A Concept for Quasiliving Nitroxide-Mediated Radical Copolymerization

Michail Yu. Zaremski,* Anna V. Plutalova, Michail B. Lachinov, and Vladimir B. Golubev

Polymer Science Department, Faculty of Chemistry, Moscow State University, Vorob'evy Gory, Moscow 119899, Russia

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ABSTRACT: A principle conception for quasiliving TEMPO-mediated radical copolymerization was advanced. It was concluded that TEMPO-mediated copolymerization of styrene with other monomers (which are not able to polymerize via quasiliving mechanism) may proceed via quasiliving mechanism in two regimes—"azeotropic" and "gradient" according to the reactivity ratio of comonomers. The "azeotropic" regime gives an almost linear increase in molecular weight with conversion and provides controlled synthesis of copolymers with a low polydispersity index. "Gradient" copolymerization proceeds via a dead-end mechanism with formation of gradient copolymers. A simple kinetic scheme was proposed for "azeotropic" copolymerization. Experimental kinetic data correlating with the advanced concept were obtained for quasiliving copolymerization of styrene with methyl and butyl acrylates, methyl methacrylate, and acrylonitrile ("azeotropic" regime); and for styrene copolymerization with *N*-vinyl pyrrolidone and vinyl acetate ("gradient" regime).

Introduction

A general concept for quasiliving free radical homopolymerization in the presence of reversible inhibitors (such as cobalt−porphyrin complexes, nitroxides, etc.) was advanced by B. Smirnov.[1] A principle idea of this technique involves an addition of a reversible inhibitor (T) to a conventional polymerization system (monomer−initiator) in order to prevent irreversible bimolecular termination between macroradicals (P) and to provide reversible recombination of P with T:

$$P^{\bullet} + T^{\bullet} \underset{k_{-T^{\bullet}}}{\overset{k_T}{\rightleftarrows}} PT \tag{1}$$

Dissociation of adduct PT regenerates the active radical P, which can then add more monomer units before the next reversible termination etc.

Nitroxide-mediated polymerization was studied in many works starting from pioneering contributions by Rizzardo[2] and Georges,[3] which opened a simple route for the preparation of polymers with a precisely controlled molecular weight and narrow polydispersity (<1.2). However, only styrene was found capable of polymerization in the presence of nitroxides (TEMPO, di-*tert*-butyl nitroxide, etc.) at 110−130 °C via "ideal" quasiliving mechanism with a linear M_n−conversion relationship and a low polydispersity index. However, not all styrene derivatives are able to polymerize via a quasiliving mechanism. It was demonstrated that polymerization of methyl-,[4,5] *tert*-butyl-,[6] methoxy-,[4,7] dimethoxy-,[5] acetoxy-,[8] chloromethyl-,[7,9] chloro-,[5,7] bromo-,[10] sulfonate-,[11] and gluconamide-[12] ring-substituted styrenes can polymerize according to the quasiliving manner, whereas, under the same conditions, polymerization of trifluoromethylstyrene[7] proceeds according to a nonliving mechanism.

In the case of other vinyl monomers, no data are available in the literature, confirming the quasiliving nature of their polymerization under the conditions of reversible inhibition of styrene polymerization. According to one experimental data,[5] methacrylates are not able to polymerize in the presence of TEMPO, whereas as shown in refs 13 and 14 they polymerize via a dead-end mechanism. Polymerizations of acrylates proceed with a reaction rate of one monomer unit per hour and stop at the stage of the formation of oligomers.[15] Similar results were obtained for the nitroxide-mediated polymerization of dimethyl acrylamide, sodium acrylate, dienes, vinyl acetate, vinyl pyrrolidone, and acrylonitrile.[16−18] The only exception from this universal pattern is a quasiliving ring-opening TEMPO-mediated polymerization of oxepans.[19] As concluded by many authors,[15,20,21] a principle reason for the absence of quasiliving nature of TEMPO-mediated polymerization of these monomers is a permanent increase in TEMPO concentration during polymerization. This leads to the shift of equilibrium (1) to the formation of non-dissociated adducts. (In the case of styrene an increase in TEMPO concentration is reduced by the spontaneous initiation and possible addition of TEMPO to styrene.) To shift equilibrium 1 to the formation of the dissociated form, several approaches were made: TEMPO was replaced by more active nitroxides, the temperature was increased up to 145−155 °C, and the concentration of TEMPO was decreased by the reaction with reducing agents.[14,20,22]

The quasiliving TEMPO-mediated copolymerization was first described by Georges and co-workers in 1993:[3] a copolymer of styrene and butadiene with a low polydispersity was prepared in a TEMPO-mediated suspension. Recently a few papers on the investigation of free radical quasiliving copolymerization of styrene with other monomers (butyl acrylate, acrylonitrile, and methyl methacrylate) in the presence of nitroxide radicals were published.[15,17,23,24] As was shown, copolymers with controlled molecular weight and low polydispersity index may be synthesized only in the systems containing an excess of styrene. Copolymers of styrene with *N*-vinyl carbazole, *N*-vinyl pyrrolidone, HEMA with a low polydispersity were also obtained in the presence of nitroxides.[23]

In previous papers[18,25] we studied the kinetics of TEMPO-mediated copolymerization in several systems, and the equilibrium constant $K = k_{-T}/k_T$ of reversible

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dissociation (eq 1) was determined. For the styrene−acrylates copolymerizations, K was found to be 10^{-11} mol/L and close to that for styrene homopolymerization and the copolymerization proceeded via quasiliving mechanism. In this work a principle conception for quasiliving TEMPO-mediated copolymerization is proposed and its experimental evidence is presented and discussed.

