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Mechanism of Rate Enhancement Using Organic Acids in Nitroxide-Mediated Living Free-Radical Polymerizations

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A recent series of publications[1−18] has described the dramatic progress in the development of a nitroxide-mediated free-radical polymerization (*s*table *f*ree-*r*adical *p*olymerization or SFRP). The first publication from this laboratory described a bulk styrene polymerization mediated by TEMPO radicals, providing polymers with narrow molecular weight distributions (MWD) but requiring 69 h to achieve 90% conversion at 125 °C.[1] Subsequently, this process was extended to produce narrow polydispersity (<1.3) homopolymers, block copolmers, and random copolymers,[2,10] with 90% conversion in as little as 4 h.[5−7,13,15] One key to this rate improvement was the addition of camphorsulfonic acid (CSA), a strong organic acid,[9] which was added in an attempt to suppress autopolymerization.[19] In contrast, the weaker acid benzoic acid, a byproduct of benzoyl peroxide (BPO) initiator decomposition, inhibits styrene autopolymerization but is not a dramatic rate enhancer.[3] Finally, some salts of organic acids act as both autopolymerization inhibitors and rate enhancers.[13]

The key steps of the SFRP process are shown in Scheme 1:

Scheme 1

$$P_i^\bullet + T^\bullet \overset{K_L}{\rightleftarrows} L_i \qquad (1)$$

$$P_i^\bullet + M \xrightarrow{k_p} P_{i+1}^\bullet \qquad (2)$$

$P_i^\bullet$ is the *active* growing polymer chain, $T^\bullet$ is the nitroxide radical, L_i is the reversibly capped polymer chain, which we denote as the *dormant* or *living chain*, and M is monomer. The polymerization rate is inversely proportional to $[T^\bullet]$, due to the equilibrium between growing and nitroxide-capped chains:

$$K_L = \frac{k_L}{k_{-L}} = \frac{L}{TP} \qquad (3)$$

Here $T = [T^\bullet]$, $P_i = [P_i^\bullet]$, $P = \sum_{i=1}^{\infty} P_i$, $L = \sum_{i=1}^{\infty}[L_i]$, and k_L and k_{-L} are the rate constants for trapping of growing chains by nitroxide and for the release of growing chains, respectively. Note that L is constant once initiation is complete, as then $L \gg T$ *(or P)*. The quantitative adherence of the SFRP process to eq 3 has been recently shown, using electron spin resonance (ESR) to measure the concentration of the nitroxide radical *in situ* during the polymerization.[5,6]

The purpose of this paper is to define the role of organic acids, such as CSA, as they affect the concentration of the nitroxide in reaction 1. The dramatic rate enhancement of CSA will be explained in terms of this equilibrium.

The experimental details have been published previously.[5,6] Briefly, BPO was used to initiate bulk styrene polymerizations at 125 °C, with TEMPO as the nitroxide mediator. After about 5 min at 125 °C, when initiation was complete, the CSA was added. In this way, interference of CSA in initiation was avoided. The experimental data are shown in Figures 1−4, with and without CSA at an initial 1.3:1 TEMPO:BPO molar ratio, and for comparison, without CSA at a lower initial 1.1:1 TEMPO:BPO ratio.

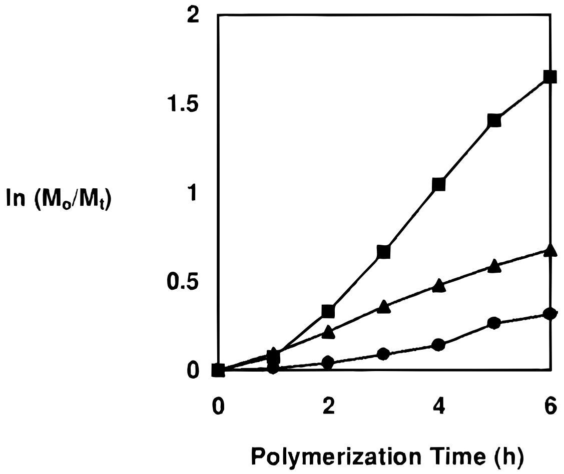

Figure 1. Rate for bulk styrene SFR polymerization (initial [BPO] = 0.036 M at 125 °C): (■) 0.016 M CSA added at 10 min, initial [TEMPO]/[BPO] = 1.3:1; (●) no CSA added, initial [TEMPO]/[BPO] = 1.3:1; (▲) no CSA added, initial [TEMPO]/[BPO] = 1.1:1.

