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Notes

On the Mechanism and Kinetics of TEMPO-Mediated Radical Copolymerization

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Introduction

Nitroxide-mediated quasi-living radical polymerization of styrene and its derivatives is successfully used for preparing polymers with narrow polydispersity ($M_w/M_n < 1.2$) and controlled molecular mass.[1] The key part here is the reversible reaction between macroradical $P^\bullet$ and nitroxyl molecule $T^\bullet$. This reaction at the high temperature (>110 °C) is described by

$$P^\bullet + T^\bullet \underset{k_{-T}}{\overset{k_T}{\rightleftharpoons}} PT \qquad (1)$$

and is characterized by the equilibrium constant $K = k_{-T}/k_T$.

Numerous papers have been devoted to investigation of the kinetics of nitroxide-mediated styrene polymerization. The value of K for styrene polymerization in the presence of TEMPO was found to be equal to $(1.5-3) \times 10^{-11}$ mol/L at 120−125 °C.[2,3]

Unfortunately, other monomers, such as acrylonitrile, acrylates, methacrylates, vinyl acetate, etc., do not polymerize under the above conditions. The possible reason for the absence of polymerization is still unclear.

A few papers on the investigation of radical quasi-living copolymerization of styrene with other monomers in the presence of nitroxide radicals were recently published.[4−7] It was shown that the molecular mass of copolymers grows proportionally to the degree of conversion of monomers. Polydispersity indexes measured in the cases of copolymerizations of styrene with acrylonitrile, butyl acrylate, and methyl methacrylate induced by adducts of TEMPO and low molecular radicals or macroradicals are rather low.[4,5] Similar results were obtained for copolymerization of styrene with butyl acrylate and *N*-vinyl pyrrolidone initiated by common radical initiators AIBN and benzoyl peroxide in the presence of TEMPO.[6] This was also reported in the synthesis of block[5] and gradient[6,7] copolymers via nitroxide-mediated quasi-living copolymerization. However, no papers provide the kinetic data characterizing these processes.

In the present work the kinetics of TEMPO-mediated styrene/methyl acrylate copolymerization was studied in comparison with TEMPO-mediated styrene homopolymerization. Such comparative study permitted clarification of the copolymerization mechanism. The effective equilibrium constant K_{ef}, characterizing interaction of TEMPO with growing radicals, was also determined.

Experimental Section

Copolymerizations were carried out as follows: freshly distilled styrene and methyl acrylate (MA) in a 81:19 molar ratio (azeotropic ratio), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), and recrystallized benzoyl peroxide (BP) were charged into a vial, degassed by several freeze−thaw cycles at reduced pressure and sealed off. The mixture was heated at 120 °C.

Copolymerization kinetics was studied by isothermal calorimetry with a Calvet type microcalorimeter DAK-1,1-A. The rate of copolymerization was measured by direct registration of the rate of heat release. For the calculation of the reaction rate, a value for the heat of copolymerization of 72 kJ/mol was used.[8]

Concentration of TEMPO in the polymerizing system was measured using an ESR spectrometer, RE-1307, working at the X-band. Experiments were carried out directly in the resonator of the spectrometer at 120 °C or at ambient temperature after heating the sample in oil bath for a definite time. The discrepancy between both measurements did not exceed 10%.

GPC analysis was performed in THF with a Waters instrument equipped with a RI-410 detector. A combination of three Ultrastyragel columns (10^3 Å, 10^5 Å, and linear) maintained at 35 °C was used. Chromatograms were processed with a Data Module-730. An average molecular weight of the copolymer samples was calculated according to the procedure described previously.[9] Copolymers obtained for GPC analysis were isolated from the reaction mixture by lyophilization with benzene at reduced pressure after definite periods of copolymerization.

Copolymer composition was determined by IR spectroscopy with spectrometer Specord-M80 using the linear ratio between the relative absorbance of the carbonyl band of the acrylate unit (1730 $\mathrm{cm^{-1}}$) to that of the phenyl ring of styrene (1600 $\mathrm{cm^{-1}}$) and the relative fraction of MA to styrene in copolymer, as described previously.[10]

Results and Discussion

To simplify the kinetic analysis, TEMPO-mediated styrene/MA copolymerization has been studied at the azeotropic comonomer ratio styrene/MA = 81:19 (mol). At this ratio copolymer composition does not depend on the degree of conversion. In fact the mole fraction of styrene in the copolymer was found to be equal to 78 ± 3%, coinciding with the composition of the monomer composition. If this condition is met, the heat of copolymerization remains constant during the process.

