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Mechanism of Controlled/“Living” Radical Polymerization of Styrene in the Presence of Nitroxyl Radicals. Kinetics and Simulations

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ABSTRACT: The polymerization of styrene in the presence of a stable radical, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), has been simulated using a Predici simulations package. On the basis of the experimental data, a kinetic model for the TEMPO-mediated polymerization of styrene is proposed. In order to simulate the experimental data properly, it was necessary to include thermal self-initiation, transfer, and irreversible decomposition of intermediate alkoxyamines in addition to the reversible cleavage of the TEMPO-polymeric radical adduct. This model, combined with the values of the rate constants of propagation (k_p), termination (k_t), transfer (k_{trm}), and alkoxyamines decomposition (k_{decomp}), was then employed to estimate the kinetic and thermodynamic parameters for the exchange between dormant and active species. The equilibrium constant, K, was estimated to be approximately 10^{-11} mol·L^{-1}, the deactivation rate constant, $k_d = 8 \times 10^7$ mol^{-1}·L·s^{-1}, and the activation rate constant, $k_a = 8 \times 10^{-4}$ s^{-1}, for bulk styrene polymerization at 120 °C.

Introduction

The description of a mechanism of polymerization requires the definition of all elementary reactions involved in the process, i.e., initiation, propagation, chain breaking reactions (transfer and termination), and other reactions such as exchange, isomerization, etc. The absence of chain breaking reactions results in a living polymerization; however, in homogeneous radical polymerization it is impossible to suppress bimolecular termination between growing radicals entirely. Therefore, radical polymerizations can be only apparently living (or “living”) or just controlled in the sense that the preparation of polymers with predetermined molecular weights, low polydispersities, and terminal functionalities is possible.

Radical polymerization, in spite of its commercial importance, has been difficult to control at the level attained for anionic and cationic polymerization. A rational design and approach to controlled/“living” radical polymerization has been presented only very recently.[1] This approach is based on the reversible formation of growing radicals from various types of dormant species. The reversible homolytic cleavage of dormant species can be accomplished by either thermal, photochemical, or catalytic activation. The most successful approaches are as follows: homolytic cleavage of alkoxyamines[2−10] and dithiocarbamates,[11−13] use of various organometallic species,[14−19] and catalyzed atom transfer radical polymerization.[20−26] These approaches could be supplemented with the bimolecular degenerative transfer process.[27,28]

The use of a stable radical, TEMPO (2,2,6,6,-tetramethyl-1-piperidinyloxy), as a moderator in the radical polymerization of styrenes has been studied most extensively, but the exact mechanism and the reasons why well-defined polymers can be prepared are still obscure. The objective of this paper is to summarize the experimental data obtained from different, but comparable, systems and to provide a comprehensive view on the polymerization of styrene in the presence of TEMPO and other alkoxyamines. We will analyze the effect of various reactions occurring in this system, including self-initiation, termination, transfer, decomposition of alkoxyamines, and the effect of the dynamics of exchange on kinetics, molecular weights, and polydispersities. In a subsequent paper we will analyze the effect of various reaction conditions as well as the polymerization of other monomers which do not self-initiate.

A computer simulation of the polymerization process can be relatively simple if only one deviation from the ideal living system is considered. It has been demonstrated that such an approach can be extremely useful in studying the mechanism of controlled/living polymerizations such as group transfer, carbocationic, and other polymerizations.[29−32] However, as will be shown later, a radical polymerization involves several elementary reactions, and therefore a clean analytic solution is not available, and oversimplification may lead to an incorrect conclusions.[33] It has been reported recently that the Predici computer simulation program can be used successfully for the simulation of multistep polymerization systems and that it provides an excellent agreement with purely analytical solutions.[34] Therefore, we have used the Predici program to simulate the TEMPO-mediated radical polymerization of styrene. Even though the accuracy of the estimation of the rate and the equilibrium constants is ±50%, the main purpose of this paper is to show the order of magnitude of the rate constants and the effect of various reactions on the rate of polymerization, molecular weights, and polydispersities.

Brief History of the TEMPO-Mediated Polymerization of Styrene

The first use of nitroxyl radicals and alkoxyamines in a radical polymerization was reported by Rizzardo and Solomon[2,3] for a variety of vinyl monomers, but it was generally limited to low-molecular weight polymers and oligomers. Subsequent extensive studies by Georges and co-workers on the polymerization of styrene in the presence of TEMPO demonstrated that well-defined polymers with low polydispersities can be prepared in this system.[4,35−39] Alkoxyamines have been employed

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in three different ways to control the polymerization of styrene. First, alkoxyamines, themselves, have been used as well-defined initiators, in a way similar to the Rizzardo and Solomon original work.[2,5,7,9,40,41] It should be stressed that this approach yields polymers with the lowest polydispersities and it provides the most lucid picture of the reactions occurring in such a system. Second, alkoxyamines may be formed *in situ* by using peroxides and/or diazo compounds and corresponding nitroxyl radicals.[4,35−39,42] In this case it is important to use a concentration of the radical scavenger exceeding that of the radicals formed by the decomposition of the initiator. Third, alkoxyamines can also be formed *in situ* by using nitroxyl radicals in thermally self-initiated polymerization.[6,42−45] Unfortunately, a TEMPO-mediated system is efficient only for styrene (co)polymerization and cannot be used succesfully in a polymerization of (meth)acrylates and other polar monomers.[10,46] As will be discuss later, this could be directly related to the inability of self-initiation of these monomers.

Modifications to the above systems generally involve the addition of a catalytic amount of a relatively strong organic acid or some other additive.[47,48] The acids can be either externally added or built into nitroxyl species and act in the intramolecular fashion.[6] Their role is not clear, and in this paper we will refrain from a detailed analysis of the effect of these additives. It has been postulated, though, that these additives may reduce the rate of self-initiation,[49] reduce the concentration of TEMPO,[48] or catalyze the exchange reactions.

