

RAPID COMMUNICATION

TEMPO-Mediated Polymerization of Styrene: Rate Enhancement with Dicumyl Peroxide

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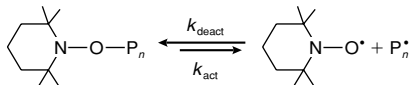
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The concept of applying stable nitroxyl radicals to control a free-radical polymerization was developed in late 1980's by Solomon and Rizzardo¹ for a variety of monomers, but this original approach was limited to low molecular weight polymers. Subsequently, Georges and co-workers adapted this approach to polymerization of styrene initiated by benzoyl peroxide (BPO) in the presence of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO)² yielding high molecular weight polymers with low polydispersities and molecular weights increasing linearly with conversion. Other authors have reported that well-defined polymers can also be obtained in thermal polymerization of styrene in the presence of TEMPO³ as well as in the polymerization of styrene initiated by various TEMPO adducts^{4,5} and other alkoxyamines.^{6,7} Additionally, copolymers of styrene and other vinyl monomers have also been synthesized in a controlled manner by using this technique.^{8–10}

Control of the polymerization is achieved by cleavage of the dormant alkoxyamine that reversibly produces propagating radicals:



Thus, because the above equilibrium is shifted strongly to the left side, the concentration of the active species is lower in the TEMPO-mediated polymerization than in a conventional free radical polymerization. Consequently, the rate of bimolecular termination, which is second order with respect to radical concentration, is

lower and does not lead to a broadening of the molecular weight distributions, in contrast to conventional polymerizations. However, the rate of propagation (first order with respect to radical concentration) is also affected, although much less than the termination.

The most important disadvantage of this process is the long time required for completion of the polymerization, even at relatively high temperatures and independent of initiator concentration. For example, in a bulk polymerization of styrene at 120°C it takes 20 h to reach 60% conversion and 44 h to reach ~90% conversion at TEMPO adduct concentration of 0.01M. The reason for the slow polymerization rate is a low stationary concentration of the propagating radicals. The equilibrium constant:

$$K_{eq} = \frac{[P^{\bullet}] \cdot [T^{\bullet}]}{[PT]}$$

where $P^{\bullet}$ = propagating radicals, $T^{\bullet}$ = TEMPO and PT-dormant chains, at 120°C is on the order of $10^{-11} \text{ mol L}^{-1}$.^{11,12} The experimentally determined stationary concentration of TEMPO is approximately 0.1% of the original concentration of TEMPO or its adduct.^{12,13} Thus, the stationary concentration of propagating radicals, $[P^{\bullet}] = K_{eq} \cdot [T^{\bullet}] / [PT]$, is about $10^{-8} \text{ mol L}^{-1}$.

The rate of the polymerization of styrene in the presence of TEMPO and some other nitroxides⁶ is independent of the concentration of the alkoxyamine (nitroxide adduct) and remarkably close to the rate of thermal polymerization under similar conditions. It has been shown that it is thermal self-initiation of styrene that provides a concentration of propagating radicals sufficient for obtaining reasonable, albeit slow, polymerization rates.^{11,12,14} The thermally produced radicals compensate for the radicals lost due to termination by coupling and prevent an excessive accumulation of

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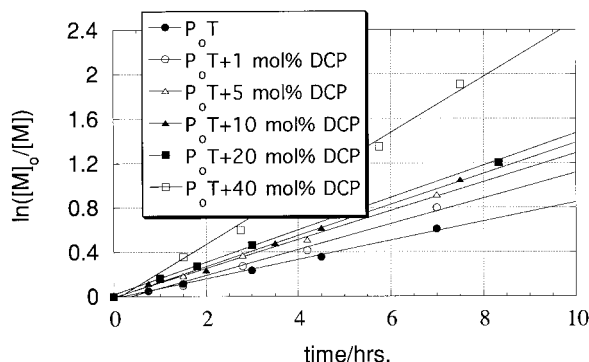


Figure 1. Kinetic plots of $\ln([M]_0/[M])$ vs. time for bulk polymerization of styrene in the presence of 1-phenylethyl-TEMPO adduct, $[P_0T]_0 = 0.010 \text{ mol L}^{-1}$, and variable amounts of DCP; temperature, 120°C .

TEMPO. If the thermal initiation were absent, the polymerization would be even slower. Based on the above observations the conclusion might be drawn that the rate of the TEMPO-mediated polymerization of styrene can be enhanced by decreasing the concentration of TEMPO and thereby increasing the concentration of propagating radicals. Since the polymerization is controlled by the excess of TEMPO (a persistent radical effect¹⁵), this approach would undoubtedly lead to a higher rate of bimolecular termination and an increase in polydispersities if the concentration of TEMPO is brought too low and the rate of the trapping of the growing chains becomes lower than the rate of propagation. This might be avoided if the concentration of radicals is only few times higher than the concentration of radicals provided by thermal self-initiation, and the excess of TEMPO is continuously but slowly being removed from the system.