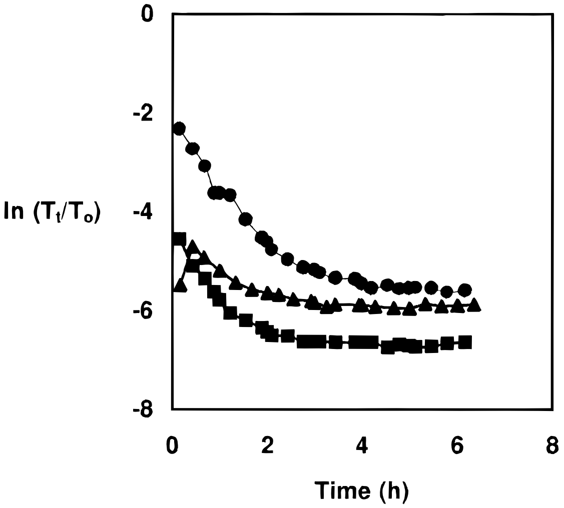

Figure 2. TEMPO concentration determined by ESR spectroscopy for bulk styrene SFR polymerization ([BPO] = 0.036 M at 125 °C): (■) 0.016 M CSA added at 10 min, initial [TEMPO]/[BPO] = 1.3:1; (●) no CSA, initial [TEMPO]/[BPO] = 1.3:1; (▲) no CSA, initial [TEMPO]/[BPO] = 1.1:1.

Figure 1 shows the dramatic effect of CSA: a 2.5−4-fold rate increase. The largest effect is early in the polymerization, where the rate without CSA is particularly slow. The rate *without* CSA can be increased by reducing the initial TEMPO concentration, from 1.3:1 to 1.1:1 TEMPO:BPO. Even so, the rate with CSA at the 1.3:1 ratio is faster than without CSA at the 1.1:1 ratio.

Figure 2 shows that the TEMPO concentration, measured *in situ* by ESR, drops rapidly during initiation (the first 5 min), primarily due to trapping of the initiated polymer chains by nitroxide.[8] Once initiation is complete, CSA is added, further reducing the TEMPO

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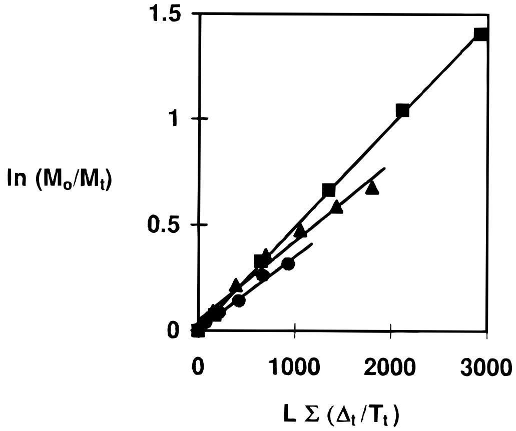

Figure 3. Rate of bulk styrene SFR polymerization corrected for TEMPO concentration (initial [BPO] = 0.036 M at 125 °C): (■) 0.016 M CSA added at 10 min, initial [TEMPO]/[BPO] = 1.3:1; (●) no CSA, initial [TEMPO]/[BPO] = 1.3:1; (▲) no CSA, initial [TEMPO]/[BPO] = 1.1:1.