In our previous works[3] we found out that styrene homopolymerization initiated by BP in the presence of TEMPO (mol ratio TEMPO/BP = 1.15−1.54) proceeds as a two-stage process. At the beginning of the reaction (at the first 2−3 h) the reduced (divided by instantaneous monomer concentration) rate (R^*) of polymerization decreases or increases rapidly in dependence on ratio TEMPO/BP and initial TEMPO concentration (nonstationary stage). Then R^* becomes almost constant

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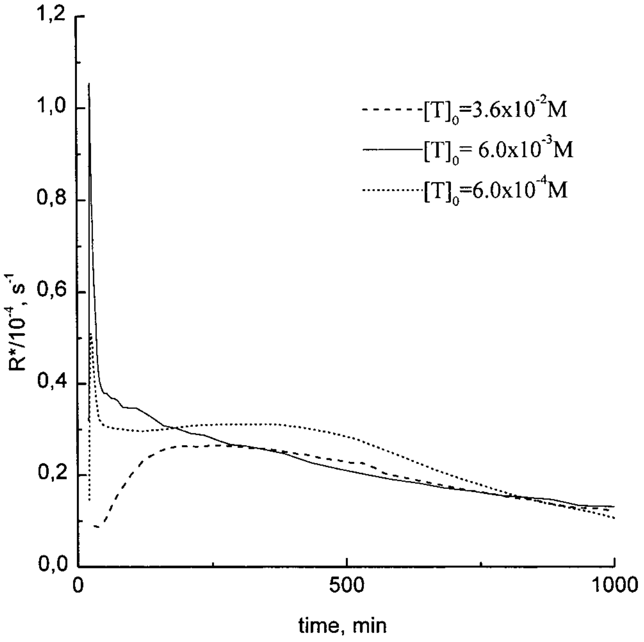


Figure 1. Plot of reduced rate *R** vs time for TEMPO-mediated copolymerization of styrene with MA at 120 °C.

up to complete conversion (stationary stage). The concentration of TEMPO drastically decreases during the first 10−13 min and changes insignificantly at the stationary stage.

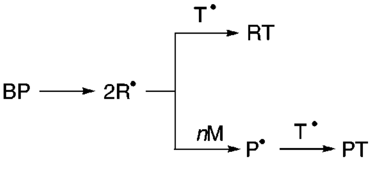
Figure 1 shows the plots of the reduced rate of styrene−MA copolymerization vs time for different initial concentration of TEMPO. All kinetic curves show a short initial nonstationary region 1−2 h, over which *R** changes rapidly. Such behavior of *R** is similar to that observed for styrene homopolymerization. After this period *R** continues to decrease slightly in the course of the reaction. For all systems, the absolute value of *R** is reduced by a factor of 2 during a reaction time of 1000 min. That is why we call this region "quasi-stationary" in contrast to the "stationary" stage in the homopolymerization of styrene.

The decrease in *R** at the quasi-stationary stage is similar for all the systems under study independent of initial concentration of TEMPO. These results suggest that the concentration [P•] of active propagating radicals decreases during the copolymerization since *R** and [P•] are related as

$$R^* = k_p[P^\bullet] \tag{2}$$

Speculations on the possible reasons for the observed *R** decrease will be given below.

In all copolymerizations, the concentration of TEMPO is reduced a few orders of magnitude during the first 10−15 min (Figure 2) in accordance with the fast decomposition of BP:



(3)

(The rate of BP decomposition depends on the initial TEMPO concentration, but the average half-life time of BP does not exceed 2.5 min in all the systems.) Starting from a specific period of the reaction, the concentration of TEMPO becomes almost constant. The time period of 1−2 h, which is necessary for TEMPO to achieve a stationary concentration, $[T]_{st}$, coincides exactly with the time of the transition of copolymerization rate to quasi-stationary regime. In the intermediate time (15 min−1 h), the TEMPO concentration increases from its minimum value to $[T]_{st}$ as well as in the styrene homopolymerization system. This phenomenon could be associated with a release of TEMPO radicals in the bimolecular recombination of primary oligomeric radicals, since two nitroxyls become "free" in each act of recombination. The value of $[T]_{st}$ increases along with an increase in the initial concentration $[T]_0$ of TEMPO.