Georges et al. reported that addition of a small amount of camphorsulfonic acid (CSA)¹⁶ or 2-fluoro-1-methylpyridinium *p*-toluenesulfonate¹⁷ to a polymerization of styrene initiated by BPO in the presence of TEMPO increased the rate of polymerization significantly. But the addition of CSA or the salt also caused broadening of polydispersities, particularly at the beginning of the polymerization. In the case of CSA as an additive, the authors showed that the concentration of TEMPO is decreased in the presence of CSA, possibly by a fast direct reaction of TEMPO with the acid.¹⁸ This reaction irreversibly eliminates some of the nitroxide already at the beginning of the polymerization, thereby reducing the induction period. After the initial increase of the rate, the polymerization proceeds with a virtually unchanged rate (vide data in Ref. 16). Scaiano and co-workers¹⁹ also observed that adding a polar additive such as CSA decreases the rate of the reaction of TEMPO with carbon-centered radicals contributing to the aforementioned polymerization rate increase. The mechanism of the rate enhancement in the presence of the salt is unknown so far.

In this work, an alternative approach to rate en-

hancement of the TEMPO-mediated polymerization of styrene is demonstrated. In our approach the increase of polymerization rate was achieved by adding a small amount of a radical initiator with a long half-life time at the reaction temperature. After this communication was submitted, a similar experiment has been suggested by Fukuda.²⁰ In our system, the excess of TEMPO is continuously decreased by reaction with radicals formed by the slowly decomposing radical initiator, analogous to thermal self-initiation. The initiator of choice was commercially available dicumyl peroxide (DCP), which at the employed concentrations, decomposes with a rate comparable to the rate of thermal initiation under the polymerization conditions. The simplest system to which the rate enhancement by addition of DCP can be applied is the thermal polymerization of styrene in the presence of TEMPO. The addition of DCP to this system increases the rate of polymerization, however, the long induction period is still observed.

Figure 1 shows kinetic plots for polymerization of styrene initiated by the 1-phenyl ethyl-TEMPO adduct in the presence of a variable amount of DCP. The rate of polymerization apparently increases with the increase of the amount of DCP added. The plots are linear, indicating a steady state for propagating radicals within the conversions studied. The slopes of the plots of $\ln([M]_0/[M])$ vs. time become larger for higher DCP content suggesting an increase in the stationary concentration of the growing radicals. As calculated from the rate of decomposition at 120°C , the amount of the DCP decomposed after 10 h (an average reaction time) is about 75% of the amount added. That means that the total amount of radicals produced by decomposition of DCP is between 1×10^{-4} and $3 \times 10^{-3} \text{ mol L}^{-1}$ for the range of DCP concentrations used in this experiment.

As expected, the molecular weights of the resulting polymers are progressively lower than expected molecular weights (based on the initial concentration of the initiator) as the amount of added DCP is increased (Fig. 2). The radicals introduced by decomposition of the ini-

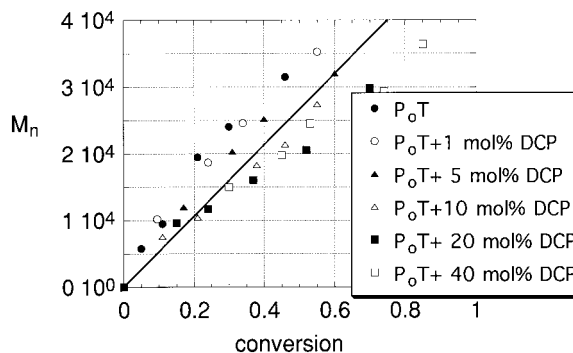


Figure 2. Evolution of molecular weights with conversion for a bulk polymerization of styrene in the presence of 1-phenylethyl-TEMPO adduct, $[P_0T]_0 = 0.010 \text{ mol L}^{-1}$, and variable amounts of DCP; temperature, 120°C . (The line serves as a visual guide.)