There is a great deal of confusion concerning the mechanism of styrene polymerization in the presence of TEMPO and other nitroxides. This confusion can be ascribed partially to the slightly different experimental conditions used by different groups, including temperature, purification of reagents, concentrations of TEMPO and conventional initiators, monomer conversion, methods of analysis of the polymers (precipitated or not), degree of oxygen exclusion, etc. However, from all of these reports a common picture emerges in which (a) the polymerization rates are first order in monomer and essentially independent of the TEMPO/alkoxyamine concentrations; (b) the molecular weights linearly increase with conversion and are relatively well controlled up to $M_n \approx 20\,000-30\,000$; (c) the polydispersities usually decrease with conversion but then may increase, depending upon the conversion and molecular weights; however, the polydispersities are usually below $M_w/M_n = 1.3$; and (d) the concentration of residual TEMPO during the polymerization is approximately 0.1−1% of the initial concentration of TEMPO (or alkoxyamine).[33,50]

The most important characteristics of controlled/living styrene radical polymerization, listed below, are missing in many articles devoted to that subject:

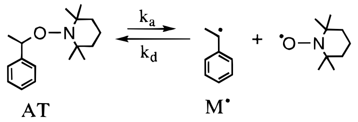
(a) The rates of polymerization, very similar to that of styrene self-initiated polymerization and independent of [TEMPO], indicate that self-initiation IS RESPONSIBLE for providing a sufficient amount of radicals to maintain reasonable polymerization rates.

(b) A majority of chains contain alkoxyamine end groups that exchange with the growing radicals present at very low concentrations.

(c) The rate of the exchange reaction is comparable to the propagation rate, but at the later stages side reactions lead to an increase of polydispersities.

(d) Regardless of the initiation mode, polymerization occurs with a large excess of counter-radicals relative to growing radicals. This persistent radical effect[51] is due to a continuously occurring bimolecular termination process which does not allow the radicals to reach equimolar concentration with TEMPO when TEMPO is added in excess or results in the rapid initial decrease of the concentration of the radicals when alkoxyamine is used as initiator. In all cases, under pseudostationary conditions, $[P_n^\circ] \ll [\mathrm{TEMPO}]$.

Scheme 1



In several cases the above observations have been, however, interpreted in very unusual and, in our opinion, erroneous way. Because the above features have not been recognized properly, incorrect conclusions have been appearing in recently published papers. For example, an agglomeration of alkoxyamine end groups to aggregates with degree of aggregation ≥ 10 was used to explain the independence of the polymerization rates of the concentration of the alkoxyamine.[7] In another publication the authors calculated the equilibrium constant on the basis of the assumption $[P_n^\circ] = [\mathrm{TEMPO}]$, although in fact $[P_n^\circ] \approx 0.001[\mathrm{TEMPO}]$. In addition, the concentration of growing radicals was reported to be $[P_n^\circ] \approx 6 \times 10^{-7}$ mol·L^{-1}, i.e., 60 times higher than the actual value ($\approx 10^{-8}$ mol·L^{-1}), because k_{obs} was reported as 2.4×10^{-3} s^{-1}, instead of 2.4×10^{-3} min^{-1} (cf. Figure 1 in the cited paper).[9] An example of misinterpretation of the experimental data can also be seen in a publication by Veregin et al.[33] in which a mathematical estimation of the value of the deactivation rate constant in the TEMPO-mediated polymerization was attempted. In this work the contribution of self-initiation and termination was not taken into account; the increase of polydispersities for [TEMPO]/[BPO] = 1.1 in comparison to 1.3 was ascribed to slower exchange in the former system rather than to contribution of chains which have not been trapped by TEMPO due to its too low concentration. Moreover, the authors mistakenly reported the concentration of TEMPO as being of the order of 10^{-3} instead of 10^{-5} mol·L^{-1}, which probably led to underestimation of k_d (cf. Figures 1 and 3 in ref 33).

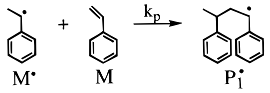
In this paper we will discuss the importance and contribution of various elementary reactions in styrene bulk polymerization in the presence of TEMPO. As it will be shown, the neglectance of some of these reactions could lead to the wrong interpretation and incorrect mechanistic picture of this important system.

Elementary Reactions Involved in the TEMPO-Mediated Styrene Polymerization

The simplest system for a TEMPO-mediated styrene polymerization includes styrene and the corresponding TEMPO adduct 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-piperidine. In the simplest mechanistic scheme the adduct undergoes a reversible homolytical cleavage producing 1-phenylethyl radical and a counter-radical TEMPO with a rate constant of activation, k_a. 1-Phenylethyl radical reacts with the counter-radical with the rate constant of deactivation (k_d) (Scheme 1).

1-Phenylethyl radical can react with monomer with a rate constant of propagation (k_p) (Schemes 2 and 3). Although it is recognized that the first addition might be faster than the subsequent steps, it is assumed that

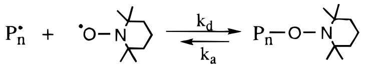
Scheme 2



Scheme 3

$$P^{\bullet}_{n} + M \xrightarrow{k_p} P^{\bullet}_{n+1}$$

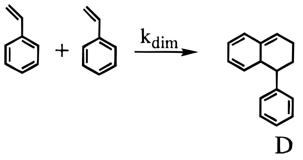
Scheme 4



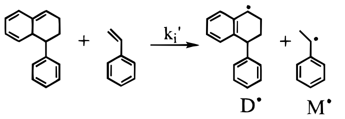
Scheme 5

$$P^{\bullet}_{n} + P^{\bullet}_{m} \xrightarrow{k_t} P_{n+m}$$

Scheme 6



Scheme 7



$k_{p1} = k_{p2} = k_{pn}$ in order to simplify the analysis. Propagation rate constants are available in the literature, and for styrene $k_p = 2 \times 10^3$ mol^{-1}·L·s^{-1} at 120 °C.[52,53]

The propagating radicals also may react reversibly with TEMPO with rate constants k_a and k_d (Scheme 4). The dynamics of this exchange reaction is not yet known, and the purpose of this paper is to estimate the two rate constants.

It is assumed here that not only the propagation rate constants but also activation and deactivation rate constants for monomeric and polymeric radicals are the same due to their close resemblance.

Both the 1-phenylethyl radical and macromolecular radicals can undergo termination. In the radical polymerization of styrene termination occurs predominantly and in this simulation exclusively by coupling. The termination rate obviously depends on the viscosity, chain length, and temperature, but in this simplified approach only one value is used for the termination rate constant $k_t = 10^7$ mol^{-1}·L·s^{-1} at 120 °C (Scheme 5).[54,55]

In addition, it is well-known that styrene can polymerize via thermal self-initiation, presumably by radicals formation from unsaturated dimers according to Mayo[56,57] (Scheme 6). The rate of thermal formation of the dimer has been determined by using various inhibitors. By interpolation of the literature data,[58,59] the rate of dimer formation at 120 °C was calculated to be approximately 2×10^{-6} mol·L^{-1}·s^{-1}. From this value, $k_{dim} = 3 \times 10^{-8}$ mol^{-1}·L·s^{-1} was then calculated.

