

SUPPORTING INFORMATION

Synthesis of poly(methyl methacrylate) and block copolymers by semi-batch nitroxide mediated polymerization

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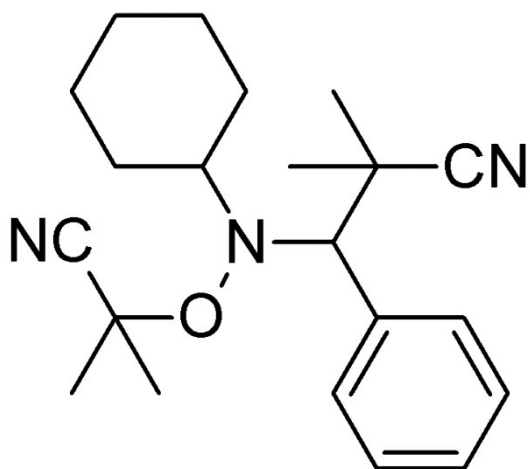


Figure S1 Structure of the alkoxyamine 3-(((2-Cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile.

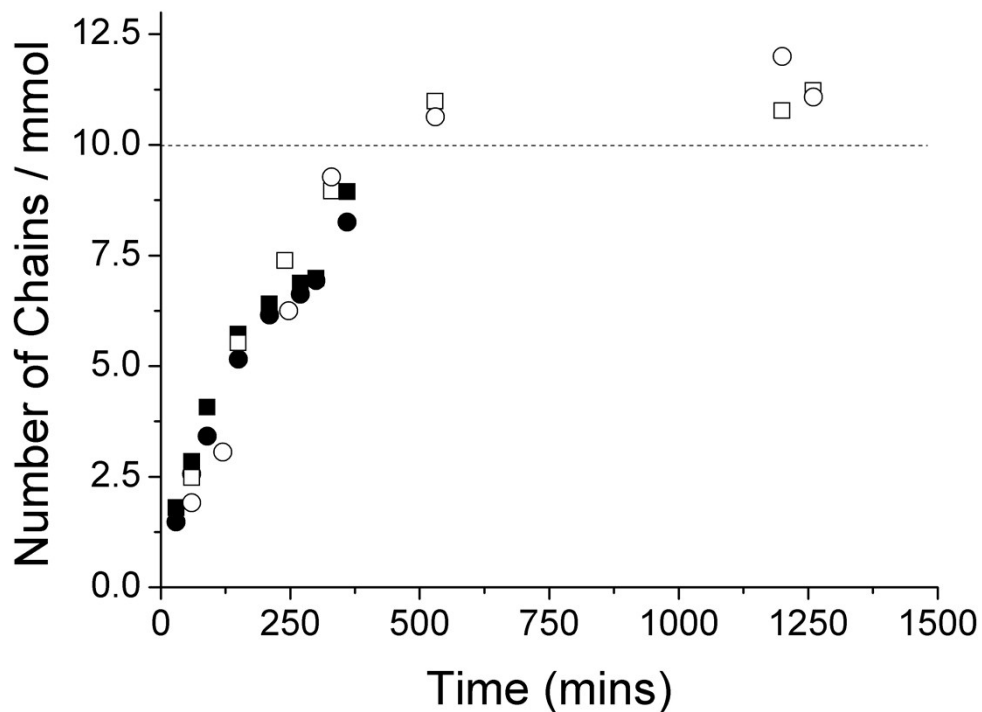
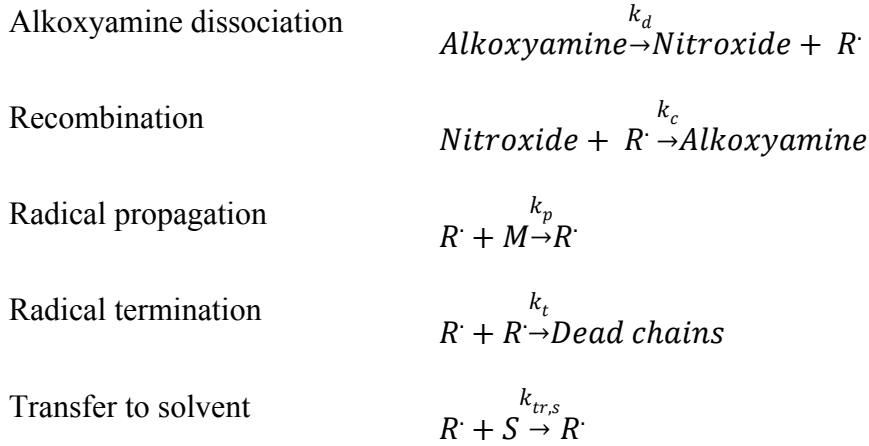


