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Effect of Regime of Addition of Initiator on TEMPO-Mediated Polymerization of Styrene

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Summary

Investigation of the TEMPO-mediated polymerization of styrene at different regimes of addition of AIBN initiator showed that the course of the polymerization could be changed dramatically by a mode of the initiator addition without using any other additives. A very significant acceleration of the polymerization was reached at a specific regime without broadening the polydispersity of the resulting polymer.

Introduction

The field of living free radical polymerization has been rapidly developed during the last decade with major advances in all methods including ATRP, RAFT, and nitroxide-mediated processes [1-3]. The nitroxide-mediated polymerization still remains technically the simplest and safest process, since it does not require additional purification of a polymer from metals or the use of strongly smelling thiocompounds. Main features of nitroxide-mediated polymerization are generally well understood due to extensive kinetic and mechanistic studies by several groups of workers [4-7]. A variety of nitroxides that control the polymerization of different vinyl monomers has been synthesized but they are expensive for industrial applications [3]. That is why the polymerization mediated by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or its simplest derivatives is still of considerable interest.

There is a general consensus that TEMPO is an ideal mediator for styrene polymerization mostly because of two factors: (1) a reasonable rate of cleavage of styrene/TEMPO bonds of the dormant alkoxyamine compared to monomer conversion and (2) thermal self-initiation of styrene polymerization that permits overcoming the persistent radical effect [8] and achieving high conversions. The use of TEMPO allows to obtain polystyrene of low polydispersity. However, the main drawback is that the polymerization is very slow even at 120-130 °C.

Several attempts have been made to find ways to increase appreciably the rate of TEMPO-mediated polymerization without any significant broadening of the polydispersity. Progress has been achieved by adding organic acids and their derivatives [9-12], such as camphorsulfonic acid, acetic anhydride, 2-fluoro-1-methylpyridinium p-toluenesulfonate, or using a combination of two initiators with different half-lives [13, 14]. In both cases the acceleration was observed because of decreasing TEMPO concentration due to irreversible binding to the additives, or reversible coupling with new growing radicals. Using such combination of initiators seems technologically preferable because it avoids adding extra components in the reaction mixture and allows to control polydispersity in a soft mode.

The application of initiators with long half-lives leads to the conjecture that suppression of the persistent radical effect, and thus an increase in the polymerization rate, could be reached by a variation of regimes of adding an initiator with a short half-life. This approach has recently been demonstrated for the AIBN-HydroxyTEMPO system when a continuous addition of the initiator results in the desirable rate enhancement (76% conversion was reached after 16 h versus usual 40 h), and the polymerization proceeds in a living fashion [15]. Here we describe that a discrete regime of AIBN addition affords significant acceleration of the TEMPO-mediated polymerization of styrene without increase in polydispersity.

Experimental

Materials

Styrene (Aldrich) was dried over $MgSO_4$ and then distilled under vacuum. AIBN (Akzo Nobel) was recrystallized from methanol. TEMPO (Aldrich) was used as received.

Polymerization

Polymerization of styrene was performed in bulk under N_2 atmosphere at 120 °C. A typical procedure was as follows. Styrene (8 mL 8.7 M), TEMPO (10 mg, 0.008 M) and AIBN (8 mg, 0.006 M; the TEMPO/AIBN molar ratio 1.3) were mixed under N_2 in a three-necked reactor equipped with a thermometer, a gas inlet tube and a condenser. The reaction mixture was thermostated in an oil-bath. An extra portion of AIBN (4 mg; 50% relative to initially added) was dissolved in 0.5 ml of toluene and this solution was then added in 5 equal volumes. Time intervals between each addition were 30, 50, 60, 75, and 120 min. Thus, five regimes of addition were tested. The final TEMPO/AIBN ratio was 0.87. The concentration of TEMPO was kept constant in all experiments, the content of AIBN was varied. Polymerizations with the TEMPO/AIBN ratios of 0.87, 1.3, and 1.8, when all AIBN was added at the very beginning, were also conducted. All experiments were run in triplicate. Each experimental point in Figure 1 is a mean value of three determinations. Monomer conversion was determined gravimetrically.

