ISSN 1560-0904, Polymer Science, Series B, 2020, Vol. 62, No. 1, pp. 1–13. © Pleiades Publishing, Ltd., 2020.
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Kinetic Features of Elementary Events in the Radical Polymerization of Methyl Methacrylate under Conditions of Nitroxide-Mediated Reversible Inhibition

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Received June 20, 2019; revised September 2, 2019; accepted September 16, 2019

Abstract—The kinetic features of the elementary events of initiation, reinitiation, and reversible termination in the radical polymerization of methyl methacrylate mediated by piperidine and imidazoline nitroxides are studied. The rate constants of these reactions and the constant of equilibrium between the dormant and growing chains are determined. In all the systems studied, the reinitiation rate constant and the equilibrium constant decrease during polymerization. The activity of imidazoline nitroxides in the termination reaction turns out to be an order of magnitude lower than that of piperidine ones, and the constant of interaction of both types of nitroxides with methyl methacrylate growing radicals is two and a half orders of magnitude lower than that with their low molecular weight counterparts.

DOI: 10.1134/S1560090420010121

INTRODUCTION

Radical polymerization carried out under conditions of nitroxide-mediated reversible inhibition is used for the controlled synthesis of a large number of vinyl polymers. However, in the case of MMA, this process, as a rule, proceeds in a decaying mode and leads to formation of a dead polymer. Although information on the polymerization of MMA operating by the mechanism of reversible inhibition involving nitroxide radicals periodically appears in the literature, in practice, the region of the living process usually does not go beyond 30–50% conversion [1–9] or is limited to producing oligomers [10, 11]. The reason for this phenomenon could be understood if the basic kinetic parameters of this process were known: the rate constants of the reactions of initiation k_d and nitroxide termination k_x, their ratio, the equilibrium constant $K = k_d/k_x$, and the rate constant of the disproportionation reaction k_{disp}. Unfortunately, such parameters are determined only for model low molecular weight compounds. Quantitative information on reactions proceeding directly in polymerization processes is extremely small and is limited to 2,2,6,6-tetramethylpiperidine-1-oxyl and SG-1 nitroxides.

It is well known that the adducts of nitroxides with low molecular weight radicals modeling the PMMA growing radical are unstable [12]. The same feature is also characteristic of high molecular weight PMMA–nitroxide adducts. Among all known polymeric nitroxide adducts, they are distinguished by the highest values of the reinitiation constants. The half-life of adduct PMMA–TEMPO at 120°C is 20 s [13], which is 50 times smaller than that of adduct PS–TEMPO. For PMMA–SG-1 and PS–SG-1, this difference exceeds 250 times. (Unfortunately, all the values given in [13–15] were obtained from the kinetic analysis of SG-1-mediated polymerization of MMA. No experimentally measured value of k_d is available for adduct PMMA–SG-1.) Therefore, from the point of view of the reinitiation reaction, there are no obstacles to the implementation of the reversible inhibition mechanism.

On the contrary, information about the kinetics of the reverse reaction, i.e., interactions of the PMMA radical or its low molecular weight analogs with nitroxides, is very contradictory. According to the published data, either the low molecular weight analogs of PMMA and PS radicals do not differ in reactivity in the reaction with nitroxides (this is typical of SG-1 [16, 17]), or the former is several times more reactive than the latter, as in the case of TEMPO or imidazoline nitroxides [16, 17].

However, in the reactions of polymer radicals with nitroxides, there is an inverse relationship: the reactivity of the PMMA radical is an order of magnitude lower than that of the PS radical. According to our data, the rate constant for the interaction of the PMMA radical with TEMPO is 2×10^6 L/(mol s); for the interaction of the PS radical with TEMPO, 1.5×10^7 L/(mol s) [18]. In the reaction with the SG-1 nitroxide, these values are of the order of 10^4 and 10^5 L/(mol s) for PMMA and PS, respectively [1]. In other words, the reactivity of the PMMA radical is significantly lower than that of its low molecular weight counterparts. In a series of radicals $(CH_3)(COOCH_3)(CH_3)C^\bullet–(C_6H_5)(CH_3)_2C–MMA^\bullet–PMMA^\bullet$, the rate constant of their interaction with TEMPO decreases by two and a half orders of magnitude [15].