Figure S2 Evolution of number of chains with reaction time for Runs 1-4. The circles represent reactions with monomer in the initial charge (Runs 1 and 2) and the squares represent reactions with no monomer in the initial charge (Runs 3 and 4). The open symbols are for reactions with 20 hr feeding time (Runs 2 and 4) and closed symbols for 5 hr feeding time (Runs 1 and 3). The dotted line represents the theoretical number of chains arising from the initial alkoxyamine.

Persistent Radical Effect in Batch Polymerization



Scheme S1 Kinetic model of nitroxide mediated polymerization.

The concentration of radicals and the buildup of free nitroxide in a batch reaction can be calculated in the same manner as used by Tang *et al.* in considering polymerizations by atom transfer radical polymerizations¹ and by Ohno *et al.* in nitroxide mediated polymerization.² The reaction scheme shown in Scheme S1 leads to

$$\frac{d[R\cdot]}{dt} = k_d[Alkoxyamine] - k_c[Nitroxide][R\cdot] - 2k_t[R\cdot]^2 \quad (S1)$$

$$\frac{d[Nitroxide]}{dt} = k_d[Alkoxyamine] - k_c[Nitroxide][R\cdot] = \frac{d[R\cdot]}{dt} + 2k_t[R\cdot]^2 \quad (S2)$$

Given that $\frac{d[Nitroxide]}{dt} \gg -\frac{d[R\cdot]}{dt}$ leading to

$$\frac{d[Nitroxide]}{dt} = 2k_t[R\cdot]^2 \quad (S3)$$

The radical concentration in the steady state is given by the equilibrium constant of the macroalkoxyamine assuming that $[I] \approx [I]_0$

$$[R] = K \frac{[I]_0}{[\text{Nitroxide}]} \quad (\text{S4})$$

Substituting into equation (S3) gives

$$\frac{d[\text{Nitroxide}]}{dt} = 2k_t \left(K \frac{[I]_0}{[\text{Nitroxide}]} \right)^2 \quad (\text{S5})$$

Upon integration this leads to

$$[\text{Nitroxide}] = (6k_t K^2 [I]_0^2 t)^{\frac{1}{3}} \quad (\text{S6})$$

From equation S4

$$[R] = \left(\frac{K[I]_0}{6k_t} \right)^{\frac{1}{3}} t^{-1/3} \quad (\text{S7})$$

The assumption that $[I] \approx [I]_0$ and that the steady state is reached places an upper and lower time limit within which these equations are valid. The steady state is commonly achieved within less than 1 second and therefore the steady state assumption is reasonable for the time ranges of interest.³ The upper limit of the time scale, t_u , is such that $[I] \approx [I]_0 \gg [\text{Nitroxide}]$ leading to

$$t_u \ll \frac{[I]_0}{6k_t K^2} \quad (\text{S8})$$

Using typical values of $[I]_0 = 0.01 \text{ M}$, $k_t = 3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and $K = 1 \times 10^{-8} \text{ M}$ leads to a value of $t_u \ll 925 \text{ h}$ which is well below the range of interest in this work. Figure S3 presents the analytical solution and that obtained by numerical solution in order to further demonstrate the applicability of the above equations.