General Concept

The main peculiarity which determines the quasiliving character of nitroxide-mediated polymerization is equilibrium between propagating (living) and nonpropagating (nonliving) species (eq 1).[26]

In the case of copolymerization of two monomers M_1 and M_2, two equilibrium reactions are possible (following the terminal model):

$$P_1T \underset{k_{T_1}}{\overset{k_{-T_1}}{\rightleftharpoons}} P_1^{\bullet} + T^{\bullet} \tag{2}$$

$$P_2T \underset{k_{T_2}}{\overset{k_{-T_2}}{\rightleftharpoons}} P_2^{\bullet} + T^{\bullet} \tag{3}$$

where P_1T and P_2T are the adducts of TEMPO with macroradicals with terminal units M_1 and M_2 respectively. The different equilibrium constants of dissociation correspond to these two reactions (eqs 2 and 3):

$$K_1 = \frac{[P_1][T]}{[P_1T]} \tag{4}$$

and

$$K_2 = \frac{[P_2][T]}{[P_2T]} \tag{5}$$

However, we can experimentally measure an overall effective constant K_{ef}, which is determined as

$$K_{ef} = \frac{([P_1] + [P_2])[T]}{([P_1T] + [P_2T])} \tag{6}$$

and characterizes each quasiliving copolymerization system.

In dependence on the values of K_1 and K_2, different mechanisms and kinetic behaviors of TEMPO-mediated copolymerization are possible.

I. When both K_1 and K_2 are enough high ($\geq 10^{-11}$ mol/L) (e.g., when both adducts P_1T and P_2T can readily dissociate to free radicals), copolymerization should proceed according to the quasiliving mechanism. Obviously, such a situation is realized in the copolymerization of styrene with its derivatives. The experimental evidence for this case was obtained by Kazmaier[9] and Hawker[23] in the copolymerization of styrene and chloromethylstyrene, induced by benzoyl peroxide (BPO) in the presence of TEMPO or induced by TEMPO−adduct. Independent of monomer feed ratio, low-polydispersity copolymers ($M_w/M_n < 1.36$) were prepared at high conversions (~80%). Styrene−vinylpyridine copolymerization may also be quasiliving, because vinylpyridine was found to be similar to styrene in TEMPO-mediated polymerization.[5]

II. The more complicated mechanism of copolymerization should be when $K_1 \gg K_2$. This situation corresponds to copolymerization of styrene with many other monomers (here and below index "1" is attributed to styrene). To our knowledge, the K_2 values for the polymerization of other monomers have not been determined. Apparently, K_2 for acrylic, methacrylic and vinyl esters, dienes, etc. should be a few orders of magnitude less than K_1. Indeed, no detectable homopolymerization of these monomers was observed when the polymerization was introduced by BPO in the presence of TEMPO. When it was initiated by TEMPO−adducts, it stopped as soon as a small excess of free nitroxides appeared in the system.[20,27] One can expect that during the process, the copolymerization in these systems should transform from quasiliving to permanently terminated proportionally to the extent of the accumulation of nonactive adducts P_2T. Another reason adducts P_2T can be considered as "dead" is due to an irreversible disproportionation between (meth)acrylate radicals and nitroxides, as described previously.[10,28]

Nevertheless, it is possible to carry out the copolymerization according to the quasiliving mechanism up to high conversions. As known, styrene radicals form "active" (able to dissociate) adducts. So, we can suggest that if styrene adducts (P_1T) were predominantly formed in the chain ends, copolymerization would proceed via mechanism similar to the quasiliving one for styrene homopolymerization. Therefore, to reach the quasiliving mechanism of copolymerization, the inequality $[P_1T] \gg [P_2T]$ should be fulfilled.

The relative probability of the formation of styrene unit at the end of the propagating radical can be estimated from the steady-state suggestion for classic radical copolymerization in accordance with the terminal model:

$$k_{12}[P_1^{\bullet}][M_2] = k_{21}[P_2^{\bullet}][M_1] \tag{7}$$

The use of terminal model seems to be quite correct here, because the reactivity ratios of comonomers in TEMPO-mediated copolymerizations coincide with those for classical copolymerizations.[17,23,25] According to (7), the ratio between concentrations of the polymer radicals is described as

$$\frac{[P_1]}{[P_2]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \tag{8}$$

or

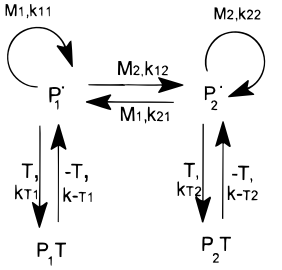
$$\frac{[P_1]}{[P_2]} = \frac{r_1 k_{22}[M_1]}{r_2 k_{11}[M_2]} \tag{9}$$

Therefore, for realization of the quasiliving mechanism of copolymerization, the inequality $r_1k_{22}[M_1] \gg r_2k_{11}[M_2]$ should be fulfilled. This means that the second comonomer should be significantly less active than styrene.