The second feature of the interaction of PMMA radicals with nitroxides is a decrease in the termination rate constant with increasing temperature (by a factor of 5 on transition from 20 to 45°C [1]).

These two circumstances indicate that nitroxide radicals "work poorly" as traps for MMA growing radicals. Attempts to describe the nitroxide-mediated polymerization of MMA without taking into account the real values of the termination rate constant [1, 13, 17, 19] significantly reduce their predictive power.

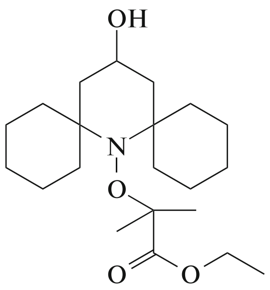
The situation is further complicated by the fact that the interaction of MMA growing radicals with nitroxides is accompanied by disproportionation, which leads to the formation of dead chains and hydroxylamine. For example, for TEMPO, the probability of such a path is 1/5 compared with reversible recombination [15]. In turn, hydroxylamine is involved in the secondary inhibition reaction, which also affords dead chains. Note that there are nitroxide radicals that are not prone to disproportionation, for example, SG-1, but during the polymerization of MMA, reversible inhibition is also not realized for them [1, 20].

It was previously experimentally shown that, when using alkoxyamines, i.e., the adducts of radical $(CH_3)(CH_3)(COOEt)C^\bullet$ with imidazoline nitroxides, the disproportionation reaction does not occur at the initiation stage. Therefore, the implementation of the reversible inhibition mechanism during the polymerization of MMA with such alkoxyamines is most likely. Recently, this assumption was verified experimentally for the first time [21].

The aim of this work is to determine the quantitative characteristics of the polymerization of MMA under conditions of reversible inhibition by imidazoline and some other nitroxides. The main attention here is paid to the reaction of the PMMA radical with nitroxides as the least studied process.

EXPERIMENTAL

In this work, methyl methacrylate, styrene, benzene, chlorobenzene, acetonitrile, and trifluoroacetic anhydride (**TFA**) were purified by standard methods and AIBN was recrystallized from ethanol. TEMPO, di-*tert*-butyl nitroxide (**DTBN**), C-phenyl-*N*-*tert*-butylnitron (**PBN,** Sigma), and chemically pure silver oxide Ag_2O were used as received. Alkoxyamines 2-(4-hydroxy-dicyclohexanespiro-2,6-piperidine-1-oxyl)ethyl isobutyrate (**A-1**), 2-(1-hydroxyethylcyclopentane-spiro-2-3-phenyl-5,5-diethyl-imidazoline-1-oxyl)ethyl isobutyrate (**A-2**), and 2-(2,5,5-triethyl-3-indole-5-*para*-phenylcarbinylimidazoline-1-oxyl)ethyl isobutyrate (**A-3**) were synthesized and characterized according to [22] in the Laboratory of Nitrogen Compounds of the Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, using the corresponding nitroxide radicals: 4-hydroxy-dicyclohexanespiro-2,6-piperidine-1-oxyl (**N-1**), 1-hydroxy-ethylcyclopentane-spiro-2-3-phenyl-5,5-diethylimidazoline-1-oxyl (**N-2**), and 2,5,5-triethyl-3-indole-5-*para*-phenylcarbinyl-imidazoline-1-oxyl:



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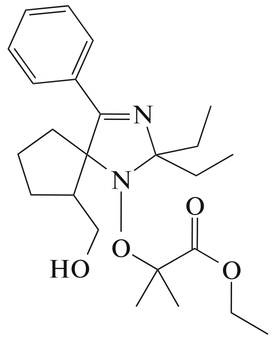

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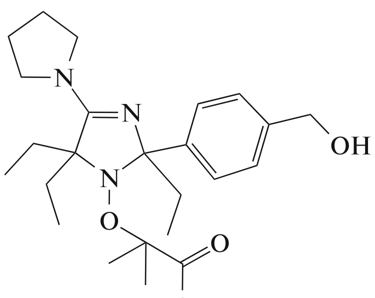


A-3

For the synthesis of macroinitiators, alkoxyamine solutions in MMA were prepared. If necessary, styrene, AIBN, and TFA were added to an alkoxyamine solution in MMA. The reaction mixture was poured into an ampoule and degassed on a vacuum unit by three freeze–vacuum–thaw cycles to a residual pressure of 5×10^{-3} mmHg, after which the ampoule was sealed. The sample was placed in a thermostat heated to the desired temperature (45–80°C) and held for the required time. The polymer was isolated by freeze drying in vacuum from benzene.