Experimental evidence for the formation of the Mayo dimer in the thermal self-polymerization of styrene is quite ample; however, the actual initiation process is not yet clear. Possibly, initiation occurs via hydrogen transfer to monomer, as shown in Scheme 7. Although an analytical model for the thermal polymerization of styrene has been developed and successfully solved,[60] the absolute values of the rate constants are still unknown. It has been assumed that the dimer radical (D•) reacts with monomer with the same rate constant as the monomeric radical (Scheme 8). Thus, in order to fit the experimental kinetic data, it was necessary to set $k_i' = 5 \times 10^{-8}$ mol^{-1}·L·s^{-1}.

Scheme 8

$$D^{\bullet} + M \xrightarrow{k_p} P^{\bullet}_{1}$$

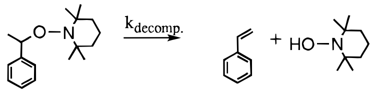
Scheme 9

$$P^{\bullet}_{n} + M \xrightarrow{k_{trm}} P_n + M^{\bullet}$$

Scheme 10

$$D + P^{\bullet}_{n} \xrightarrow{k_{trd}} D^{\bullet} + P_n$$

Scheme 11



When the thermal polymerization of styrene was simulated using the above kinetic parameters, the obtained molecular weights were approximately 100 times higher than those experimentally determined. The addition of transfer to monomer (Scheme 9) to the model did not result in a significant decrease of the molecular weights (at 120 °C, $C_{trM} = 1.4 \times 10^{-4}$;[61], i.e., $k_{trM} = 0.28$ mol^{-1}·L·s^{-1}).

Literature values of the rate constants of transfer to polymer are less reliable but usually proposed to be lower than those for transfer to monomer. Because most polymerizations were studied only to moderate conversions (<70%), transfer to polymer was not taken into account in these simulations.

On the other hand, when transfer to the Mayo dimer (Scheme 10) was incorporated into the model, the molecular weights within the range found experimentally were obtained. The optimum fit was achieved for $k_{trD} = 50$ mol^{-1}·L·s^{-1}. This value allowed us to fit accurately both the kinetic data and molecular weights. Although the precise determination of the rate constant of transfer to the Mayo dimer is beyond the scope of this publication, this relatively large rate constant is justified experimentally, as shown by Olaj and co-workers.[62,63]

It has been recently reported that 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine spontaneously thermally decomposes to styrene and the corresponding hydroxylamine (Scheme 11) with a rate constant $k_{decomp} = 3 \times 10^{-5}$ s^{-1} at 120 °C in dimethyl sulfoxide (DMSO).[64] More recent experiments conducted in our laboratories with dimeric and trimeric adducts as well as with low-molecular weight polymers ($M_n = 3000$) indicate that macromolecular species participate in a similar reaction with a rate constant $k_{decomp} \approx 1 \times 10^{-5}$ s^{-1}. The observed difference in these two constants can be ascribed to the statistical factor (three β-H atoms in the monomeric adduct versus two β-H atoms in the macromolecular species) and can be additionally lower due to solvent effects. It should be noted, though, that for the macromolecular alkoxyamine this reaction results in the formation of a polymer with a terminal double bond rather than a monomer.

In this paper we will not analyze the potential effect and contribution of the degenerative transfer which we proposed before.[44] It will be shown later that the experimentally observed polydispersities are already

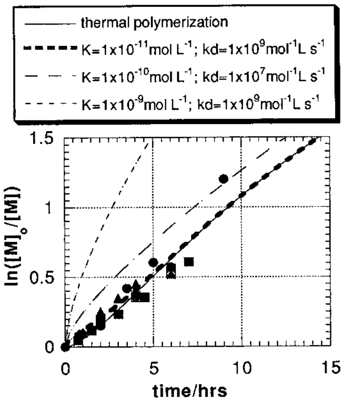


Figure 1. Kinetic plots for the simulated polymerization of styrene in the presence of adduct $[AT]_0 = 0.012$ M with variable kinetics and thermodynamics of exchange, simulated thermal polymerization of styrene, and experimental data: ●, thermal polymerization (ref 64 and this work); ■, $[AT]_0 = 0.010$ M (this work); □, $[AT]_0 = 0.012$ M;[67] ○, $[AT]_0 = 0.009$ M[67]; ×, $[AT]_0 = 0.003$ M[67]; ♦, $[AIBN]_0 = [TEMPO]_0 = 0.010$ M[44]; ▲, $[BPO]_0 = [TEMPO]_0 = 0.010$ M (this work). $[ST]_0 = 8.7$ M; temperature = 120 °C. The lines correspond to the simulated results.

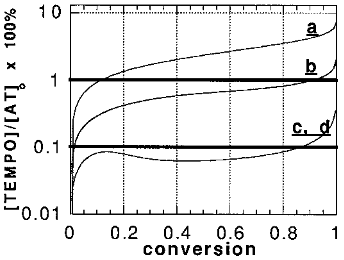


Figure 2. Simulated relative concentration of TEMPO in systems with variable kinetics and thermodynamics of exchange: a, $K = 1 \times 10^{-9}$ mol·L^{-1}, $k_d = 1 \times 10^9$ mol^{-1}·L·s^{-1}; b, $K = 1 \times 10^{-10}$ mol·L^{-1}, $k_d = 1 \times 10^9$ mol^{-1}·L·s^{-1}; c, $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^9$ mol^{-1}L s^{-1}; d, $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1}. The horizontal lines indicate the range of the experimentally observed concentrations of TEMPO. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

higher than those predicted for unimolecular exchange alone. Thus, the contribution of bimolecular exchange (degenerative transfer) would reduce the polydispersities even further below the observed values. The unimolecular exchange will be discussed in a subsequent paper along with the polymerization of other monomers.