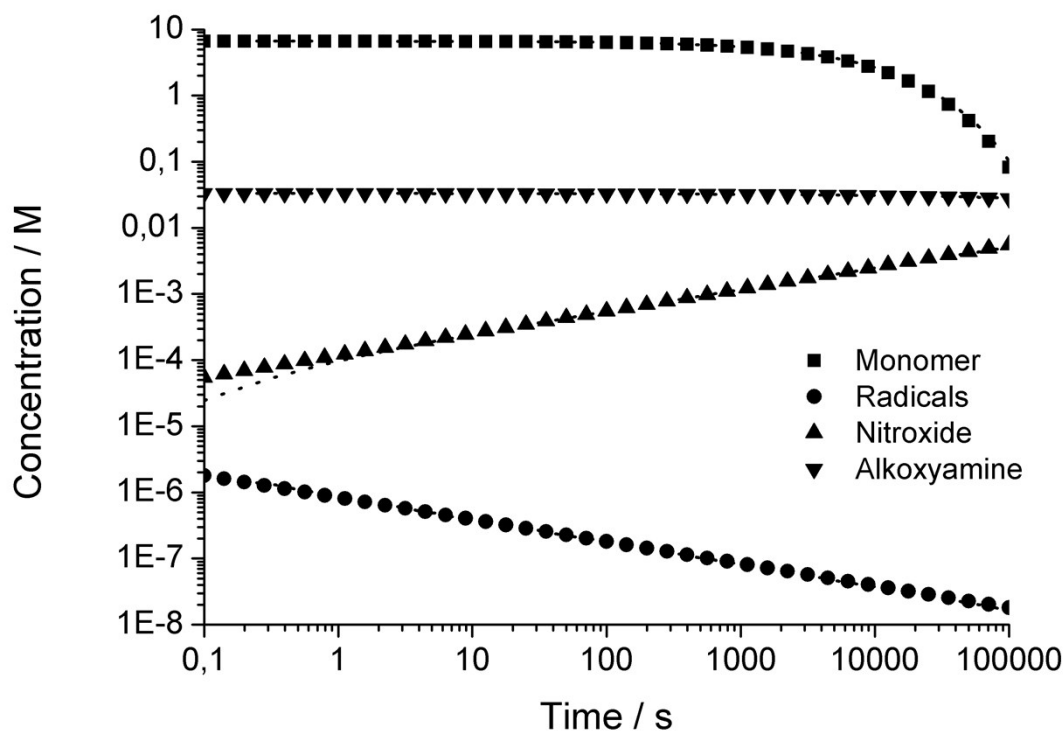


Figure S3 Concentrations of the various species during a typical nitroxide mediated polymerization in batch. The symbols represent the analytical solutions presented in Equations S6 and S7. The lines represent the numerical solution of the full reaction scheme shown in Scheme S1. The close agreement between the two solutions, except for the initial time period when equilibrium is established, demonstrate the validity of the equations within the timeframe of the polymerization. $k_p = 2.67 \times 10^6 \exp(-22360/RT) \text{ M}^{-1}\text{s}^{-1}$,⁴ $k_t = 1.98 \times 10^8 \exp(-5890/RT) \text{ M}^{-1}\text{s}^{-1}$,⁵ $k_d = 0.01 \text{ s}^{-1}$ and $K = 3 \times 10^{-9} \text{ M}$ for a 66 wt% MMA polymerization in toluene at 90 °C (MMA/Alkoxyamine = 200 mol/mol) in batch.