To determine the initiation rate constant, solutions of alkoxyamines in chlorobenzene were prepared

(10^{-4} mol/L). The mixtures were poured into ampoules, placed in a Bruker EMX EPR spectrometer sensor, and heated in a resonator cell to 60, 70, or 90°C. Afterwards, the spectra were recorded. Dissolved oxygen was used as a trap for alkyl radicals.

To determine the reinitiation rate constant, a macroinitiator solution in benzene was prepared (10^{-4} mol/L), after which PBN (0.4 mol/L) was added. The reaction mixture was poured into ampoules and degassed, the ampoules were sealed and placed in a thermostat at a temperature of 60–90°C, and the amount of the released nitroxide was recorded using a RE-1307 radiospectrometer.

The molecular weight characteristics of the samples were estimated by GPC according to polystyrene standards and recalculated to PMMA via the formula $M_{\mathrm{PMMA}} = 0.644 \times M_{\mathrm{PS}}^{1.019}$ on a Waters liquid chromatograph equipped with a refractometric detector, three columns filled with ultrastyrogel with a pore size of 10^4 and 10^5 Å, and a linear column. GPC analysis was performed in THF at 35°C; the flow rate was 0.9 mL/min. Chromatograms were processed on a Data Module-730 integrator.

The amount of hydroxylamine formed in the reaction mixture during polymerization was determined by the known method [18]. After polymerization ([alkoxyamine] = 20 mmol/L, 80°C), the ampoule was opened, silver oxide was added, the mixture was evacuated, and the ampoule was sealed. The ampoule was kept for 1.5–2 h at room temperature, and the amount of released nitroxide was measured by EPR. The amount of hydroxylamine formed by the disproportionation of alkoxyamines in an inert medium was determined in a similar manner using the alkoxyamine solution in benzene.

The rate constant of reversible termination was assessed by competitive inhibition at 40°C using a preliminarily degassed solution of TEMPO and nitroxide N-2 in methyl methacrylate.

The polymerization rate was determined by calorimetry at 40°C on a DAK-1-1a differential automatic microcalorimeter in the mode of direct registration of the rate of heat release under isothermal conditions. An ampoule with the test mixture was placed in the working cell, and an ampoule with approximately equal amounts of the already polymerized monomer was placed in the compensation cell. The rate of polymerization was calculated using the known enthalpy of MMA polymerization.

RESULTS AND DISCUSSION

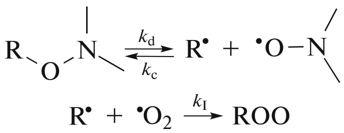
Determination of Initiation and Reinitiation Rate Constants

The initiation reaction was studied by the example of the decomposition of three alkoxyamines A-1, A-2, and A-3 in chlorobenzene at 60, 70, and 90°C. These alkoxyamines are the adducts of imidazoline nitroxides and substituted TEMPO with a low molecular weight radical simulating the MMA growing radical.

Table 1. Initiation rate constants for alkoxyamines and the activation energy of initiation

Alkoxyamine	$k_d \times 10^4$, s^{-1}			E_a, kJ/mol
	60°C	70°C	90°C	
A-1	75	13.0	135	100 ± 15
A-2	4.4	7.6	190	130 ± 30
A-3	6.1	15.0	82	85 ± 10

To determine the initiation rate constant k_d, the accumulation of nitroxide in the decomposition of alkoxyamines in a thermostatically controlled cell of the EPR spectrometer was recorded. The dissolved oxygen in the sample served as a competitive inhibitor:



The rate constant was calculated from the kinetic curve of the accumulation of nitroxide in coordinates of the first-order equation,

$$-\ln(1 - [\mathrm{N}]/[\mathrm{A}]_0) = k_d t, \tag{1}$$

and from the slope of the initial linear portion of the nitroxide accumulation curve at low temperatures: $d[\mathrm{N}]/dt = -d[\mathrm{A}]/dt = k_d[\mathrm{A}]_0$, where [N] and $[\mathrm{A}]_0$ are the current and initial concentrations of nitroxide N and adduct A and t is time.