Results

Kinetics of Polymerization. Figure 1 depicts the reported kinetic data on the thermal self-initiated polymerization of styrene, the results of polymerization in the presence of 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine, and the data available from the literature on polymerization initiated by azobis(isobutylronitrile) (AIBN) and benzoyl peroxide (BPO) in the presence of TEMPO at 120 °C, as well as the results of computer simulations of the thermal polymerization of styrene and the polymerization in the presence of the adduct. The total initial concentration of alkoxyamine in this simulation is $\approx 10^{-2}$ mol·L^{-1}, unless specifically noted otherwise.

There is a striking conclusion from the inspection of Figure 1. The polymerization rates are similar and do not depend upon the concentration of the adduct or on the way it has been formed. The polymerization rates in the presence of adducts are very similar to the rate of thermal self-initiated polymerization in the absence of adducts. Very recently a similar observation has been reported by Catala et al. for the di-*tert*-butyl nitroxide-mediated polymerization of styrene.[7] The authors attributed the independence of the polymerization rate on the concentration of the alkoxyamine to the association of alkoxyamines to inactive aggregates with a degree of association $n \leq 10$. We believe that there is neither physical nor chemical reason nor evidence for the formation of such aggregates.[65] As independently concluded by Fukuda,[50] the real origin of the similar rates in the presence of variable amounts of alkoxyamines is that self-initiation is primarily responsible for maintaining a reasonable polymerization rate. The contribution of the thermal self-initiation to the polymerization rate is significant due to extremely low values of the exchange equilibrium constant. The main role of the alkoxyamines is to control the molecular weights and polydispersities by exchanging with the thermally generated radicals. This exchange may be uni- or bimolecular. Thus, the inability to thermally self-initiate would explain why TEMPO-mediated polymerization of (meth)acrylates is much less successful than that of styrene.

For the first stage of simulations we used only Schemes 1–8 without taking into account transfer and decomposition reactions. In order to fit experimental kinetic data, we found it necessary to use equilibrium constant values $K = k_a/k_d < 10^{-10}$ mol·L^{-1}, and the best fit was found for $K \approx 10^{-11}$ mol·L^{-1}. Of course, $K = 10^{-10}$ mol·L^{-1} is the upper limit for the equilibrium constant, and lower values such as 10^{-12} mol·L^{-1} also fit the observed kinetics. Apparently the dynamics of exchange has no effect on kinetics. Using either the upper limit of the rate constant of deactivation $k_d = 10^9$ mol^{-1}·L·s^{-1} or a 100 times lower value $k_d = 10^7$ mol^{-1}·L·s^{-1} (and correspondingly $k_a = 10^{-2}$ and 10^{-4} s^{-1}) resulted in the same rate of monomer consumption.

It must be stressed here that styrene polymerization is a special case in which the growing radicals are formed by both the self-initiation and dissociation (activiation) of alkoxyamines. The ratio of the observed rate coefficient (slope in the semilogarithmic coordinates) to the rate constant of propagation equals the concentration of growing radicals $k_{obs}/k_p = [P_n°]$. Linear kinetic plots indicate a rather constant value of $[P_n°] \approx 10^{-8}$ mol·L^{-1}.

Equilibrium TEMPO Concentrations. Figure 2 presents the simulated concentration of TEMPO for a variety of equilibrium constants. The available literature EPR data and also our estimates of the concentration of TEMPO by UV–vis spectroscopy indicate that approximately 0.1–1% of TEMPO (based on the initial concentration of alkoxyamine) is formed in the reaction.[6,42,50,66] This indicates that the lower limit of the equilibrium constant is $K \geq 10^{-11}$ mol·L^{-1}. Comparison of this value with that estimated from the kinetics gives relatively good agreement and sets the value of $K = k_a/k_d = 10^{-11}$ mol·L^{-1} at 120 °C. Previously we have estimated $K \approx 10^{-10}$ mol·L^{-1},[67] on the basis of the apparently overestimated concentration of TEMPO (≥1%), probably due to the oxidation of the hydroxylamines. More precise EPR data indicate that the concentration of TEMPO is approximately 0.1%. The equilibrium constant, estimated in this way, equals

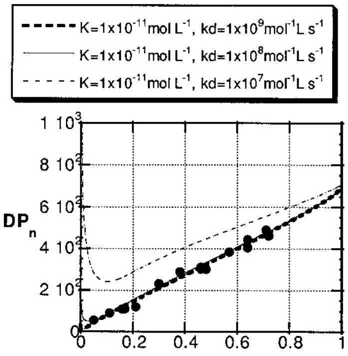


Figure 3. Simulated dependence of the number average degree of polymerization DP_n on the conversion in systems with variable kinetics of exchange and equilibrium constant $K = 1 \times 10^{-11}$ mol·L^{-1}. Solid points correspond to experimental data. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

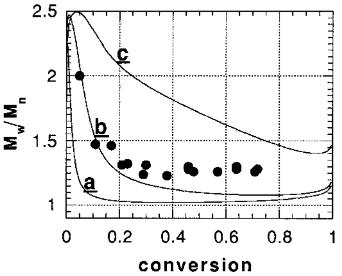


Figure 4. Simulated dependence of molecular weight distributions on conversion in systems with variable kinetics of exchange and equilibrium constant $K = 1 \times 10^{-11}$ mol·L^{-1}: a, $k_d = 1 \times 10^9$ mol^{-1}·L·s^{-1}; b, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1}; c, $k_d = 1 \times 10^7$ mol^{-1}·L·s^{-1}. Solid points correspond to experimental data. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

$$K = [P_n^\circ]\,([TEMPO^\circ]/[P_n - TEMPO]) = (10^{-8}\ \text{mol·L}^{-1}) \times 0.001 \approx 10^{-11}\ \text{mol·L}^{-1}$$

A small increase of the concentration of TEMPO with monomer conversion is due to a continuous termination process which is not being completely balanced by the progresively slower self-initiation.

Neither the kinetics of polymerization nor the determination of the equilibrium TEMPO concentrations allow one to estimate the dynamics of exchange. Here, as in some systems analyzed earlier,[30] the most useful method for determining the dynamics of this process is to analyze the evolution of polydispersities and molecular weights with conversion.

Evolution of Molecular Weights and Polydispersities with Conversion. **(a) No Transfer, No Decomposition.** Figure 3 illustrates the evolution of molecular weights with conversion for the simplest systems (without transfer and decomposition) with variable exchange rates but a constant value of $K = 10^{-11}$ mol·L^{-1}. It seems that some of the reported data agree relatively well with the simulations if the rate of deactivation is larger than $k_d > 10^7$ mol^{-1}·L·s^{-1} ($k_a > 10^{-4}$ s^{-1}). Too high initial molecular weights are calculated for smaller values of the exchange rate constants.