Instruments

Molecular weight measurements were performed by gel permeation chromatography (GPC) using a Waters 150C ALC/GPC with a refractive index detector equipped with online degasser and a Shodex Linear KF/806M column. THF was used as an eluent at 1 mL/min flow rate and 35 °C. Calibration was performed with linear polystyrene standards.

Results and Discussion

The TEMPO-mediated polymerization of styrene in the presence of AIBN as an initiator was first run at the [TEMPO]/[AIBN] (γ) ratios of 1.3 and 1.8. Under these conditions, the polymerization occurred slowly in a living fashion and the data obtained agreed well with those reported elsewhere [4]. An illustration of the kinetic plots of polymerization for γ = 1.3 is shown in Figure 1. The molecular weights and polydispersity (PD) of polystyrene obtained at γ = 1.3 were also as expected. The PD was 1.28 and 1.25 at 7 and 59% conversion, respectively. Correspondingly, at γ = 1.8 both the rate of polymerization and PDs were lower (Table 1).

Table 1. Polymerization of styrene in presence of TEMPO (0.008 M) at various regimes of addition of AIBN (τ).

TEMPO/AIBN	Conversion, %	M_nx10^{-3}	PD
τ = 0 min (all AIBN was added at the beginning)			
1.8	11 (10h)	10.7	1.22
	46 (30h)	41.3	1.17
1.3	7 (4h)	6.8	1.28
	59 (30h)	54.2	1.25
0.87	14 (1h)	12.8	2.61
	32 (3h)	24.4	1.97
	63 (25h)	32.1	1.94
τ = 30 min (5 additions in every 30 min)			
0.87	16 (2h)	17.4	2.42
	30 (4h)	26.0	2.08
	64 (25h)	27.7	2.01
τ = 50 min (5 additions in every 50 min)			
0.87	4 (1h)	3.2	2.08
	36 (3h)	29.5	1.56
	67 (6h)	45.3	1.44
	92 (25h)	52.0	1.42
τ = 60 min (5 additions in every 60 min)			
0.87	7 (2h)	7.5	1.56
	44 (4h)	30.2	1.36
	66 (5h)	43.4	1.27
	94 (7h)	52.1	1.27
τ = 75 min (5 additions in every 75 min)			
0.87	9 (2h)	7.5	2.96
	36 (4h)	20.9	2.00
	58 (6h)	35.2	1.80
	84 (25h)	40.0	1.75
τ = 120 min (5 additions in every 120 min)			
0.87	17 (4h)	18.0	2.07
	43 (8h)	29.3	2.93
	74 (25h)	30.1	2.66
Frequent Addition Regime (addition every 15 min)			
0.87	8 (0.5h)	7.2	2.64
	18 (1h)	11.9	2.21
	25 (2h)	27.5	1.66
	49 (3h)	33.3	1.50
	60 (4h)	39.4	1.39
	68 (6h)	41.5	1.41

Times to reach the conversions are given in parenthesis

As known the polymerization rates might be affected by applying different regimes of mixing the ingredients, its living character being preserved [15]. Keeping this in mind, we have attempted to vary the mode of addition of AIBN. Although the objective of decreasing the concentration of the persistent radical (TEMPO in our case) and thus speeding up the polymerization is not original [9-14], a significant acceleration of polymerization of styrene without compromising PDs has been obtained. The experiment was performed as follows. The concentration of TEMPO was kept constant from experiment to experiment and it was always added at the beginning of the process. The *total* amount of AIBN was also kept constant and [TEMPO]$_t$/[AIBN]$_t$ = 0.87. A portion of AIBN (66.7%) was introduced at the very beginning together with TEMPO, to have γ= 1.3 at time t = 0. The remaining AIBN was administered to the reaction mixture in five portions after certain time intervals (τ= 30, 50, 60, 75, and 120 min). When all AIBN was fed, γ became 0.87. The experiment with γ = 0.87 from the very beginning of the process was also performed (τ = 0). Rates of styrene polymerization at these regimes of addition are shown in Figure 1.