According to the change in ratio P_1T/P_2T during TEMPO-mediated copolymerization, three principal regimes can be realized.

IIA. "Azeotropic" Regime. If $[P_1T] \gg [P_2T]$ from the beginning to the end of copolymerization, the quasiliving nature of the process can be realized in the entire interval of conversions. Such a situation is possible, when $r_1k_{22} \gg k_{11}r_2$ and the ratio between two monomers does not change significantly during copolymerization. The ratio between comonomers remains almost constant during copolymerization when it is carried on in azeotropic ratio or under the feed compositions close to the azeotropic. It is why we call this regime “azeotropic”. Many monomer pairs satisfy to this requirement, for example styrene−(meth)acrylates and styrene−acrylonitrile. The extent of the occurrence of permanent chain breaking in each system will depend on the relation between [P_1T] and [P_2T] adducts during copolymerization. This relation depends on both the activity of monomers but and on the difference between K_2 and K_1. If $K_2 \ll K_1$, adducts P_2T will accumulate in copolymerization system rather than adducts P_1T. An increase in concentration of nonactive P_2T adducts should lead to decrease in the effective equilibrium constant K_{ef} and as consequence to decrease in the rate of copolymerization and increase in polydispersity of copolymer at high conversion.

The fraction of nonactive adducts P_2T can be evaluated from the following simplest scheme involving only two kinds of reversible termination and four reactions of the propagation:



(10)

As follows from (10):

$$\frac{d[P_2T]}{dt} = k_{T_2}[P_2][T] - k_{-T_2}[P_2T] \qquad (11)$$

We assume for simplification that adducts P_2T are not able to reinitiate polymerization and neglect the second term in the right side of eq 11:

$$\frac{d[P_2T]}{dt} = k_{T_2}[P_2][T] \qquad (12)$$

Concentrations [P_2] may be calculated from eq 9, and [P_1] from eq 4, so that finally we have

$$\frac{d[P_2T]}{dt} = k_{T_2}K_1\frac{k_{11}r_2[M_2]}{k_{22}r_1[M_1]}[P_1T] = k_{T_2}K_1\frac{k_{11}r_2[M_2]}{k_{22}r_1[M_1]}([T]_0 - [P_2T]) \qquad (13)$$

Integration of eq 13. gives the expression for “dead” chains as a function of reaction time

$$[P_2T] = [T]_0(1 - \exp(-at)) \qquad (14)$$

where $a = k_{T_2}K_1k_{11}r_2[M_2]/k_{22}r_1[M_1]$ is constant during the azeotropic copolymerization.

Using (14), the reduced rate of copolymerization in “azeotropic regime” may be written as

$$R^* = R/[M] = k_p[P^\bullet] = k_pK_1\frac{[T]_0}{[T]}\exp(-at) \qquad (15)$$

where [M] is the instantaneous total concentration of both monomers and k_p is the effective copolymer propagation rate coefficient. To obtain eq 15 we made three assumptions: (1) $k_{-T_2} \approx 0$, (2) the fractions of radicals $P_1^\bullet$ and $P_2^\bullet$ satisfy the terminal model of copolymerization, and (3) a contribution of spontaneous initiation and irreversible bimolecular termination to the rate of copolymerization is negligible.

IIB. “Gradient” Regime. If [P_1T] ≫ [P_2T] at the beginning of copolymerization, but then the ratio between [P_1T] and [P_2T] changes drastically, quasiliving copolymerization will proceed only when $r_1k_{22}[M_1] \gg k_{11}r_2[M_2]$. In the most of copolymerization systems, styrene is one of the most active vinyl monomers, and it will copolymerize faster than the second comonomer. Therefore, instantaneous fraction of styrene will decrease during the reaction. When probability of the recombination of radical P_2 with TEMPO will exceed that for addition styrene unit to P_2

$$k_{T_2}[T] > k_{21}[M_1]$$

quasiliving copolymerization will stop by permanent termination. This situation is typical for the systems, which have no azeotropic point (such as styrene−*N*-vinyl pyrrolidone, styrene−vinyl acetate) and to the systems mentioned in case IIA under the excess of second monomer. The rate of copolymerization should be a complicated function of the change in monomer concentration during copolymerization and should decrease in accordance with decrease in styrene fraction in polymerizing system. As a result of this copolymerization, gradient copolymer (copolymer with composition changing from the beginning of chain to its end) will form, so we call this regime “gradient”. The more is difference between r_1 and r_2 the more significant change in composition along copolymer chain will be obtained in copolymer.

IIC. Convenient Regime. If from the very beginning of copolymerization the probability of the formation of P_1T−adducts is less than that of P_2T−adducts, TEMPO will be consumed to formation of nonactive adducts P_2T. After the consumption of TEMPO, reaction will proceed as convenient radical copolymerization initiated by spontaneous styrene polymerization.