The linear increase of molecular weights with conversion for the simulated dependencies indicates that the proportion of chains that are self-initiated and terminated by coupling is relatively low (below a noticeable level), as will be shown below in Figure 8.

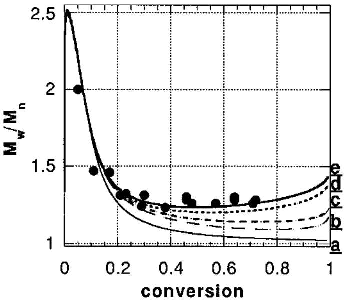


Figure 5. Effect of various side reactions on the simulated dependence of molecular weight distributions upon conversion in systems with $K = 1 \times 10^{-11}$mol·L^{-1} and $k_d = 8 \times 10^7$mol^{-1}·L·s^{-1} with the following: a, exchange and termination; b, exchange, termination, and thermal initiation; c, exchange, termination, thermal initiation, and transfer to monomer; d, exchange, termination, thermal initiation, and decomposition of alkoxyamines; e, exchange and all side reactions combined. Solid points correspond to experimental data. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

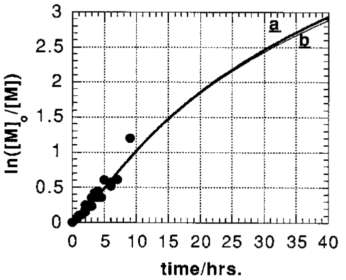


Figure 6. Effect of side reactions on simulated kinetics in systems with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with the following: a, exchange, termination, and thermal initiation; b, exchange and all side reactions (cf Figure 5) combined. Solid points correspond to experimental data. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

Figure 4 depicts the variation of polydispersities with conversion for various values of the rate constants of activation and deactivation. The initial best fit was found for $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1}, a value which is lower than the diffusion controlled values $k_d \approx 10^9$ mol^{-1}·L·s^{-1} but is very close to the rate constant for the reaction of TEMPO with 1-phenylethyl radical.[68]

In systems with slow exchange, a monotonic decrease of polydispersity with conversion is expected; however, the experimentally observed polydispersities increase at higher conversions. Thus, it appears that the simple system including only propagation, exchange, self-initiation, and termination cannot fit the observed dependence of the polydispersities on conversion for any rate constants of exchange while using the estimated earlier value of the equilibrium constant $K = 10^{-11}$ mol·L^{-1}. Therefore some additional side reactions must also contribute to the broadening of the molecular weight distribution. Taking the side reactions (namely transfer to monomer and decomposition of the alkoxyamine) into account, the optimum fit of the experimentally observed polydispersities was found for $k_d = 8 \times 10^7$ mol^{-1}·L·s^{-1} (see Figure 5).

(b) Systems with Transfer to Monomer and Decomposition of Alkoxyamines. Figure 5 demonstrates the effect of transfer to the monomer and the decomposition of alkoxyamines on molecular weight distribution. Transfer alone leads to a relatively small increase in polydispersities, much lower than experimentally observed. However, a larger increase in polydispersities that is much closer to that observed experimentally is predicted by taking into account the decomposition reaction (Scheme 11) already reported for model species.[64]

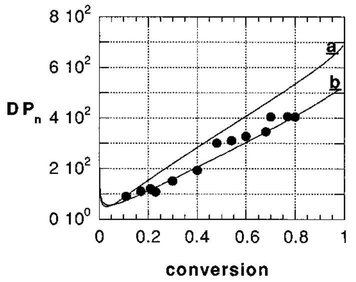


Figure 7. Effect of side reactions on the simulated dependence of the number average degree of polymerization DP_n on the conversion in systems with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with the following: a, exchange, termination, and thermal initiation, b, exchange and all side reactions (cf. Figure 5) combined. Solid points correspond to experimental data. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

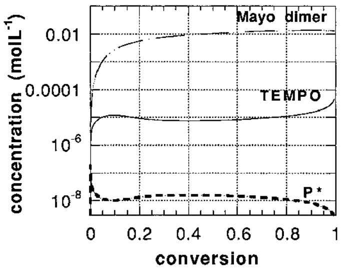


Figure 8. Simulated concentration of growing chains (P*), TEMPO, and the Mayo dimer vs conversion in a system with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with thermal intiation and no other side reactions. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

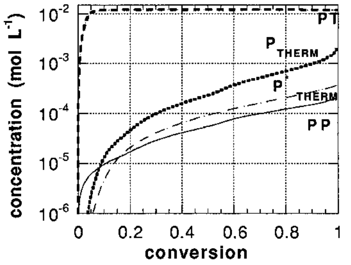


Figure 9. Simulated concentration of dormant chains (PT), chains terminated by coupling (PP), chains initiated thermally (P^*_{THERM}), and chains involved in transfer to the Mayo dimer (P_{THERM}) vs conversion in a system with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with thermal intiation and no other side reactions. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

Figures 6 and 7 illustrate the cumulative effect of transfer and decomposition on the molecular weights and kinetics of polymerization. Apparently, decomposition of alkoxyamines reduces the concentration of TEMPO in the system only slightly, resulting in only a small overall effect on the concentration of the growing radicals and the polymerization rate. Transfer to the monomer and to the Mayo dimer, on the other hand, contributes much more to the final molecular weights which are about 20 000 lower than expected on the basis of the initiator concentration.

Variation of the Concentration of Various Species with Conversion. Figures 8−11 show the variation of the concentrations of the most important species as a function of conversion for a hypothetical system with exchange, self-initiation, and termination without transfer to the monomer and the decomposition of alkoxyamines (Figures 8 and 9) and with these two reactions (Figures 10 and 11).