Both methods give values that differ by no more than 30%.

Figure 1 shows the kinetic curves of the accumulation of nitroxide radicals during the decomposition of adducts A-1, A-2, and A-3 in the coordinates of Eq. (1). The initiation rate constants and activation energies obtained from the analysis of the curves are presented in Table 1.

As can be seen, piperidine A-1 and imidazoline A-2 initiators are quite active and are close in their kinetic parameters. The latter of the initiators, A-3, is characterized by the activation energy atypically low for alkoxyamine initiators. Therefore, all further studies were carried out with the first two compounds.

To determine the rate constant of reinitiation, i.e., the decomposition of polymer adducts, a number of PMMA–N-1 and PMMA–N-2 samples were obtained by the polymerization of methyl methacrylate mediated by A-1 and A-2 under different conditions (Table 2). Then, similar experiments were carried out using PBN as a competitive inhibitor. Since PMMA–N-2 is active even at room temperature, it was isolated by freeze drying and not reprecipitated, since there was a significant loss of its activity. In this

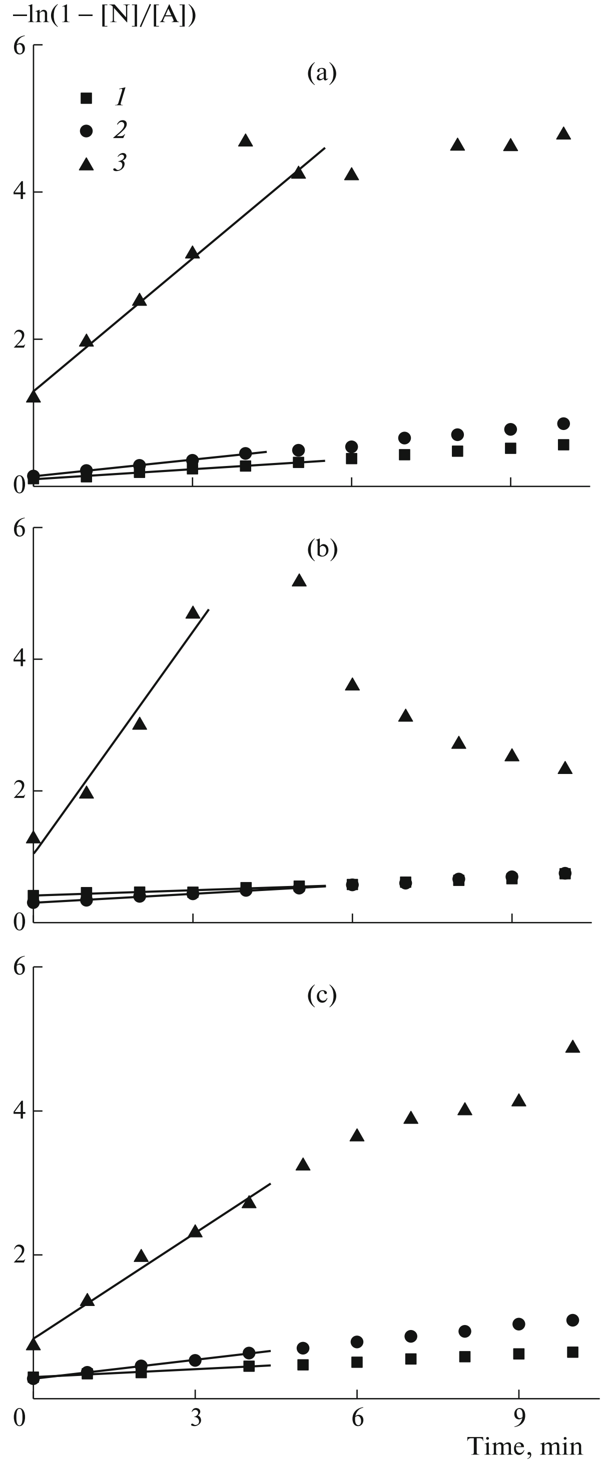


Fig. 1. Time dependence of nitroxide radical concentration in the coordinates of Eq. (1) during the decomposition of (a) A-1, (b) A-2, and (c) A-3 alkoxyamines in chlorobenzene solution at a temperature of (*1*) 60, (*2*) 70, and (*3*) 90°C.

