Supporting Information for *"Nitroxide mediated controlled synthesis of glycidyl methacrylate-rich copolymers enabled by SG1-based alkoxyamines bearing succinimidyl ester groups"*

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In Figure 3, the apparent rate constants (k_p[P·] where k_p is the propagation rate constant and [P·] is the concentration of propagating macroradicals) determined experimentally from the $\ln[1/(1-X)]$ versus time plots (X = monomer conversion) were plotted as a function of initial monomer feed composition ($f_{GMA} = 1 - f_{ST}$) for glycidyl methacrylate (GMA)/styrene (ST) mixtures. The apparent rate constants dramatically increase at high GMA feed compositions and an expression was derived for k_p[P·] in an attempt to predict the experimental observations. Below is how a predictive expression for k_p[P·] was derived and compared to the experimental data.

First, the k_p is actually an average k_p for the mixture and is denoted herein as $\langle k_p \rangle$. Expressions for $\langle k_p \rangle$ have been derived using terminal or penultimate kinetic copolymerization models[1]. Here, we use the penultimate model as such a model can better describe most copolymerization kinetic systems, even though the copolymer composition can be predicted well by a terminal model[1]. For an implicit penultimate model, $\langle k_p \rangle$ is given by:

$$\langle k_p \rangle = \frac{r_{ST} f_{ST}^2 + 2 f_{ST} f_{GMA} + r_{GMA} f_{GMA}^2}{r_{ST} \dfrac{f_{ST}}{\overline{k_{p,ST}}} + r_{GMA} \dfrac{f_{GMA}}{\overline{k_{p,GMA}}}} \qquad [1]$$

where r_{ST} and r_{GMA} are the monomer reactivity ratios for ST and GMA, respectively, f_{ST} and f_{GMA} ($f_{GMA} = 1 - f_{ST}$) are the feed compositions of ST and GMA, respectively. Also, $\overline{k_{p,ST}}$ and $\overline{k_{p,GMA}}$ are given by:

$$\overline{k_{p,ST}} = k_{p,ST} \frac{r_{ST} f_{ST} + f_{GMA}}{r_{ST} f_{ST} + \dfrac{f_{GMA}}{s_{ST}}} \qquad [2a]$$

$$\overline{k_{p,GMA}} = k_{p,GMA} \frac{r_{GMA} f_{GMA} + f_{ST}}{r_{GMA} f_{GMA} + \dfrac{f_{ST}}{s_{GMA}}} \qquad [2b]$$

where $k_{p,ST}$ and $k_{p,GMA}$ are the homopolymerization propagation rate constants of ST and GMA, respectively and s_{ST} and s_{GMA} are the radical reactivity ratios. All of the monomer and radical reactivity ratios were taken from Wang and Hutchinson[2] while the propagation rate constants were taken from the appropriate literature[3,4]. All of the parameters used for the estimation of k_p[P·] are summarized in Table S1.

Next, we need to evaluate [P·] for a nitroxide mediated controlled radical polymerization. For this, we use the expression derived by Fischer[5]. It assumes that irreversible termination is not omitted from the polymerization mechanism.

$$[P\cdot] = \left(\frac{\langle K \rangle [I]_0}{3 \langle k_t \rangle} \right)^{1/3} t^{-1/3} \qquad [3]$$

In Equation [3] above, $\langle K \rangle$ is the average equilibrium constant, $[I]_0$ is the initial concentration of nitroxide , $\langle k_t \rangle$ is the average termination rate constant and t is the time. For the implicit penultimate model, Charleux and co-workers derived the following expression for $\langle K \rangle$[6].

$$\langle K \rangle = \frac{\dfrac{r_{ST} f_{ST}}{k_{p,ST}} + \dfrac{r_{GMA} f_{GMA}}{k_{p,GMA}}}{\dfrac{r_{ST} f_{ST}}{k_{p,ST} K_{ST}} + \dfrac{r_{GMA} f_{GMA}}{k_{p,GMA} K_{GMA}}} \qquad [4]$$

Note that the individual equilibrium constant for ST is available from experimental data[7] but that of GMA is not available and was estimated by the available data from the related methyl methacrylate (MMA)[8]. Finally, $\langle k_t \rangle$ was taken for the penultimate model using the following expression[9]:

$$\langle k_t \rangle = \left(p_{ST} k_{t,ST}^{1/2} + p_{GMA} k_{t,GMA}^{1/2} \right)^2$$

where $k_{t,ST}$ and $k_{t,GMA}$ are the homo-termination rate constants for ST and GMA, respectively. Furthermore, p_{ST} and p_{GMA} were given by:

$$p_{ST} = \frac{\dfrac{r_{ST} f_{ST}}{k_{p,ST}}}{\dfrac{r_{ST} f_{ST}}{k_{p,ST}} + \dfrac{r_{GMA} f_{GMA}}{k_{p,GMA}}} \quad \text{and} \quad p_{GMA} = 1 - p_{ST}.$$

$k_{t,ST}$ was taken from Beuermann and Buback[4] while $k_{t,GMA}$ was not available from the literature and thus the termination rate constant for MMA was substituted in its place[10]. Thus, the product of $\langle k_p \rangle [P\cdot]$ can be determined. Note however, that due to the [P·] term, the expression is time dependent. To account for this, [P·] at each composition was plotted as a function of time. [P·] dramatically decreased and leveled to nearly a constant value after only a few minutes (Fig. S1). The concentration at 10 minutes was then taken as the steady value for [P], which would have been reasonable during the time-scale of the experiments. Table S2 lists the [P·] after 10 minutes as a function of feed composition. The [P·] values were then multiplied by the expression for $\langle k_p \rangle$ and plotted in Figure 3 of the manuscript along with the experimental data.