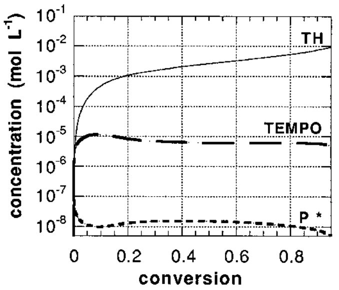


Figure 10. Simulated concentration of growing chains (P*), TEMPO and hydroxylamine (TH) vs. conversion in a system with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with thermal intiation, transfer to monomer, and decomposition of alkoxyamine. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

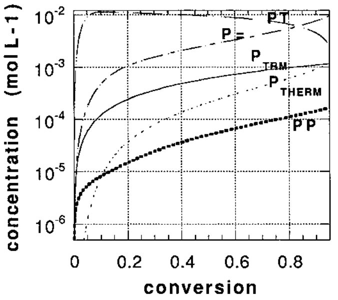


Figure 11. Simulated concentration of dormant chains (PT), chains terminated by transfer (P_{TRM}), alkoxyamine decomposition (P=) and coupling (PP), and chains involved in transfer to the Mayo dimer (P_{THERM}) vs conversion in a system with $K = 1 \times 10^{-11}$ mol·L^{-1}, $k_d = 1 \times 10^8$ mol^{-1}·L·s^{-1} with thermal initiation, transfer to monomer, and decomposition of alkoxyamine. $[AT]_0 = 0.012$ M; $[ST]_0 = 8.7$ M; temperature = 120 °C.

Figure 8 shows the variance in the concentration of the Mayo dimer, TEMPO and growing radicals in the absence of transfer and decomposition. The concentration of a Mayo dimer reaches 10^{-2} mol/L at 40% conversion and stays rather constant. The concentration of the Mayo dimer is influenced the most by transfer, and the error in the determination of k_{trd} will be reflected by either too low or too high concentration. However, since the simulated kinetics of polymerization agrees very well with the experimental one (directly related to the concentration of the Mayo dimer), the value of k_{trd} used in these simulations is probably close to the true value. The relatively low concentration of the Mayo dimer is consistent with the spectroscopic difficulty in directly observing these species. Olaj and co-workers[63] reported even lower concentration of the Mayo dimer and higher k_{trd}, but the product k_{trd}[D] was nearly the same as the product k_{trd}[D] of the values used in this work. This discrepancy could most likely originate from overestimating the extinction coefficient for the Mayo dimer in the spectroscopic measurements conducted by Olaj.

The alkoxyamines cleave homolytically, providing high initial concentration of radicals $[P°]_0 = [TEMPO]_0 = (K[P{-}TEMPO]_0)^{1/2}$. However, in a very short time, the excess of the radicals recombine, leading to a new stationary concentration of $[P_n°] \approx 10^{-8}$ mol·L^{-1} and $[TEMPO] \approx 10^{-5}$ mol·L^{-1} (Figure 8) which corresponds to the value $K \approx 10^{-11}$ mol·L^{-1}. The stationary concentration of TEMPO corresponds to approximately 0.1% concentration of the initial concentration of the alkoxyamine. Simulations beginning with BPO and TEMPO as starting compounds provide similar stationary conditions.

Figure 9 shows that the concentration of dormant chains (PT) is roughly equal to the initial concentration of the adduct (10^{-2} mol/L). Only a very small number of chains terminate by coupling ([PP] ≈ 2%). The amount of the terminated chains (PP) is equal to exactly half of the amount of the radicals formed thermally (P^*_{THERM}). Because of very efficient transfer to the Mayo dimer, the proportion of chains marked by transfer to the Mayo dimer and self-initiated (P^*_{THERM}) is much higher (up to 20% at the end of polymerization). A sufficiently low concentration of TEMPO (and therefore high enough concentrations of growing radicals and reasonable polymerization rates) is attained by scavenging TEMPO with the continuously formed radicals from the self-initiation process. The concentration of TEMPO rapidly increases to 10^{-5} mol/L and then stays roughly constant.

Figure 10 describes similar changes in the concentration of different species present in the system when monomer transfer and decomposition are included in the model. Both reactions are important and lead to continuous decrease of the concentration of dormant chains accompanied by an increase in polydispersities. The molecular weights are not affected because the decomposition does not change the total number of chains. The kinetics is also not affected very strongly because the concentration of TEMPO and the growing radicals is rather constant, even at high conversions.

Figure 11 depicts the dependence of the concentration of chains that were terminated, self-initiated, or participated in the transfer and decomposition upon conversion. At 60% conversion approximately 80% of the chains are still active and carry an alkoxyamine end group. The proportion of self-initiated and terminated chains is below 1% and of chains that have lost activity by either transfer or decomposition is about 20%. However, at 80% conversion nearly half of the chains have lost activity, and at complete conversion less than 20% of chains are potentially active. This means that it is still possible to prepare relatively well-defined homopolymers and block copolymers from a starting block up to molecular weights ≈ 60 000 (i.e., at 60% conversion with the initial concentration of alkoxyamine 0.01M). For higher concentrations of alkoxyamines and for shorter chains, the control over the polymerization can be extended even to higher conversions.

Discussion

Effects of Self-Initiation and Termination. Termination and self-initiation are inherent elementary reactions in bulk polymerization of styrene at temperatures ≥ 100 °C. In the TEMPO-mediated polymerization the termination by recombination leads to the concentration of TEMPO a few orders of magnitude higher than that of growing radicals. This persistent radical effect[51] occurs regardless of the initiating system and provides similar stationary concentration of growing radicals and counterradicals irrespectively of whether the alkoxyamines, TEMPO alone, and TEMPO with conventional initiators such as AIBN and BPO are used in the polymerization. Small differences between various systems originate in a lack of stoichiometric balance between the concentrations of scavanger and initiator and in some side reactions occurring during the initiation. Alkoxyamines seem to be the best initiators since they do not lead to any side reactions at the initiation stage, provide perfect balance between scavenger and polymeric chains, eliminate any induction periods, and could be used together with a controlled excess of TEMPO.

Self-initiation is responsible for maintaining reasonable polymerization rates in the presence of TEMPO due to the very low value of the equilibrium constant. In some other systems with more stericaly hindered nitroxides[9] or in atom transfer radical polymerization (ATRP)[21] where the equilibrium constants are higher, the polymerization rates are also significantly higher. In these systems, the proportion of chains formed by self-initiation is low and does not affect the overall molecular weights and polydispersities for $M_n < 50\,000$.

In the absence of self-initiation, for example in polymerization of (meth)acrylates and acrylonitrile, the control of molecular weights and polydispersities is much less satisfactory. However, notably, random copolymers of acrylates and acrylonitrile with styrene have been successfully prepared.[10,46] This can be, at least partially, ascribed to the self-initiation of styrene and to slower styrene polymerization.