Summarizing our postulates, in Table 1 we classified monomers in accordance with their ability to copolymerize with styrene via quasiliving manner. (Here we did not consider any possible side processes leading to deviation from the quasiliving mechanism.)

Results and Discussion

Azeotropic Regime. At the azeotropic ratio, both comonomer and copolymer compositions do not depend on degree of conversion. This fact simplified significantly the kinetic analysis and allowed us to reveal the mechanism of TEMPO-mediated copolymerization. From the kinetic point of view, we can consider the azeotropic copolymerization as homopolymerization of effective monomer with effective molecular weight, propagation rate coefficient, heat of copolymerization etc. Transformation of GPC curves of obtained copolymers reflects only a change in MWD of macromolecules.

Here we have studied the copolymerization of styrene with several monomers from group IIA−methyl acrylate (MA), butyl acrylate (BA), acrylonitrile (AN), and methyl methacrylate (MMA) in the azeotropic molar ratios [styrene]/[MA] = 81:19, [styrene]/[BA] = 77:23, [styrene]/[AN] = 62:38, and [styrene]/[MMA] = 53:47. The ratio

Table 1. Possibility of Quasiliving Nitroxide-Mediated Copolymerization

type of monomer system	$r_1k_{22}/k_{11}r_2$	r_1	second monomer	possibility of "livingness"
1			alkylstyrenes, alkoxystyrenes, chlorostyrene, bromostyrene, chloromethylstyrene, acetoxystyrene	quasiliving mechanism at any monomer ratio
IIA	$\gg 1$	<1	acrylonitrile, methacrylates, acrylates	quasiliving mechanism at azeotropic (or close to it) monomer ratio; dead-end mechanism under excess of M_2
IIB	$\gg 1$	>1	*N*-vinyl pyrrolidone, vinyl acetate, *N*-vinyl carbazole	quasiliving mechanism at $f_2{}^a < 0.1-0.2$; dead-end mechanism at any other monomer ratio
IIC	<1	<1	butadiene, methacrylonitrile	quasiliving mechanism at $f_2 < 0.03-0.05$; convenient mechanism at any other monomer ratio

[a] Here and in Tables 2–4, *f* and *F* are molar fraction of monomer in monomer feed mixture and in copolymer obtained, respectively.

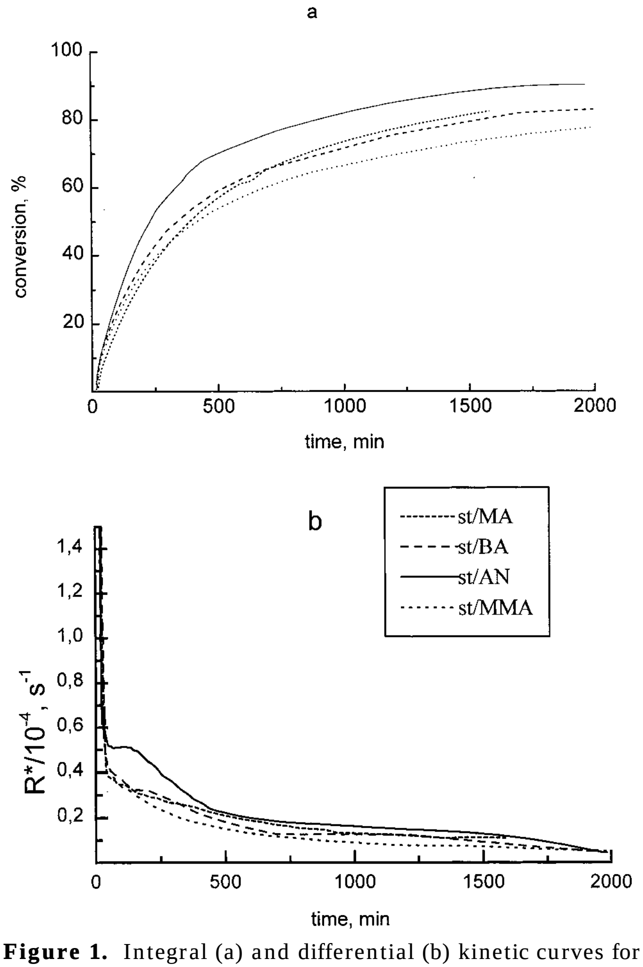


Figure 1. Integral (a) and differential (b) kinetic curves for TEMPO-mediated copolymerization at 120 °C, $[T]_0/[BPO]_0 = 1.2$, and $[T]_0 = 6.0 \times 10^{-3}$ M.

$[TEMPO]/[BPO]$ was 1.2:1, and the concentration of BPO was 5.0×10^{-3} M in the all feed systems.

Figure 1 shows the plots of integral and differential kinetic curves in different systems. All kinetic curves have a short initial nonstationary region 1–2 h, during which the reduced (divided by instantaneous monomer concentration) rate (R^*) of copolymerization drops rapidly.[29] After nonstationary period R^* continues to decrease slightly in the course of the reaction. The decrease of the R^* at this region is similar for all systems under study. We call this region "quasi-stationary" because the decrease of R^* does not exceed a factor of 2 during 1000 min. The reaction continues up to almost complete conversion.