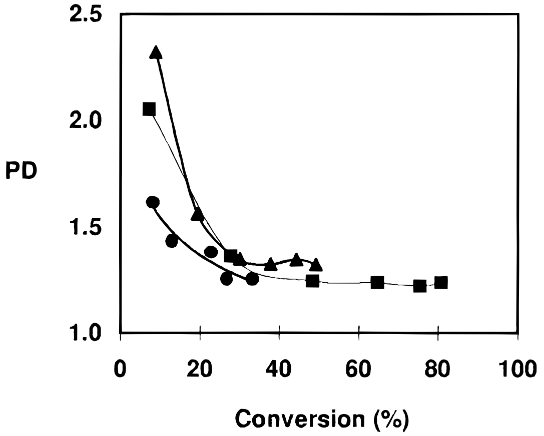

Figure 4. Polydispersity for bulk styrene SFR polymerization (initial [BPO] = 0.036 M at 125 °C): (■) 0.016 M CSA added at 10 min, initial [TEMPO]/[BPO] = 1.3:1; (●) no CSA, initial [TEMPO]/[BPO] = 1.3:1; (▲) no CSA, initial [TEMPO]/[BPO] = 1.1:1.

concentration. At 15 min (the first data point), 10 min after CSA addition, the TEMPO concentration has been reduced by a factor of 10 compared to the reaction without CSA. Indeed, the TEMPO concentration with CSA and 1.3:1 TEMPO:BPO is similar to that without CSA at the lower 1.1:1 TEMPO:BPO ratio. Thus, CSA increases the consumption of TEMPO during the polymerization. The polymerization rates *qualitatively* agree with Scheme 1: a reduction in TEMPO concentration results in an equivalent increase in the polymerization rate. As show previously, the effect of the [TEMPO] on the polymerization rate can be *quantitatively* accounted for using the differential rate equations describing the polymerization.[5] The equilibrium between growing chains and capped dormant chains, described by eq 3, and conventional free-radical kinetics gives[5]

$$\frac{-\mathrm{d}M}{\mathrm{d}t} = k_\mathrm{p} M \frac{L}{TK_\mathrm{L}} \tag{4}$$

$$\int_{t=0}^{t} \frac{\mathrm{d}M}{M} = \frac{Lk_\mathrm{p}}{K_\mathrm{L}} \sum_{t=0}^{t} \frac{\Delta t}{T_t} \tag{5}$$

$$\ln\left[\frac{M_0}{M_t}\right] = \frac{Lk_\mathrm{p}}{K_\mathrm{L}} \sum_{t=0}^{t} \frac{\Delta t}{T_t} \tag{6}$$

k_p is the polymerization rate constant, while M_0 and M_t are the monomer concentrations at times $t = 0$ and $t = t$, respectively. Δt is a time interval over which the [TEMPO] is assumed constant, with an average value of T_t. In practice, T_t was calculated over 1 h intervals from the ESR data. We have previously shown that this approach results in an excellent agreement with the experimental data.[5]

The rate data from Figure 1 were corrected using eq 6, and TEMPO concentrations from Figure 2. The corrected rates are plotted in Figure 3 as $\ln[M_0/M_t]$ versus $L\sum(\Delta t/T_t)$. The slope is $k_\mathrm{p}/K_\mathrm{L}$, the ratio of the styrene polymerization rate constant to the equilibrium constant between active and growing chains. The curves in Figure 3 are linear, both with and without CSA. All data sets give y intercepts of zero, giving slopes ($k_\mathrm{p}/K_\mathrm{L}$) of $(1.23 \pm 0.14) \times 10^{-7}$ s^{-1} and $(0.95 \pm 0.12) \times 10^{-7}$ s^{-1} with and without CSA at 1.3:1 TEMPO:BPO and a slope of $(1.03 \pm 0.18) \times 10^{-7}$ s^{-1} without CSA at 1.1:1 TEMPO:BPO, respectively. Thus, the polymerizations without CSA give the same value of $k_\mathrm{p}/K_\mathrm{L}$, within the quoted 95% confidence limits. While the value for the polymerization with CSA is statistically different, the difference is only about 30%. Thus, the majority of the CSA rate enhancement arises from the reduction in nitroxide concentration, more than an order of magnitude more important than this secondary rate enhancement.