Exchange Reactions. The exchange between radicals continuously generated by self-initiation and dormant alkoxyamines is a key feature of the controlled/living polymerization of styrene in the presence of TEMPO. This reaction allows good control over polydispersities and molecular weights, which are predetermined by the ratio Δ[M]/[TEMPO], if the initial concentration of TEMPO is higher than that of the radicals formed by the decomposition of the initiator.

The rate of exchange is comparable to the propagation rate, and therefore, the polydispersities decrease with conversion during the initial stages of the polymerization. At the beginning of the reaction, but after the equilibrium has established (ca. at 2% conversion), the propagation seems to be 20 times faster than deactivation which leads to the formation of oligomers with DP ≈ 20. This value, observed experimentally, can also be estimated from the following expression:

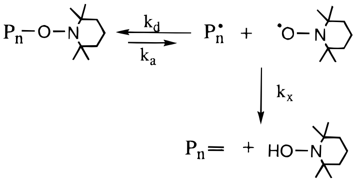
$$\mathrm{DP}_{n0} = R_{p0}/R_{d0} = k_p[\mathrm{M}]_0[\mathrm{P}_n{}^\circ]/k_d[\mathrm{TEMPO}]_{st}[\mathrm{P}_n{}^\circ] = k_p[\mathrm{M}]_0/k_d[\mathrm{TEMPO}]_{st}$$

$$\mathrm{DP}_{no} \approx ((2 \times 10^3\ \mathrm{mol}^{-1}\cdot\mathrm{L}\cdot\mathrm{s}^{-1}) \times (10\ \mathrm{mol}\cdot\mathrm{L}^{-1}))/((10^8\ \mathrm{mol}^{-1}\cdot\mathrm{L}\cdot\mathrm{s}^{-1}) \times (10^{-5}\ \mathrm{mol}\cdot\mathrm{L}^{-1})) \approx 20$$

The above calculations also indicate that recently estimated value of $k_d \approx 1.5 \times 10^7$ mol^{-1}·L·s^{-1} [33] is too low, because if this value were correct, at the begining of the polymerization polymers with $\mathrm{DP}_n \approx 100$ should be obtained.

The k_d values estimated in this study are very close to those determined directly for the model reactions of the 1-phenylethyl radical with TEMPO. The relatively slow exchange should lead to a continuous decrease of polydispersities throughout the polymerization. But in fact it was found that the polydispersities increase at higher conversions. This observation can be explained in two ways. One is that the exchange rate is progressively reduced in comparison with the propagation rate and another one is that additional side reactions become important. It is possible that, at higher conversion due to increased viscosity, the diffusion rate limit is reduced below 10^8 mol^{-1}·L·s^{-1} and therefore k_d becomes smaller while k_p is not yet affected. The latter case will be discussed in the subsequent section.

Scheme 12



We refrained here from discussing the contribution of bimolecular degenerative transfer. The polydispersities are already higher than those predicted for a system with the unimolecular exchange only. The addition of bimolecular exchange (degenerative transfer) would reduce the polydispersities even further below the experimentally observed values. In principle, the polydispersities at final conversion can be described by the following equations for conventional exchange and degenerative transfer, respectively:

$$M_w/M_n = 1 + (k_p[I]_0)/(k_d[\mathrm{TEMPO}])$$

$$M_w/M_n = 1 + (k_p)/(k_{dtr})$$

It is predicted that the polydispersities should depend on $[I]_0$ only in the former case. The limiting polydispersity for the conventional exchange is estimated to be $M_w/M_n = 1.01$ for $[I]_0 = 0.01$ mol·L^{-1}, whereas values higher than 1.3 are actually observed. This value is even higher than that estimated for the $k_d \approx 10^7$ mol^{-1}·L^{-1}·s^{-1} ($M_w/M_n = 1.1$), and therefore, it is impossible to assess the contribution of degenerative transfer in this system. However, the rate constant of degenerative transfer must be much faster than that of propagation in order to lead to the significant reduction of polydispersities. Such a process has been observed for alkyl iodides but not yet for alkoxyamines which are more sterically hindered. Because free TEMPO is observed during the TEMPO-mediated polymerization of styrene, the unimolecular exchange has to take place.

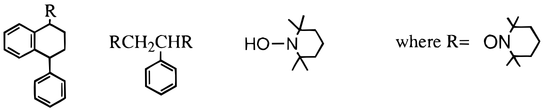
Side Reactions. In this study it was assumed that the rate constants for all of the elementary reactions were identical to those in conventional radical polymerization. This assumption was applied to transfer to the monomer. As in most radical polymerization, transfer to styrene is not very important, even at 120 °C. Less than 10% of chains participated in the transfer at complete conversion, as shown in Figure 11, and at lower conversion and higher initiator concentration this value is below the detection limit.

On the other hand, it appears that the decomposition of alkoxyamines is a more important process. At 60% conversion, 20% of the chains decomposed, and, at 80% conversion, half of the chains lost activity.

Decomposition was described previously as an unimolecular process. However, it is possible that TEMPO may attack not only a carbon atom of the growing radical but it may also abstract β-hydrogen atoms (Scheme 12).

Taking into account the observed rate constant for the oligomeric/polymeric species, $k_{\mathrm{decomp}} = 10^{-5}$ s^{-1}, and the determined equilibrium constant, $K = 10^{-11}$ mol·L^{-1}, one can estimate $k_x = k_{\mathrm{decomp}}/K \approx 10^6$ mol^{-1}·L·s^{-1}, which is approximately 100 times slower than the deactivation process. This means that the chemoselectivity of TEMPO reacting with the carbon-centered radical versus hydrogen atom abstraction is approximately 99% for polystyryl radicals.

Chart 1



In previous studies of the mechanism of self-initiated styrene polymerization in the presence of TEMPO, several by-products were identified (Chart 1) [59].

The presence of 1,2-bis(2,2,6,6-tetramethyl-1-piperidinyloxy)(1,2-bis(TEMPO) adduct in the reaction mixture indicates that TEMPO can initiate the polymerization. However, the proportion of this species was low, and the use of a large excess of TEMPO in these experiments led to long induction periods during which polymerization was not possible but rather side reactions could be detected. Although such reactions should be taken into account, we believe that their contribution is rather small; otherwise they would prevent the formation of well-defined polymers.