The concentration of nitroxide is a direct measure of the extent of termination in the reaction. In addition, from the radical concentration an estimate on the extent of concentration of dead chains formed by chain transfer reactions, $[C_s]$, can be evaluated. In

the present case, transfer to solvent is assumed to contribute to the greatest extent and in this case, the concentration of chains that have undergone transfer is given by

$$\frac{d[C_s]}{dt} = k_{tr,s}[S][R\cdot] = k_{tr,s}[S]\left(\frac{K[I]_0}{6k_t}\right)^{1/3}t^{-1/3} \quad (S9)$$

Which upon integration gives

$$[C_s] = \frac{3}{2}k_{tr,s}[S]\left(\frac{K[I]_0}{6k_t}\right)^{1/3}t^{2/3} \quad (S10)$$

Persistent Radical Effect in Semi-Batch Polymerization

Above we have dealt with a batch reaction system where all components are added from the outset of the reaction. In a semi-batch polymerization in which in the initial charge is solvent and initiator with volume, V_0 , and the monomer is fed at a given rate, f_m , over a given time, t_{feed} , the radical concentration and number of dead chains can be similarly calculated. In this case equation S3 becomes

$$\frac{d[Nitroxide]}{dt} = 2k_t[R\cdot]^2 - \frac{f_m[Nitroxide]}{V_0 + f_m t} \quad (S11)$$

The concentration of radicals is calculated by

$$[R\cdot] = \frac{K[I]_0 V_0}{[Nitroxide](V_0 + f_m t)} \quad (S12)$$

Substituting into S11 gives

$$\frac{d[Nitroxide]}{dt} = 2k_t \left(\frac{K[I]_0 V_0}{[Nitroxide](V_0 + f_m t)} \right)^2 - \frac{f_m[Nitroxide]}{V_0 + f_m t} \quad (S13)$$

Which can be integrated to give

$$[Nitroxide] = \left(\frac{6k_t [I]_0^2 K^2 V_0^3 t + 3f_m k_t [I]_0^2 K^2 V_0^2 t^2}{V_0^3 + 3V_0^2 f_m t + 3V_0 f_m^2 t^2 + f_m^3 t^3} \right)^{1/3} \quad (S14)$$

By combination with equation S12, the radical concentration is therefore given by

$$[R] = \frac{K[I]_0V_0}{\left(\frac{6k_t[I]_0^2K^2V_0^3t + 3f_mk_t[I]_0^2K^2V_0^2t^2}{V_0^3 + 3V_0^2f_mt + 3V_0f_m^2t^2 + f_m^3t^3}\right)^{1/3}(V_0 + f_mt)} \quad (S15)$$

As for the case of batch polymerizations, the above equations are only valid once the steady state has been achieved, which typically takes place on the order of less than 1 s. The upper limit for the validity of the above as dictated by the relationship $[I]_0 \ll [\text{Nitroxide}]$. Figure S4 presents the analytical solution of equations S14 and 15 and that obtained by numerical integration of the full reaction Scheme shown in S1 in order to further demonstrate the applicability of the above equations within the timeframe of interest.