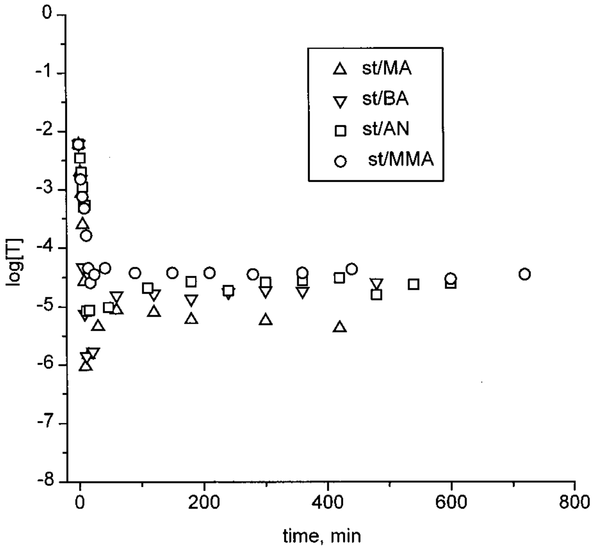
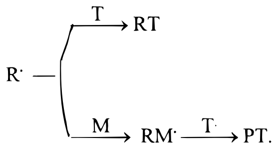


Figure 2. Plot of TEMPO concentration vs time for TEMPO-mediated copolymerization at 120 °C.

In all copolymerizations, the concentration of TEMPO decreases drastically during the first 10–13 min in accordance with the rapid decomposition of BPO (Figure 2):

$$\mathrm{BPO} \xrightarrow{k_d} 2\mathrm{R}^{\bullet} \qquad (16)$$



(17)

The rates of TEMPO consumption are similar: the half-live times do not exceed 2 min in all systems. At the quasi-stationary stage, concentration of TEMPO (T_{st}) remains constant up to high conversions. The time period of 1–2 h, which is necessary for TEMPO to achieve T_{st}, coincides exactly with the time of the transition of copolymerization rate to quasi-stationary regime. In intermediate time (15 min–1 h), the concentration of TEMPO increases from its minimum value to T_{st}. This phenomenon may be associated with a release of TEMPO radicals in the bimolecular recombination of primary oligomeric radicals since 2 nitroxyls become "free" in each act of recombination. The value of T_{st} is of 2 orders of magnitude less than its initial concentration T_o.

In our previous works,[30] we found out that under the same conditions styrene homopolymerization proceeds

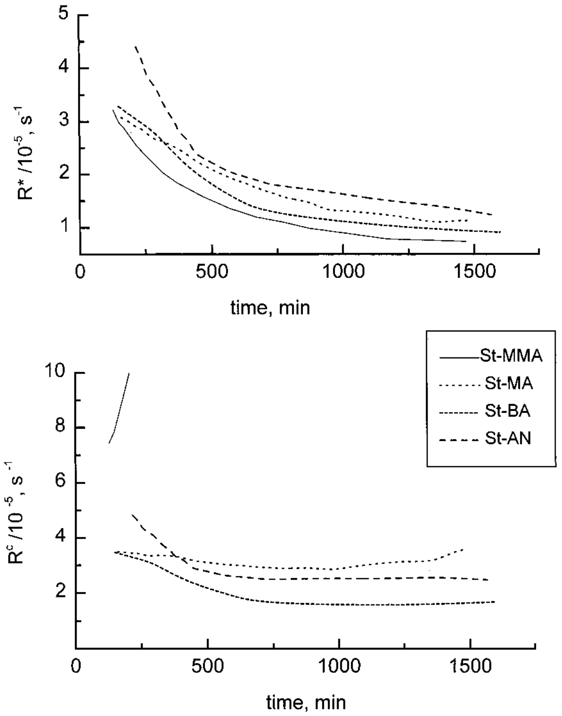


Figure 3. Plots of R^* and R^c vs time for TEMPO-mediated copolymerization.

also as a two-stage process. At the beginning of the reaction (at the first 1−2 h) the reduced R^* decreases rapidly (nonstationary stage), and then R^* becomes almost constant up to complete conversion (stationary stage). The concentration of TEMPO changes in the course of the styrene homopolymerization and copolymerization by the same manner. Therefore, the copolymerizations in the systems styrene/AN, styrene/(meth)-acrylates are quite similar to the styrene homopolymerization, as was predicted above. The principal difference between homo- and copolymerizations comprises in constancy of R^* in homopolymerization at the second stage in contrast with slight decrease of R^* in the copolymerization. The latter may be good experimentally evidence of the predicted accumulation of nonactive adducts P_2T during the copolymerization.

The accumulation of P_2T at quasi-stationary stage was calculated according to (14) using known values of kinetic constants.[31] In Figure 3 corrected $R^c = R^*/([T]_0 - [P_2T])$ plots, involving only the contribution of active adducts to the copolymerization are presented. As was expected, the copolymerizations of styrene with MA, BA and AN give almost horizontal R^c plots, except decrease in R^c at the beginning of quasi-stationary stage in styrene/BA and styrene/AN copolymerizations.