In model studies, we have previously shown that CSA in xylene (in the absence of monomer and initiator) rapidly consumes TEMPO,[13] consistent with the known disproportionation of nitroxides to oxammonium and hydroxylamino species in the presence of strong acids.[20] This is the likely mechanism for the consumption of TEMPO during the polymerization.

The small secondary effect of CSA increases $k_\mathrm{p}/K_\mathrm{L}$ by about 30%. We know of no precedent that k_p for styrene is affected by acids. If CSA effects K_L, then CSA must either decrease k_L, the rate of chain trapping by TEMPO, or increase the rate of chain release, $k_{-\mathrm{L}}$. The former has a precedent: more polar solvents do lead to slower nitroxide trapping rates.[21] However, changing the solvent from benzene (a reasonable model for styrene) to a hydrogen-bonding polar solvent (a reasonable model for CSA) reduces the trapping rate by only 30%. It seems unlikely that addition of only 0.016 M CSA could effect the solvent polarity enough to explain the observed 30% trapping rate decrease. Finally, an acid could affect $k_{-\mathrm{L}}$, by protonating the N−O−C bond or again by changing solvent polarity. The effect of the latter on $k_{-\mathrm{L}}$ is unknown. A protonated nitroxide radical has been observed using ESR,[22] but again it is not known if this would lower the energy required to release the growing chain.

Figure 4 shows the polydispersity of the resultant polymers with conversion. At the 1.3:1 TEMPO:BPO ratio, the polydispersity is initially increased by CSA addition. However, the PD narrows with conversion, resulting in little PD difference above 30% conversion. In addition, comparsion of the TEMPO concentrations in Figure 2, with the respective PDs at low conversion in Figure 4, shows that a high initial PD arises from a low TEMPO concentration, not from the presence of CSA. A lower TEMPO concentration slows the trapping of growing polymer chains (reaction 1), leading to the broader initial polydispersity. This effect has been recently discussed for the SFRP process[6] and is similar to effects observed in other polymerizations involving dormant chains.[23]

Beyond 30% conversion, the polydispersity with CSA at the initial 1.3:1 TEMPO:BPO is better than the polydispersity without CSA at the lower initial 1.1:1 ratio, while the former still gives a higher overall polymerization rate. This is the advantage to using CSA to increase polymerization rates, compared to simply reducing the initial TEMPO concentration. As shown in Figure 2, starting with the lower 1.1:1 TEMPO:BPO without CSA gives a lower initial TEMPO concentration than with 1.3:1 TEMPO:BPO with CSA. This lower TEMPO concentration may be a disadvantage early in the reaction. As CSA consumes TEMPO, this situation reverses: polymerization *with* CSA at 1.3:1 TEMPO:BPO ultimately has less TEMPO. The different TEMPO concentration profile with conversion in the presence of CSA apparently results is a better polydispersity at high conversions.

Previous work has shown that there is an optimum CSA concentration due to the competition between the rate enhancement and broadening of PDs, a result of the reduction in the nitroxide concentration by CSA.[9] Very low nitroxide levels ultimately result in significant irreversible termination ($\propto k_t P^2$); however, before that level is reached the slowing of the reversible trapping rate also broadens the polydispersity, as explained in ref 6.

In summary, the primary rate enhancement mechanism due to organic acids, such as CSA, in nitroxide-mediated polymerizations involves the consumption of nitroxide radicals. The lower nitroxide concentration affects the equilibrium between growing and dormant chains, increasing the number of growing chains, and hence the polymerization rate. While similar rate enhancements can be obtained without CSA, by simply decreasing the initial nitroxide concentration, the best compromise between fast rates and narrow polydispersities is obtained with CSA. There is a small secondary rate enhancement by CSA, a result of either an increase in the polymerization rate constant, a rate increase for nitroxide release from growing chains, or a rate decrease for chain trapping by nitroxide.

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