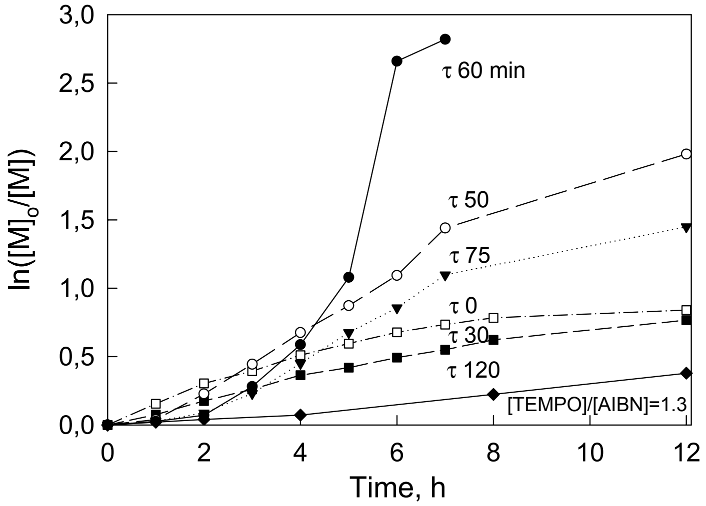

Figure 1. Plots of ln([M]$_0$/[M] versus time for bulk polymerization of styrene at 120 °C in the presence of 0.008 M TEMPO and variable regimes of addition of AIBN. Initial [AIBN] = 0.006 M; extra 0.003 M (50% from the initial) was added in 5 portions at different time intervals (τ). [TEMPO]/[AIBN] ratios: initial 1.3, final 0.87.

When all AIBN is added at the very beginning (γ = 0.87; τ = 0), the polymerization accelerates drastically at low conversions without any induction period. Then the rate decreases and finally the polymerization nearly stops—merely 63% conversion has been reached after 25 h (Table 1, Fig. 1). The polymer obtained was characterized by broad PD (> 2 at low and ca. 2 at higher conversions) and its molecular weights did not depend on conversion after 30% (Fig. 2). The kinetic curve at τ = 30 (addition every 30 min) is very similar to that described above for τ= 0. A slight difference is that the acceleration is not so pronounced at the very beginning but the same tendency is obvious. The PD was also above 2 at low and ca. 2 at high conversions. The molecular weights were significantly lower than expected [16] and did not show any dependence on conversion even at conversions lower than in the previous case (Fig. 2). The kinetic curve with the longest addition time interval (τ = 120 min) does not demonstrate such acceleration from the beginning due to lower concentration of the initiator. However, it levels off later and a higher conversion (74%) has been obtained after 25 h (Table 1) comparing with the τ = 0 and 30 regimes (63-64%). The PD of the produced polystyrene was ca. 2 at low conversions but it broadened as the conversion increased (Table 1). Evolution of molecular weights of the resulting polymer with conversion reminds of that for the τ = 0 and 30 min regimes. The molecular weights were conversion-independent after reaching a 40% level and progressively lower than the calculated weights (Fig. 2).

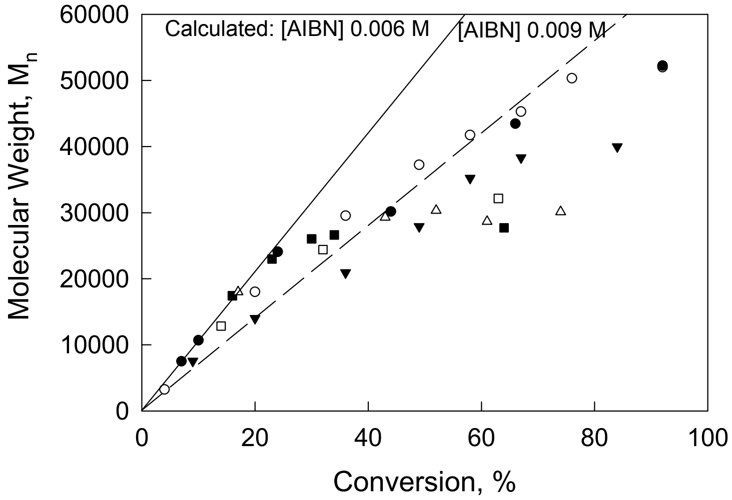

Figure 2. Evolution of number average molecular weights with conversion for bulk polymerization of styrene at 120 °C in the presence of 0.008 M TEMPO for various regimes of addition of AIBN. [TEMPO]/[AIBN] ratios: initial 1.3, final 0.87. Calculated molecular weights at AIBN 0.006 M and 0.009 M are solid and dashed lines, respectively. (□) 0.009 M AIBN was added at the beginning (τ = 0); (■) τ = 30 min; (○) τ = 50 min; (●) τ = 60 min; (▼) τ = 75 min; (△) τ = 120 min.

