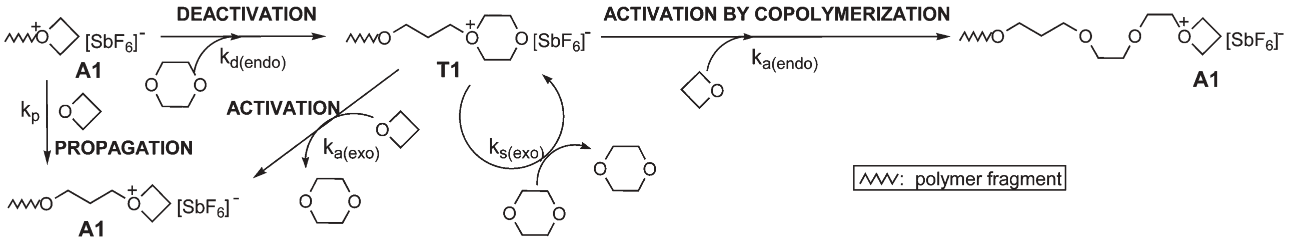


Fig. 2 Dependence ln([Ox]$_0$/[Ox]$_t$) *vs.* time in 1,4-dioxane at 35°C, where [Ox] = 1.125 M and [3-PPD] = 0.00114 M.†

Considering the above equations as well as the linear dependence $M_{n\ (GPC)}$ on conversion (*i.e.* c_0 = [A1] + [T1] remains constant during the polymerization process), the curved nature of slope of ln([Ox]$_0$/[Ox]$_t$) *vs.* time (Fig. 2) can only be explained if k_p (L·mol^{-1}s^{-1}) is larger than k_a (L·mol^{-1}s^{-1}).[10] Such factors are



Scheme 2

believed to be responsible throughout the polymerization process for the narrowness and constancy of the polydipersivity ($M_w/M_{n\ (GPC)} \approx 1.2$†). This polidispersivity is slightly broader than predicted by Poisson behaviour,[3] which we believe is attributable to the possibility of solvent exchange reactions of the dormant speices T1 (rate constant $k_{s(exo)}$). Because living ACE growing species coexist in the form of "active" and "dormant" species, respectively A1 and T1, the polymerization of oxetane initiated by 3-PPD in 1,4-dioxane at ambient temperature can be classified as a *terminative quasiliving polymerization process*. This is the first reported effective living polymerization based on *irreversible end-capping reactions* in which the rate of activation of the "dormant" species is governed by the concentrations of "dormant" species [T1] and of the monomer [Ox] (see Eqn. (2)). This is also the first example of living CROP of cyclic ethers in which $M_{n\ (GPC)}$ increases linearly with conversion throughout the polymerization.[11] We envisage an extension of this new concept of polymerization for the control of polymerization of various cyclic ethers and nucleophile monomers.

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Notes and references

† Electronic supplementary information (ESI) available: experimental data and Figs. S1–S5. See http://www.rsc.org/suppdata/cc/b4/b417076h/

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