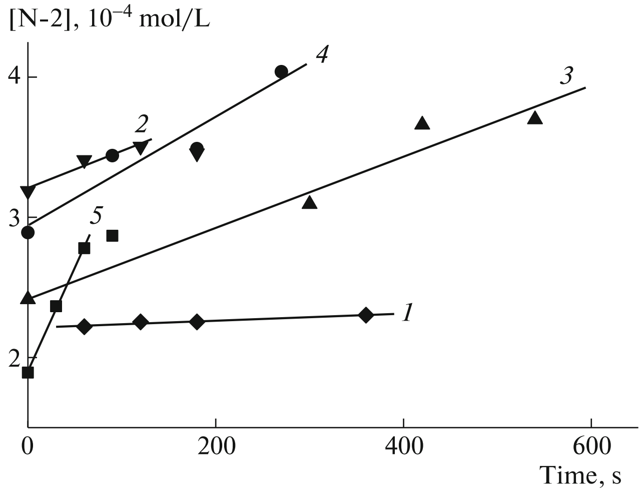


Fig. 2. Kinetic curves of nitroxide accumulation during the decomposition of PMMA–N-2 (2) in the presence of PBN at temperature T = (*1*) 60, (*2*) 70, (*3*) 72, (*4*) 80, and (*5*) 90°C. [PMMA–N-2 (2)] = 10^{-4} mol/L.

case, the polymer adduct contained a large amount of the residual free nitroxide, which is a good competitive inhibitor by itself; therefore, the PBN spin trap was taken as a competitor. The trap concentration (0.4 mol/L) was selected experimentally, so that the initial rate of nitroxide accumulation did not depend on the concentration of PBN. When analyzing the kinetics of the reaction, the growth of the nitroxide concentration was divided in half, since two nitroxide radicals are released per event of decomposition of the PMMA macroinitiator. Under these conditions, the rate of accumulation of the nitroxide radical and the rate of decomposition of the initiator coincide.

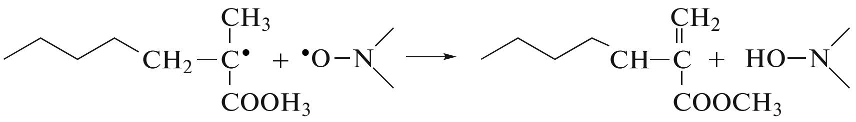
The kinetic curves of PMMA–N-2 (2) decomposition are shown in Fig. 2, and the values of the decomposition constant are listed in Table 3. The calculated activation energy of decomposition is 128 ± 19 kJ/mol, which is typical of nitroxide macroinitiators [23].

A comparison of the k_d and E_a values for low molecular weight alkoxyamine A-2 and the polymer formed in its presence shows that they have approximately the same activity as initiators. However, the constant of macroinitiator decomposition decreases by three to four times during polymerization, which is probably due to the gradual accumulation of dead chains (shown below).

In contrast, the PMMA–N-1 polymer has a significantly lower (close to zero) initiating ability; that is, almost all chains of this polymer are dead.

Disproportionation Reactions in the Polymerization of Methyl Methacrylate

The supposed accumulation of dead chains in PMMA–N-1 and PMMA–N-2 is associated with the disproportionation of growing radicals with nitroxides, which leads to the formation of hydroxylamine and macromolecules with a terminal double bond:



Initially, this possibility was investigated in an inert medium for the alkoxyamines themselves. Hydroxylamine formation was monitored using a silver mirror reaction [18]. For this purpose, a solution of A-2 in benzene was heated in vacuum for 5 min. Then, the ampoule with the sample was opened and an excess of silver oxide was added to it and kept for 1.5–2 h. If hydroxylamine is present in the medium, the release of nitroxide and the formation of silver mirror should proceed.