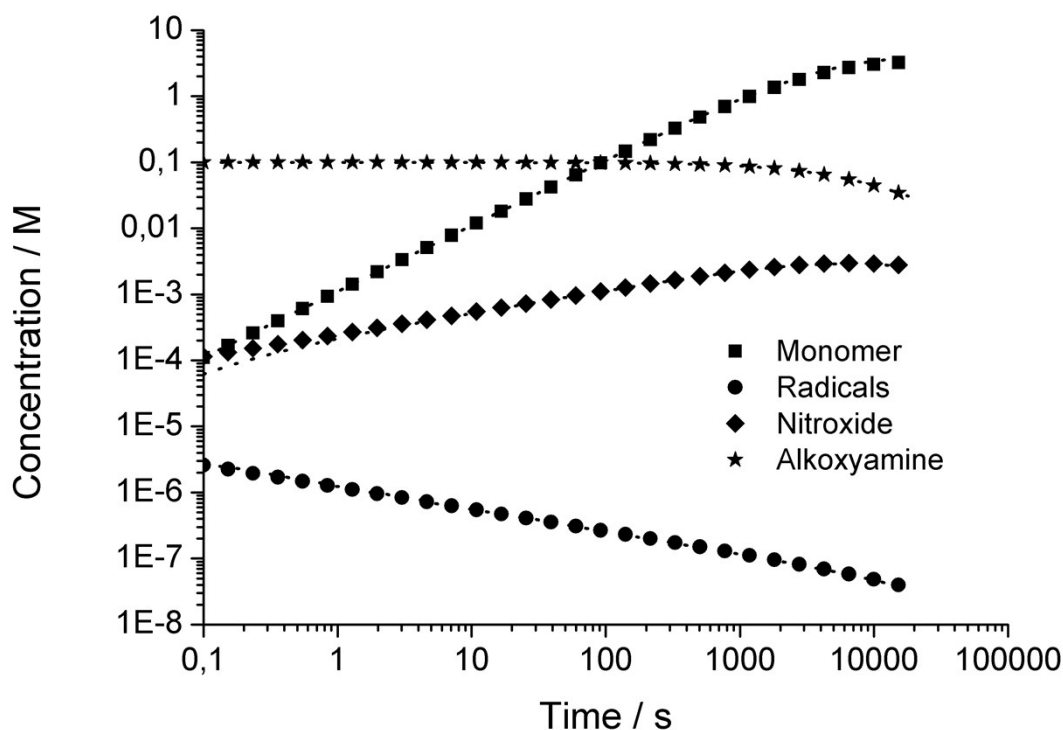


Figure S4 Concentrations of the various species during a typical nitroxide mediated polymerization in semi-batch. The symbols represent the analytical solutions presented in Equations S14 and S15. The lines represent the numerical solution of the full reaction scheme shown in Scheme S1 with the monomer fed over 5 hr. The close agreement between the two solutions, except for the initial time period when equilibrium is established, demonstrate the validity of the equations within the timeframe of the polymerization. $k_p = 2.67 \times 10^6 \exp(-22360/RT) \text{ M}^{-1}\text{s}^{-1}$,⁴ $k_t = 1.98 \times 10^8 \exp(-5890/RT) \text{ M}^{-1}\text{s}^{-1}$,⁵ $k_d = 0.01 \text{ s}^{-1}$ and $K = 3 \times 10^{-9} \text{ M}$ for a 66 wt% MMA polymerization in toluene at 90 °C ([MMA]/[Alkoxyamine] = 200 mol/mol) in semi-batch.

Similar to the above case the number of chains that have undergone termination is given by the nitroxide concentration and the number of chains which undergo transfer to solvent is given by

$$\frac{d[C_s]}{dt} = k_{tr,s}[S][R] - \frac{f_m[C_s]}{V_0 + f_m t} = k_{tr,s} \frac{[S]_0 V_0^2 K [I]_0}{\left(\frac{6k_t[I]_0^2 K^2 V_0^3 t + 3f_m k_t [I]_0^2 K^2 V_0^2 t^2}{V_0^3 + 3V_0^2 f_m t + 3V_0 f_m^2 t^2 + f_m^3 t^3} \right)^{1/3} (V_0 + f_m t)^2} - \frac{f_m[C_s]}{V_0 + f_m t}$$

(S16)

The monomer conversion can be calculated by considering the mass balance of the monomer in the system

$$\frac{d[M]}{dt} = -k_p[M][R] - \frac{f_m[M]}{V_0 + f_m t} + \frac{f_m[M]_{feed}}{V_0 + f_m t} \quad (\text{S17})$$

This equation can be solved numerically using the radical concentration according to equation S15 to give the monomer concentration after a given time and thus the monomer conversion can be calculated.

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- (2) Ohno, K.; Tsujii, Y.; Miyamoto, T.; Fukuda, T.; Goto, M.; Kobayashi, K.; Akaike, T. Synthesis of a Well-Defined Glycopolymer by Nitroxide-Controlled Free Radical Polymerization **1998**, *9297*, 1064–1069.
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