It is worth noting that in spite of the rate enhancement observed at these three regimes the polymerization was not completed even after 25 h.

The most surprising result was obtained at τ = 60. The data in Figure 1 demonstrate that the addition of AIBN at time interval of 60 min provides substantially higher polymerization rate than all other regimes tested, particularly at high conversions. The polymerization is actually complete in 7 h under these conditions. Moreover, such dramatic rate enhancement is achieved without any significant increase in PD compared to the polymerization performed at TEMPO/AIBN ratio of 1.3 (Table 1). The PD was less than 1.6 at 7% conversion and gradually decreased, reaching a value as low as 1.27. Molecular weights of the polymer grew up almost linearly with conversion though they were somewhat lower than the calculated molecular weight based on total added concentration of the initiator (Fig. 2).

Since the 60 min regime leads to a distinct polymerization kinetics, regimes close to 60 min with $\tau = 50$ and 75 min have also been investigated. Both these regimes result in considerable acceleration of the polymerization compared to 0, 30 and 120 min regimes but it was not as pronounced as $\tau = 60$ min (Fig. 1). The rate of conversion at $\tau = 50$ min was almost as high as at $\tau = 60$ min at low conversions but slowed down at high conversions. Molecular weights of the polymer obtained at this regime also increased with conversion very similarly to those observed at $\tau = 60$ min (Fig. 2). However, PD was broader, around 2 at low conversions but decreased gradually below the theoretical limit of 1.5 (Table 1).

The $\tau = 75$ min regime afforded more polydisperse polymer as compared with $\tau = 50$ and 60 min regimes. Its PD is still around 1.8 at high conversion and thus is narrower than PDs for regimes a $\tau = 0$, 30 and 120 min (Table 1).

Since the $\tau = 60$ min regime seems optimal, we verified the role of the frequency of AIBN addition, as suggested by the reviewer. The extra amount of AIBN introduced in the system was divided in 20 equal portions and added every 15 min. Thus, the same amount of AIBN was added in a period of 5 h as at $\tau = 60$ but the frequency of addition was 4 times higher (see Frequent Addition Regime in Table 1). The kinetics observed did not match that for the $\tau = 60$ regime. At low conversions ($\leq 25\%$), the polymerization occurred as for the $\tau = 0$ without induction period. However, at higher conversions the polymerization was as fast as that for the $\tau = 50$ and 60 min regimes but slowed down rather abruptly after 4 h (60% conversion). Only 68% conversion was reached after 6 h to be compared with 90% conversion at the $\tau = 60$ min. Molecular weights also grew up with conversion till 60% quite similar to the $\tau = 60$ and 50 min regimes but PDs were pretty close to $\tau = 50$ min and slightly broader than those at the $\tau = 60$ min addition. Thus, the frequency of addition is also an important factor.

The polymerizations at $\tau = 0$, 30, 60 and 120 min were simulated using Predici, a commercial software package (developed by M. Wulkow of CiT). The reaction mechanism applied was formulated elsewhere [17]. Its key steps are styrene initiation by AIBN and thermal self-initiation, propagation, radical termination, transfer to monomer and dimer, dormant-growing chain exchange and alkoxyamine decomposition. The semi-batch addition of AIBN was modeled using the “Reactors” option, which implied creating a user defined file with times and volumetric amounts of the feed stream, and providing the corresponding concentration of AIBN in the feed. The presence of toluene was neglected.

The modeling has shown that the regime of addition of AIBN may strongly affect the polymerization. When diffusion controlled effects were not considered, no significant acceleration was observed at different τ. The rate enhancement was much smaller than that observed experimentally. Moreover, the simulation showed a rate increase with increasing τ. The $\tau = 120$ min regime was slightly faster than all others. Predicted number average molecular weights corresponded fairly well to the experimental ones while predicted PDs were always lower.