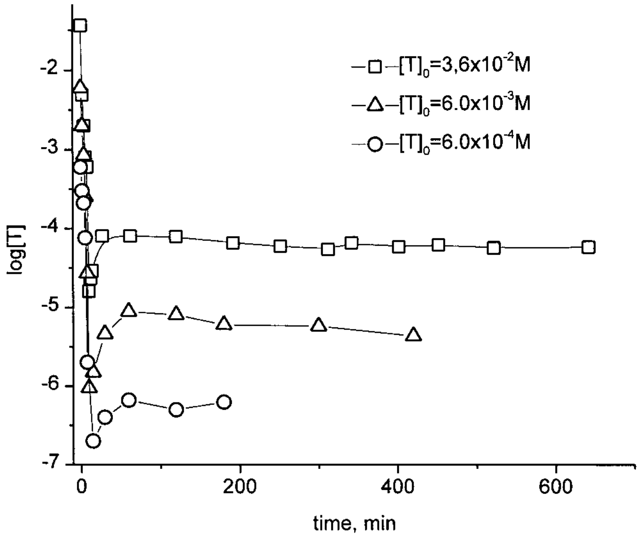


Figure 2. Plot of TEMPO concentration vs time for TEMPO-mediated copolymerization of styrene with MA at 120 °C.

According to the equilibrium

$$K = \frac{[P][T]_{st}}{[PT]} \tag{4}$$

the equilibrium constant *K* of reversible dissociation of the polymer−TEMPO adduct PT in the quasi-stationary region was calculated. $[T]_{st}$ was obtained directly from ESR data. [P] was calculated according to (2) using k_p equal to 2040 L/(mol s).[11] [PT] was assumed to be equal $[T]_0 - [T]_{st} \cong [T]_0$, because this assumption has been experimentally proved for homopolymerization of styrene and its derivatives in numerous works.[12] The obtained results are presented in Table 1.

As can be seen, the average value of *K* for MA/styrene copolymerization is in a good agreement with the one for styrene homopolymerization. However, it decreases slowly during copolymerization along with a decrease in the concentration of the propagating radicals [P]. As was mentioned earlier, *K* is a time-independent value for homopolymerization of styrene; therefore, a slight decrease in *K* can be related specifically to copolymerization. In the copolymerization system two kinds of equilibria are possible:

$$P_ST \underset{k_{T1}}{\overset{k_{-T1}}{\rightleftharpoons}} P_S^\bullet + T^\bullet \tag{5}$$

$$P_AT \underset{k_{T2}}{\overset{k_{-T2}}{\rightleftharpoons}} P_A^\bullet + T^\bullet \tag{6}$$

Table 1. Experimentally Determined Kinetic Parameters for MA/Styrene TEMPO-Mediated Copolymerization at 120 °C[a]

$[T]_o$, 10^{-3} mol/L	time, min (time, s)	$[P]_{st}$, 10^{-8} mol/L	$[T]_{st}$, 10^{-6} mol/L	K_{ef}, 10^{-11} mol/L
36	192 (11500)	1.3	65	2.3
	252 (15100)	1.3	59	2.1
	312 (18700)	1.3	54	1.9
	342 (20500)	1.3	65	2.2
	402 (24100)	1.2	58	1.9
	452 (27100)	1.2	61	1.9
	522 (31300)	1.1	56	1.7
	642 (38500)	0.9	57	1.4
6.0	120 (7200)	1.7	8.0	2.2
	180 (10800)	1.5	6.0	1.5
	300 (18000)	1.3	5.7	1.3
	420 (25200)	1.2	4.3	0.9
0.6	60 (3600)	1.5	0.66	1.7
	120 (7200)	1.4	0.50	1.2
	180 (10800)	1.5	0.62	1.6

[a] $[T]_0/[BP]_0 = 1.2$.