As far as styrene−MMA copolymerization is concerned, calculation according to eq 14 predicts death of all the growing chains after 500 min from the beginning of the copolymerization. Nevertheless, the copolymerization continues further with high R^*. The reason for this significant discrepancy is not clear now; we may suggest that k_{T_2} is less than 10^7 L/mol·s or that k_{-T_2} increases because of penultimate effect of styrene unit on dissociation of P_2T adducts.

The decrease in R^* at the quasi-stationary stage is the result of a decrease in the concentration $[P^\bullet]$ of active propagating radicals since R^* and $[P^\bullet]$ are related as

$$R^* = k_p[P^\bullet] \qquad (18)$$

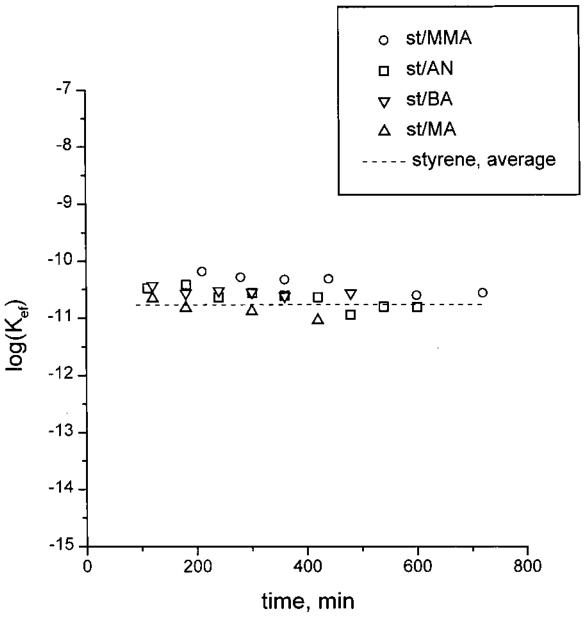


Figure 4. Dependence of K_{ef} on reaction time, 120 °C.

where $[P^\bullet] = [P_1^\bullet] + [P_2^\bullet]$. Nevertheless, [P] remains about 2−3 orders of magnitude lower (10^{-8} M) than T_{st} during the whole copolymerization. This should lead to the suppression of the reaction of bimolecular termination.

According to eq 6, the equilibrium constants K_{ef} of reversible dissociation of the copolymer-TEMPO adducts PT were calculated in the quasi-stationary region. $[T]_{st}$ was obtained directly from ESR data. [P] was calculated according to (18).[31] [PT] was assumed to be equal $T_0 - T_{st} \cong T_0$. The obtained results are presented in Figure 4. As can be seen, the average values of K are similar for four investigated systems and close to the one for styrene homopolymerization. However, K_{ef} decreases slowly during copolymerization because of the increase in the concentration of nonactive adducts P_2T, while K is a time-independent value for homopolymerization of styrene.

On one hand, the high value of K_{ef} in copolymerizations of styrene with (meth)acrylates and AN (close to the one for styrene) should provide growth of molecular weight vs conversion. On the other hand, a permanent increase in concentration of the nonactive P_2T adducts should lead to an enhancement of polydispersity index of copolymers formed at high conversions. This was sustained by GPC measurements. M_n of styrene copolymers grows in the course of copolymerization as well as in the styrene homopolymerization (Figure 5). The almost linear relationship between M_n and conversion confirms the quasiliving mechanism of the copolymerization. Polydispersity indexes of both copolymers and polystyrene decrease from 1.8 to 2.5 in the nonstationary region to 1.3 in the middle of the quasi-stationary region; but for high conversions MWD of polystyrene remains narrow, while MWDs of copolymers become broader (1.45−1.7) (Figure 6).

The obtained results confirmed that TEMPO-mediated copolymerizations of styrene with (meth)acrylates and AN proceed via quasiliving mechanism (with slight deviation from it at high conversion), similar to the one established for TEMPO-mediated homopolymerization of styrene. Thus, TEMPO-mediated copolymerization in

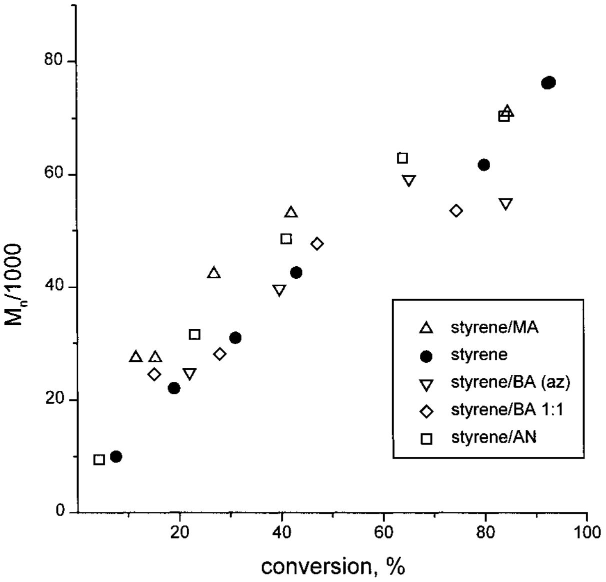


Figure 5. M_n–conversion relationship for TEMPO-mediated copolymerizations.