Table S1: List of parameters used for the estimation of the apparent rate constants for the nitroxide mediated copolymerization of styrene/glycidyl methacrylate mixtures at 90 °C.

Parameter	Value
r_{ST}	0.292 [ref. 2]
r_{GMA}	0.528 [ref. 2]
s_{ST}	0.278 [ref. 2]
s_{GMA}	1.046 [ref. 2]
$k_{p,ST}$ (**L mol^{-1} s^{-1}**)	900 [ref. 3]
$k_{p,GMA}$ (**L mol^{-1} s^{-1}**)	3000 [ref.4]
K_{ST} (**mol L^{-1}**)	4.0×10^{-10} [ref. 7]
K_{GMA} (**mol L^{-1}**)	1.0×10^{-7} [ref. 8,a]
$k_{t,ST}$ (**L mol^{-1} s^{-1}**)	1.3×10^{8} [ref. 4]
$k_{t,GMA}$ (**L mol^{-1} s^{-1}**)	2.6×10^{7} [ref. 10,b]
$[I]_0$ (**(mol L^{-1}**)	0.020 [c]

[a] Since K_{GMA} was not available, the equilibrium constant for methyl methacrylate, K_{MMA}, was used in its place.
[b] Since $k_{t\ GMA}$ was not available, the termination rate constant for methyl methacrylate, k_{tMMA}, was used in its place.
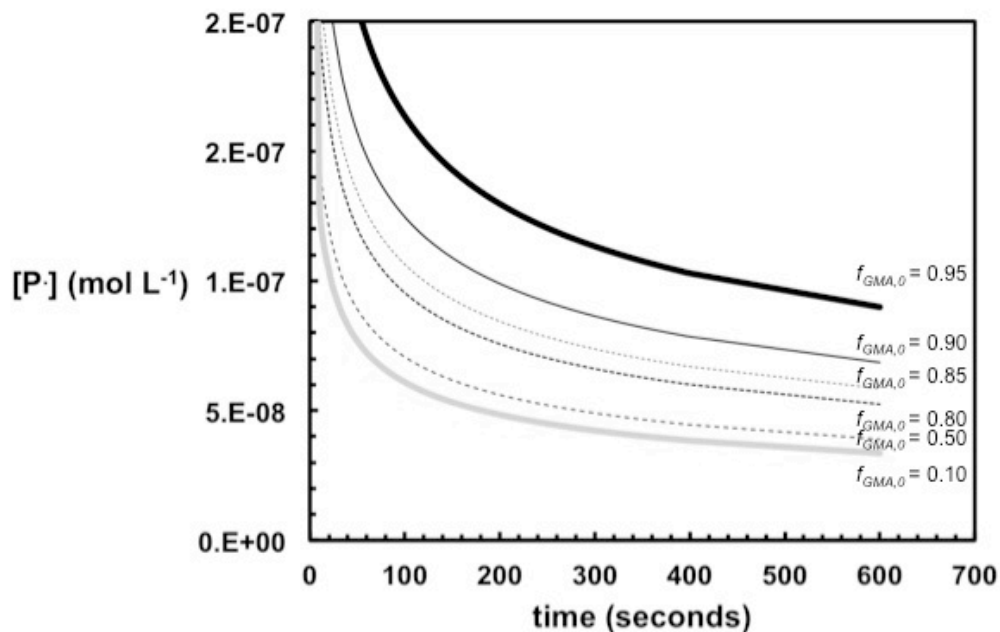[c] $[I]_0$ is the initial alkoxyamine concentration.

Fig S1. Plot of concentration of propagating radicals [P·] as a function of time (using Equation 3).

Table S2: Estimates of the propagating radical concentration [P·] as a function of feed glycidyl methacrylate (GMA)/styrene (ST) feed compositions.

GMA feed composition $f_{GMA,0}$	$[P·]_{t = 10\ min}$ (mol L^{-1})
0	3.2 x 10^{-8}
0.1	3.4 x 10^{-8}
0.2	3.5 x 10^{-8}
0.3	3.6 x 10^{-8}
0.4	3.7 x 10^{-8}
0.5	3.9 x 10^{-8}
0.6	4.1 x 10^{-8}
0.7	4.5 x 10^{-8}
0.8	5.2 x 10^{-8}
0.85	5.8 x 10^{-8}
0.9	6.9 x 10^{-8}
0.95	9.0 x 10^{-8}
1	3.5 x 10^{-7}

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