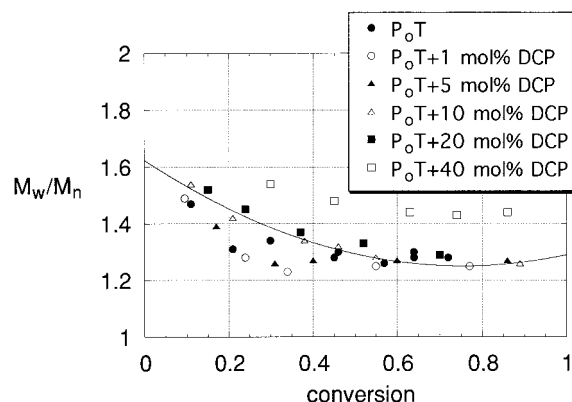


Figure 3. Dependence of molecular weights distribution upon conversion for a bulk polymerization of styrene in the presence of 1-phenylethyl-TEMPO adduct, $[P_0T]_0 = 0.010 \text{ mol L}^{-1}$, and variable amounts of DCP; temperature 120°C . (The line serves as a visual guide.)

tiator react with TEMPO, increasing the total number of chains. However the decrease of molecular weights is significant only at higher concentrations of DCP ($\geq 40 \text{ mol } \%$). Another observation that can be made after inspecting Figure 2 is that for the polymerizations with a higher initial content of DCP, the plots of molecular weights versus conversion are linear even at high conversion ($>80\%$), in contrast to a polymerization in the presence of the adduct alone, where the plots of molecular weights versus conversion show a tendency to level off at high conversions.

Introducing an additional source of radicals in the form of a radical initiator to the TEMPO-mediated polymerization of styrene reduces the stationary concentration of TEMPO and correspondingly, the rate of deactivation, and should lead to a broadening of molecular weight distributions of the resulting polymers. Indeed, when DCP is added to a polymerization of styrene initiated by the 1-phenylethyl-TEMPO adduct, a small increase in polydispersities is observed (Fig. 3), but it is significant only at the highest content of DCP ($M_w/M_n \leq 1.45$ at $40 \text{ mol } \%$) and even then it is lower than the limiting polydispersity for a conventional radical polymerization $M_w/M_n = 1.5$. At moderate content of the radical initiator the polydispersities are as low as in the presence of the adduct only.

A similar approach to rate enhancement (e.g., by addition of DCP) was also tested for a polymerization of styrene initiated by 2,2'-azobis(isobutyronitrile), AIBN in the presence of an equimolar amount of TEMPO. The polymerization procedure and polymer characterizations were identical to that for the polymerizations in the presence of 1-phenylethyl-TEMPO adduct. In this system, addition of DCP has an even more pronounced effect on the polymerization rate for the previously described system (Fig. 4) but the polydispersities are much higher ($M_w/M_n = 1.55$ vs. 1.30 in the absence of the DCP). The broadening of polydispersities occurs because, initially, the rate of propaga-

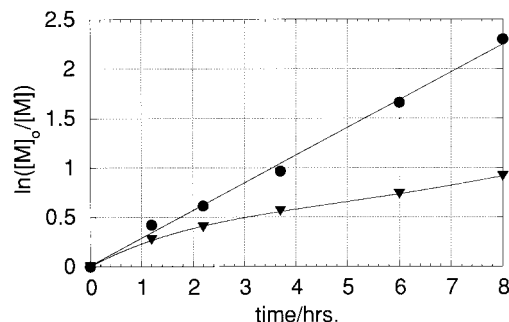


Figure 4. Kinetic plots of $\ln([M]_0/[M])$ vs. time for bulk polymerization of styrene initiated by AIBN (0.010 mol L^{-1}) in the presence of TEMPO (0.010 mol L^{-1}) with ($\blacktriangledown$) 0% of DCP, and ($\bullet$) $20 \text{ mol } \%$ of DCP; temperature, 120°C .

tion in the AIBN-initiated system is already higher than the rate of the trapping of the radicals with TEMPO and adding an additional source of radicals accelerates the initial rate of propagation even further. Thus, a high polymer is formed at very low conversions, leading to the broadening of overall molecular weight distributions. However, despite higher polydispersities, the molecular weights increase linearly with conversion (Fig. 5) indicating that the polymerization proceeds in a controlled manner.

This approach can also be successfully applied to modify the procedure invented by Georges et al.²¹ in which the reaction mixture containing monomer, initiator (BPO), and excess of TEMPO (1.3 times in respect to the concentration of BPO) is first thermostated at 90°C for 3.5 h to produce the corresponding alkoxyamine from BPO and TEMPO, and subsequently heated to 120°C , the temperature at which polymerization begins. In the modified procedure the rate enhancement is achieved by using a mixed initiator (BPO + $20\text{--}30 \text{ mol } \%$ of DCP). The reaction is approximately 2–3 times faster than in the absence of DCP. At the same