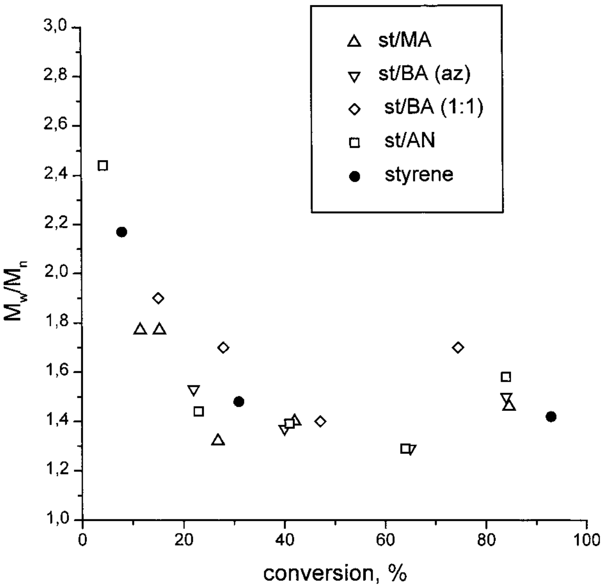


Figure 6. M_w/M_n–conversion relationship for TEMPO-mediated copolymerizations.

these systems may be successfully utilized for the synthesis of well-defined copolymers.

The evidence of quasiliving manner was demonstrated also by Fukuda[17] for styrene/AN azeotropic copolymerization, initiated by PS-TEMPO adduct, and by Hawker[23] for copolymerization of styrene with BA in three mixtures: 8:2, 7:3, and 6:4. However, Fukuda explained the quasiliving manner of copolymerization by the penultimate effect of styrene units on lability of P_2T–adducts.

Gradient Regime. As examples of type IIB, we studied copolymerization in the systems styrene–vinyl acetate (VA) and styrene–*N*-vinyl pyrrolidone (NVP) under different feed composition. The results obtained are presented in Figure 7 and Table 2. As can be seen, the rate of copolymerizations and yields of copolymers decrease proportionally to the decrease in ratio M_1/M_2 in the feed mixture. The copolymerizations do not continue up to complete conversions, but stop earlier. The value of limited conversions (q^*_{exp}) depends on the chemical nature of second comonomer and ratio M_1/M_2 (Table 3).

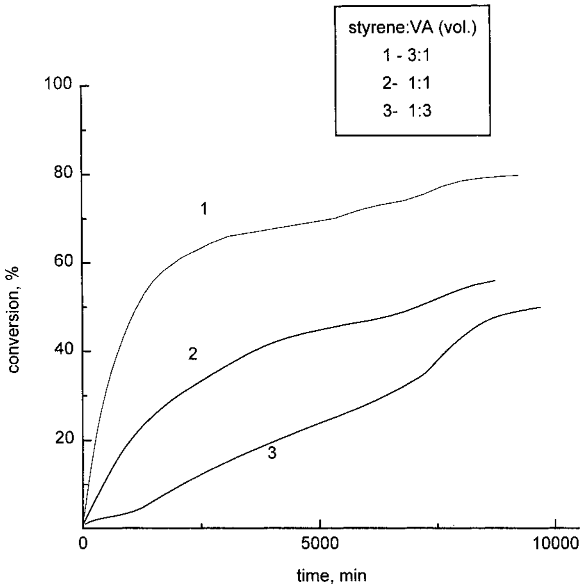


Figure 7. Kinetic curves for TEMPO-mediated styrene–VA copolymerization at 120 °C, $[T]_0/[BPO]_0 = 1.2$, and $[T]_0 = 1.2 \times 10^{-2}$ M.

Table 2. Yield of Styrene–NVP Copolymer after 8-h TEMPO-Mediated Copolymerization

f_1	yield of copolymer, %[a]
0	54
0.1	53
0.2	40
0.5	14
1.0	0

[a] [AIBN] = 5.0×10^{-3}M; $T_0/[AIBN]_0 = 1.2$.

Table 3. Limited Conversions in TEMPO-Mediated Copolymerizations

system	T_0,[a] M	f_1	q^*_{exp}, %	$q^*_{predicted}$, %
styrene–VA[b]	0.012	0.21	53.4	37
		0.45	65	57
		0.71	79.5	73
styrene–NVP[c]	0.006	0.5	86	68

[a] T_0/[initiator] = 1.2. [b] Initiator: BPO. [c] Initiator: AIBN.