Trommsdorf Effect and Chain Length Dependent Termination. In order to simplify the simulations in this study, we assumed that all of the rate constants do not vary with the chain length. We realize that this is a gross oversimplification and plan to make the corresponding corrections in the future. By using diffusion controlled rate constant of termination between two 1-phenylethyl radicals $k_{t1} = 10^9$ mol^{-1}·L·s^{-1}, we observed no significant variation of kinetics, molecular weights, and polydispersities. However, when all of the rate constants of termination were increased to $k_t = 10^9$ mol^{-1}·L·s^{-1}, a significantly slower polymerization was observed due to lower concentration of growing radicals and higher concentration of TEMPO. This is in disagreement with the reported data.

Although the simulated concentrations of chains involved in bimolecular termination was low, the real values might have been even lower, because the reaction rate between two polymeric radicals may be significantly reduced at higher conversion and high viscosity. It is assumed that for conventional free radical polymerization at high conversion the macromolecular radical can react only with a small initiating or oligomeric radical.[69] In contrast, in controlled/living systems there are no low molecular weight radicals because all chains grow simultaneously and the proportion of low-molar mass styrene-based radicals is very low. The average value of termination between two macroradicals may be as low as $k_t \approx 10^2$ mol^{-1}·L·s^{-1}.[69] In conventional systems such a strong reduction in the termination rate leads to the Trommsdorf effect, i.e., a rapid increase in radicals concentration, acceleration of the polymerization, a loss of control, and, potentially, explosions. It has been reported that the Trommsdorf effect is absent in TEMPO-mediated polymerizations.[70] The main reason for the absence of the Trommsdorf effect is that in these systems the primary mode of termination is a reversible reaction of the macromolecular radical with a low-mass scavenger, and as such this reaction is not significantly slower for longer chains or at higher viscosity. In a conventional radical polymerization at high conversions, termination occcurs mainly by recombination of two macromolecular radicals. This reaction becomes extremely slow for longer chains or at high viscosity resulting in a sudden increase in the concentration of radicals and uncontrollable acceleration of the polymerization.

In summary, the values of the rate constants used in this work lead to a successful simulation of the observed rates, molecular weights, polydispersities, and TEMPO concentrations. The apparently simple polymerization of styrene mediated by TEMPO includes several other reactions: self-initiation, termination, transfer, and decomposition of alkoxyamines. These reactions affect the polymerization in very different but important ways.

Conclusions

The TEMPO-mediated polymerization of styrene proceeds with a very low stationary concentration of radicals generated by the homolytic cleavage of alkoxyamines. Polymerization rates in the absence and in the presence of variable concentrations of alkoxyamines are nearly the same, indicating that while the total number of chains equals to that of the alkoxyamine molecules, the propagating radicals are produced mainly by self-initiation. The equilibrium constant for the reversible cleavage of alkoxyamines at 120 °C is $K \approx 10^{-11}$ mol/L as estimated from the kinetics and the stationary concentration of TEMPO in the polymerization. The rate constant of deactivation (reaction of growing radicals with TEMPO) is in the range of $k_d \approx 1 \times 10^8$ $\mathrm{mol^{-1} \cdot L \cdot s^{-1}}$. Correspondingly, the rate constant of deactivation (cleavage of alkoxyamines) is approximately $k_a \approx 1 \times 10^{-3}$ $\mathrm{s^{-1}}$. In addition to self-initiation, propagation, exchange, and termination, two other side reactions, namely, transfer and decomposition of alkoxyamines, are present. The role and contribution of the elementary reactions are summarized below:

The reversible homolytic cleavage of alkoxyamines is an important process which leads to a reduction of polydispersities and allows synthesis of well-defined polymers. The equilibrium constant of exchange is extremely low ($K \approx 10^{-11}$ $\mathrm{mol \cdot L^{-1}}$), and therefore the propagating radicals are mainly generated by self-initiation.

Self-initiation is responsible for maintaining a reasonable polymerization rate. Without self-initiation the polymerization would be slower (approximately 3 times); however, only 2% of the total number of chains are formed by thermal initiation at $[\text{alkoxyamine}]_0 \approx 10^{-2}$ $\mathrm{mol \cdot L^{-1}}$. Thermal initiation provides a self-correcting system in which a small amount of radicals is continuously supplied, making styrene polymerization an unique system.

Termination occurs as it does in any radical system, but the contribution of termination is very low, especially at low radical concentration. The proportion of terminated chains is negligible as compared to the total number of chains. Additionally, termination leads to a persistant radical effect, i.e., much higher concentration of scavenger than that of growing radicals.

Transfer to monomer occurs at elevated temperatures, and its contribution is significant, especially for relatively high-molecular weight polymers. The proportion of chains marked by transfer is below 10% at $[\text{alkoxyamine}]_0 = 10^{-2}$ mol/L, but the molecular weights are lower than expected.

The decomposition of alkoxyamines strongly affects the polydispersities and the kinetics at higher conversions. At 60% conversion, 20% of the alkoxyamines have decomposed, and at 80% conversion, 50% of the chains have decomposed.

Experimental Section

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine was synthesized either from ethylbenzene, *tert*-butyl hydroperoxide, and TEMPO as described before[8] or in 90% yield at 20 °C via entrapment by TEMPO of the 1-phenylethyl radical produced from 1-phenylethyl bromide and CuCl/$(\mathrm{Bipy})_2$ (Bipy = 2,2′-bipyridine) in benzene. The adduct was purified by column chromatography, and its purity as determined by NMR was >98%. Dimer/trimer mixtures were prepared in an analogous way.

Polymerizations were performed with freshly distilled styrene and a controlled amount of the adduct in sealed glass tubes. The reactions were stopped by quenching to low temperatures after variable times. The polymers were dissolved in tetrahydrofuran (THF), precipitated into methanol, dried, and analyzed by SEC. Conversions were determined either by gravimetric method or by GC by following the amount of unreacted styrene.

The simulations were performed using a simulation package Predici which is based on an adaptive Rothe method[71,72] as a numerical strategy for time discretization. The package uses a discerete Galerkin h−p method to represent chain length distribution and allows one to follow the concentrations of all substrates and low- and high-molecular weight products and intermediates as well as molecular weights and the corresponding distributions of all types of macromolecules.[73] It has been previously reported that the agreement between full analytical solutions and results obtained using the Predici package was excellent.[34]

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