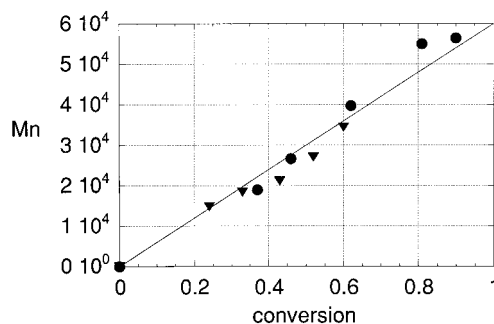


Figure 5. Evolution of molecular weights with conversion for bulk polymerization of styrene initiated by AIBN (0.010 mol L^{-1}) in the presence of TEMPO (0.010 mol L^{-1}) with ($\blacktriangledown$) 0% of DCP and ($\bullet$) $20 \text{ mol } \%$ of DCP; temperature, 120°C . (The line serves as a visual guide.)

time, the resulting polymers retain low polydispersities ($M_w/M_n \leq 1.30$) (Figs. 6 and 7).

EXPERIMENTAL

Materials Styrene (Aldrich) was dried over CaH_2 and distilled under vacuum prior to the polymerization. The initiators, AIBN (Eastman Kodak) and BPO (Aldrich), were purified by recrystallization from methanol. Dicumyl peroxide (Aldrich, 98% pure) was used as received. The 1-phenylethyl-TEMPO adduct was synthesized as described previously.¹¹

Polymerizations A series of polymerizations of styrene in the presence of the 1-phenylethyl-TEMPO adduct with variable amounts of DCP were performed. A typical polymerization procedure was as follows: monomer, adduct or initiator (AIBN or BPO), and DCP (a stock solution in styrene) were added to a Schlenk flask under argon and the reaction mixture was thermostated in an oil-bath at 120°C. Samples were taken from the reaction mixture after variable times. The monomer conversion was determined gravimetrically. The molecular weight measurements by gel permeation chromatography were performed on the samples from the reaction mixture after diluting with tetrahydrofuran.

The modified procedure was carried out as follows: the monomer, TEMPO, and mixed initiators (BPO + 20 mol % of DCP based on the concentration of BPO) were added under argon to a Schlenk flask and thermostated at 90°C for 3.5 h and then heated to 120°C. The monomer conversion and molecular weights were determined as described above.

CONCLUSIONS

In this work, it has been demonstrated that a rate enhancement of the TEMPO-mediated polymerization of

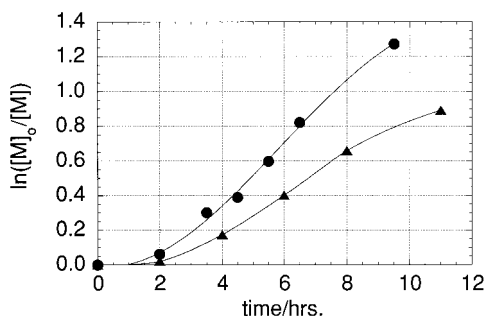


Figure 6. Kinetic plots of $\ln([M]_0/[M])$ vs. time for bulk polymerization of styrene initiated by BPO (0.010 mol L^{-1}) in the presence of TEMPO (0.013 mol L^{-1}) with (▼) 0% of DCP and (●) 20 mol % of DCP; temperature, 120°C.

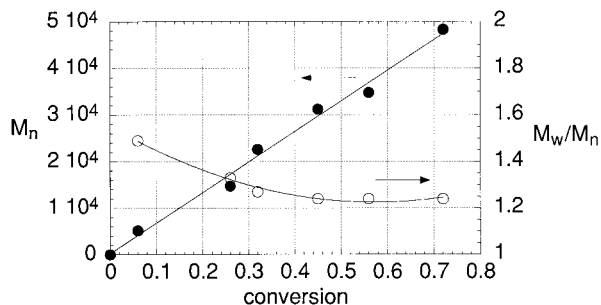


Figure 7. Evolution of (▼) molecular weights and (●) molecular weights distributions with conversion for bulk polymerization of styrene initiated by BPO (0.010 mol L^{-1}) in the presence of TEMPO (0.013 mol L^{-1}) and 20 mol % of DCP; temperature, 120°C.

styrene can be achieved upon addition of a small amount of a radical initiator with a long half-life time at the polymerization temperature. The TEMPO-mediated polymerization of styrene with DCP added in the amount up to 40 mol % proceeds with a higher rate than analogous polymerization in the absence of the radical initiator. At the same time, molecular weights increase linearly with conversion and are only slightly lower than expected when $\leq 40 \text{ mol } \%$ of the initiator is added. Additionally, the polydispersities remain low and close to those obtained in the systems without an additional initiator.

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