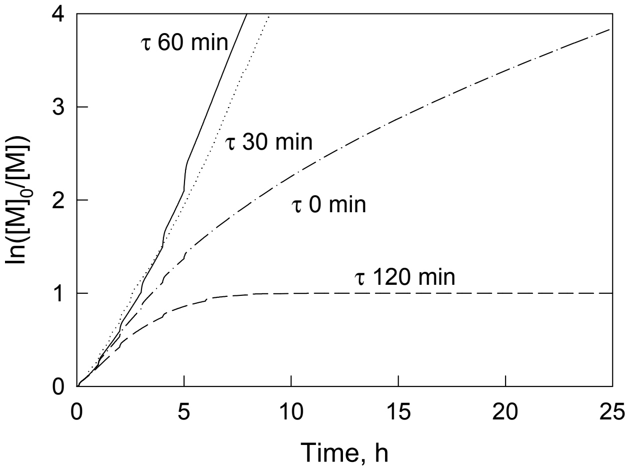

Figure 3. Simulation of kinetics of TEMPO-mediated polymerization of styrene at different regimes (τ) of AIBN addition. Free volume parameters (according to model equations in ref 18) used for propagation, termination, activation, and deactivation equal 0.1, 0.45, 0.01, and 0.1, respectively.

The polymerization rates became considerably τ dependent when the diffusion effects on radical termination, propagation, activation, and deactivation were taken into account. The free-volume expressions given in Table 2 and very moderate free volume parameters (column 3 in Table 2) were used. A maximum rate at high conversions was obtained for $\tau = 60$ min. Major acceleration was also noticed for $\tau =$ 30 min particularly at low conversions. The polymerization at $\tau = 120$ min was the slowest (Fig. 3). PDs for dead polymer were predicted around 1.4 for all regimes, while a growth of molecular weights with conversion till very high conversions was observed only for $\tau = 60$ and 30 min. Thus, the simulation demonstrated that the TEMPO-mediated polymerization could be affected by the regime of initiator addition. There is an optimal regime at which the polymerization rate is the highest.

The effect is not easy to explain and it is presumably due to quite complicated viscosity effects on the rate constants, especially for propagation, termination, and deactivation steps. Further work is being done in our group in order to better understand the role of diffusion-controlled kinetics and propose optimal operation policies in the nitroxide-mediated polymerization from a non-linear dynamics optimization point of view.

Table 2. Mathematical expressions implemented in Predici® for diffusion-controlled effects. The reaction mechanism used is given in the ref 17.

	Expression	Parameters used and comments
Propagation	$k_p = k_p^0 \exp\left[-\beta_p\left(\frac{1}{v_f}-\frac{1}{v_{f0}}\right)\right]$	β_p=0.1; k_p^0= 2.05x10^3 L mol^{-1} s^{-1}
Bimolecular Termination	$k_{tjn} = k_{tj}^0 \exp\left[-\beta_t\left(\frac{1}{v_f}-\frac{1}{v_{f0}}\right)\right], \quad j = c, d$	β_t=0.45; k_{tc}^0= 3.34x10^8 L mol^{-1} s^{-1}; "c" in equation on the left accounts for combination, and "d" for disproportionation
Activation	$k_a = k_a^0 \exp\left[-\beta_a\left(\frac{1}{v_f}-\frac{1}{v_{f0}}\right)\right]$	β_a=0.01; k_a^0= 2x10^{-3} s^{-1}
Deactivation	$k_d = k_d^0 \exp\left[-\beta_d\left(\frac{1}{v_f}-\frac{1}{v_{f0}}\right)\right]$	β_d=0.1; k_d^0= 2.1x10^8 L mol^{-1} s^{-1}
Fractional Free-volume	$v_f = \sum_{i=1}^{\#\text{of components}} \left[0.025+\alpha_i\left(T-T_{gi}\right)\right]\frac{V_i}{V_t}$	See ref 18 for nomenclature and further explanations

Conclusion

It has been demonstrated that a course of the TEMPO-mediated polymerization of styrene can be modified dramatically by regimes of discrete addition of the initiator. Significant rate enhancements of the polymerization have been achieved at several specific regimes while preserving the main features of a living process. Molecular weights were lower than expected but increased linearly with conversion. Polydispersities remained narrow and close to those obtained in the classical styrene-TEMPO systems.

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