The obtained results may be explained in accordance with reactivity of comonomers. Styrene is of 3 orders of magnitude more active than VA ($r_1 = 60$, $r_2 = 0{,}06$) and NVP ($r_1 = 6.3$, $r_2 = 0.01$). At the beginning of copolymerization, styrene polymerizes preferentially in comparison with second comonomer, the latter acts as "solvent" for styrene homopolymerization rather than "comonomer" for copolymerization. Apparently, the more styrene fraction in feed mixture, the more is initial rate of copolymerization. It was predicted above that the "death" of copolymerization would occur when no styrene will remain in reaction mixture ($q^*_{predicted}$). Our calculations in accordance with terminal model revealed that $q^*_{predicted}$ did not coincide exactly with experimental data, but were always less than q^*_{exp}. The one of the possible reasons for $q^*_{exp} > q^*_{predicted}$ is that terminal model does not work correctly at low f_1, the second is the post-homopolymerization of monomer M_2, initiated by P_1T adducts remained in copolymer.

As far as copolymerizations are going on, molecular weight of copolymers increases in both systems (Table

Table 4. Characteristics of Copolymers Obtained in "Gradient" Regime[a]

system	f_1	conversion, %	$M_n/10^3$	M_w/M_n	F_1
styrene–VA[b]	0.21	5.2	3.6	1.7	0.885
		13.4	10.5	1.6	0.866
		18.3	14.0	1.7	0.864
		31	21.2	2.6	0.686
		53	26.1	3.3	0.429
styrene–NVP[c]	0.5	3.5	7.3	1.8	
		12.4	19.7	1.5	0.860
		17.3	41.0	1.4	0.825
		55	68.5	1.4	0.785
		86	70.1	1.5	0.585

[a] T_0/[initiator] = 1.2. [b] [BPO] = 0.010 M. [c] [AIBN] = 0.005 M.

4). Polydispersity index maintains low in the system styrene–NVP ($f_1 = 0.5$), while it enhances in the system styrene–VA ($f_1 = 0.21$). In the course of copolymerization, the styrene content in the copolymers is reduced along with consumption of styrene in the monomer mixture. The growth of molecular weight of copolymers in combination with the change in copolymer composition leads to the formation of gradient copolymers in limited conversion.

Thus, TEMPO-mediated copolymerizations of styrene with vinyl acetate and *N*-vinyl pyrrolidone start as quasiliving and finish as a dead-end. Despite violation of the quasiliving manner, gradient copolymers could be synthesized with high yield.

Conclusion

In summary, the general concept for TEMPO-mediated copolymerization was advanced. Copolymerization of two comonomers can proceed via a quasiliving manner if it satisfies to following requirements: (1) the first comonomer should be able to polymerize in accordance with the quasiliving mechanism ($K_1 > 10^{-11}$ M) (styrene is a typical example); (2) the second comonomer should be significantly less active than the first ($r_1k_{22} \gg r_2k_{11}$); (3) the first comonomer should remain in the polymerizing system during copolymerization.

When these requirements are fulfilled, active polymer adducts P_1T will be preferentially formed at the end of growing chains, and copolymerization will proceed likewise in a quasiliving homopolymerization of the first monomer. Two principal regimes of TEMPO-mediated quasiliving copolymerization may be realized. When ratio between monomers M_1/M_2 maintains close to constant, monomers will copolymerize in accordance with quasiliving manner up to high conversions ("azeotropic" regime). When active monomer is consumed in the course of copolymerization, it will start as quasiliving and stop as dead-end ("gradient" regime).

Experimental confirmations of this concept were demonstrated in copolymerizations of styrene with MA, BA, MMA, and AN ("azeotropic" regime) and styrene with VA, and NVP ("gradient" regime). Thus, TEMPO-mediated styrene copolymerization may be effective and simple route to well-defined random and gradient copolymers.

Experimental Section

Materials. All monomers—styrene, MA, BA, MMA, AN, VA, and NVP (Aldrich) were distilled under reduced pressure prior to use. Benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) (AIBN) were recrystallized from ethanol. 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) was used as obtained from Sigma.

Copolymerization. Copolymerization mixtures were prepared as follows: initiator and TEMPO were weighted into 2 mL vial followed by addition of monomers. The reaction mixtures were degassed by several freeze–thaw cycles in a vacuum down to 10^{-2} mmHg and sealed off. All the samples for calorimetry, GPC, and EPR analysis were prepared from one mixture. Here, 0.2–0.4 mL of reaction mixture was charged into vials for calorimetric study or GPC, and 0.03–0.04 mL for ESR analysis. The copolymerization was carried out at 120 °C.

Kinetics. Copolymerization kinetics was studied by an 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.[32] For the calculation of copolymerization rate and reduced rate R^*, we used the method taking into account the dependence of overall heat of copolymerization on monomer composition as described previously.[33] Concentration of TEMPO in polymerizing system was measured by a ESR spectrometer RE–1307 working at 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%. Concentration of TEMPO was determined by double integration of the ESR spectrum.

Characterization. GPC analysis was performed in THF with a Waters instrument equipped with RI-410 detector. A combination of three Ultrastyragel columns (10^3 Å, 10^5Å, and linear) maintained at 35 °C was used. Chromatograms were processed with a Data Module-730.[35] Copolymers obtained for GPC analysis were isolated from reaction mixture by a lyophilization with benzene in a vacuum after definite time of copolymerization. Copolymer composition was determined by IR spectroscopy with a spectrometer Specord-M80.

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