Here P_ST and P_AT are adducts of TEMPO with macroradicals, which have styrene and methyl acrylate terminal units. The following equilibrium constants correspond to these two equations (eqs 4 and 5):

$$K_1 = \frac{[P_S][T]_{st}}{[P_ST]} \tag{7}$$

$$K_2 = \frac{[P_A][T]_{st}}{[P_AT]} \tag{8}$$

The expression for the experimentally determined effective constant K can be written as follows:

$$K_{ef} = \frac{([P_S] + [P_A])[T]_{st}}{([P_ST] + [P_AT])} \tag{9}$$

The value of K_{ef} is close to K_1 if $[P_ST] \gg [P_AT]$ or to K_2 if $[P_AT] \gg [P_ST]$. If the ratio between the adducts P_ST and P_AT remains constant, the value of K_{ef} does not change during the process of copolymerization; otherwise, it transforms according to the change in the P_ST/P_AT ratio.

In our case, the equilibrium constant K_1 is rather high and equals 1.5×10^{-11} L/(mol s). On the contrary, the value of K_2 is implied to be a few orders of magnitude less than K_1, because no detectable homopolymerization of MA was observed. So, we may consider adducts P_AT as "dead" in comparison with "dormant" adducts P_ST. Another reason adducts P_AT can be considered as "dead" is due to an irreversible dissociation by disproportionation as described previously.[12] Both factors lead to the accumulation of inactive macromolecules in copolymerization system rather than active adducts P_ST. An increase in concentration of inactive species should lead to decrease in the effective equilibrium constant K_{ef} and, therefore, to a decrease in concentration of propagating radicals P. The latter was experimentally confirmed by decrease in R^* in the course of MA/styrene copolymerization as was described above.

On the other hand, a permanent increase in concentration of the inactive species should lead to an enhancement of polydispersity index of copolymer formed at high conversions. To confirm this assumption, molecular weight characteristics of copolymers obtained at various conversions were analyzed by GPC. As was expected, the polydispersity index decreases from 1.77 in the nonstationary region to 1.3 at the beginning of the quasi-stationary region and then increases up to 1.46 for limited conversions (Table 2).

Table 2. Molecular Weight Characteristics of Styrene/MA Copolymer Prepared by TEMPO-Mediated Copolymerization[a]

time, min	conversion, %	M_n, 10^3	M_w, 10^3	M_w/M_n
15	11.5	27.4	48.6	1.77
30	15.3	27.4	48.6	1.77
120	26.8	42.3	55.4	1.30
300	42.0	53.0	74.3	1.40
1500	84.6	71.0	104	1.46

[a] $[T]_0 = 6.0 \times 10^{-3}$ mol/L; $[T]_0/[BP]_0 = 1.2$.

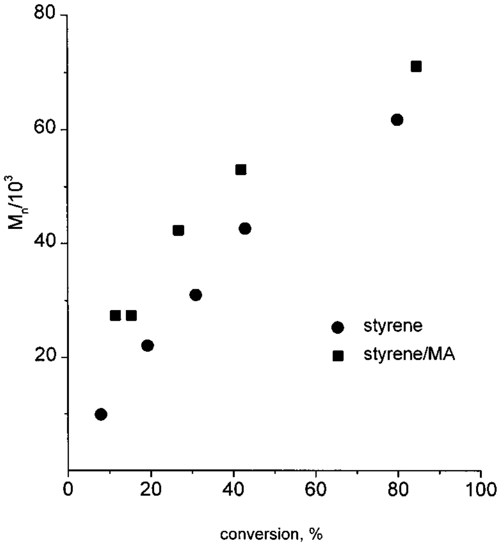


Figure 3. M_n-conversion relationship for copolymerization of styrene with MA. $[T]_0 = 6.0 \times 10^{-3}$ M.

Figure 3 shows that the M_n of the copolymer grows with conversion similarly to that for homopolystyrene obtained under the same conditions. M_n grows linearly at low and middle conversions, but at high conversions, a deviation from the linear M_n–conversion plot is observed. This deviation could be associated with an increase in the total number of polymer chains due to spontaneous styrene polymerization.

The obtained results suggest that styrene/MA TEMPO-mediated radical copolymerization proceeds in accordance with the quasi-living mechanism, similar to the one established for homopolymerization of styrene. However, at high conversions, a small deviation from the living mechanism is observed due to the continuous accumulation of inactive macromolecules in the system. Nevertheless, TEMPO-mediated copolymerization could be successfully utilized for the synthesis of styrene/MA copolymers with controlled molecular weight and low polydispersity.

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