Table 2. Synthesis conditions and molecular weight characteristics of PMMA samples used to determine the reinitiation constant

Macro-initiator	Time, min	$[A_i]$, mmol/L	$M_n \times 10^{-3}$	$Đ$
		PMMA–N-2		
(1)	10	3	9.3	2.3
(2)	10	10	10.0	1.5
(3)	13	10	11.1	1.4
(4)	20	3	21.6	1.5
(5)	120	30	7.6	1.9
(2a)*	10	10	11.7	1.5
		PMMA–N-1		
(1)	180	10	5.9	1.3
(2)**	40	–	8.9	3.4

* Obtained in the presence of 5 mmol/L of AIBN.

** For synthesis, 10 mmol/L AIBN and 10 mmol/L N-1 were used.

Table 3. Decomposition constants for PMMA-based macroinitiators

Macroinitiator	T, °C	$k_d \times 10^3$, s^{-1}
	PMMA–N-2	
(2)	90	12.0
	80	2.5
	72	1.8
	70	0.51
	60	0.25
(1)	–	3.6
(3)	–	1.3–2.0
(4)	–	2.2
(5)	–	0.9
(2a)	80	1.8
	PMMA–N-1	
(1)	80	<0.3
(2)	80	<0.2
(2)	60	<0.03

However, as follows from the EPR analysis of the reaction products, the concentration of nitroxide before and after the addition of silver oxide coincided up to the measurement error (Table 4). This indicates the absence of the disproportionation reaction between low molecular weight radicals—the products of decomposition of A-2.

When the inert reaction medium is replaced by the MMA monomer, the picture changes: already 5 min after the start of the reaction, the system contains 3% hydroxylamine, the concentration of which increases to ~15% after 20 min and does not change further. This result allows one to conclude that, even in the case where the decomposition products of the alkoxyamine initiator cannot disproportionate themselves, this possibility appears as soon as MMA growing radicals are formed in the system.

The same pattern was observed in the study of alkoxyamine A-1. During its thermolysis in an inert medium, the probability of disproportionation is small, although in the monomer medium almost all nitroxide is converted to hydroxylamine already after 15 min.

Thus, the following conclusions can be made. First, the probability of disproportionation of the piperidine nitroxide is significantly higher than that of the imidazoline nitroxide. Secondly, the disproportionation reaction in the monomer occurs much faster than that in an inert solvent; that is, the probability of disproportionation for a high molecular weight growing radical is significantly higher than that for a low molecular weight one. Thirdly, in the case of A-1-mediated polymerization, the high probability of disproportionation leads to an almost complete termination of growing chains already within 15 min after the start of polymerization. Just this circumstance is responsible for the “zero” activity of the obtained PMMA–N-1 as a macroinitiator. Finally, the accumulation of dead chains due to disproportionation in the case of A-2-mediated polymerization of MMA leads to a decrease in the initiating ability of PMMA–N-2. However, the observed decrease in the rate constant of initiation is much larger than the expected one owing to the termination of chains in the disproportionation reaction.

Table 4. Silver mirror reaction results

System	Time, min	Concentration of N (mmol/L) before/after adding Ag_2O	Content of hydroxylamine, %
A-2–benzene	5	0.43/0.36	~0
A-2–MMA	5	1.0/1.8	2.8
	20	2.4/1.1	16
	40	1.6/5.3	13
	60	5.0/4.6	17
A-1–benzene	35	0.2/1.1	7
	90	1.6/2.3	6
A-1–MMA	9	1.8/1.6	38
	15	8.8/20	~100

Reversible Termination Rate Constant k_x

The higher the general rate of interaction between the growing radical and nitroxide, the higher the rate of their disproportionation. Therefore, knowledge of the termination rate constant k_x of PMMA radicals is required to understand the mechanism of polymerization. To estimate this value, two generally accepted approaches, linearization of the distribution of macromolecules over the chain length and competitive inhibition, were used [24, 25].

The first method makes it possible to determine k_x directly under conditions of polymerization. To do this, linearization of the distribution of macromolecules over the chain length $P(M)$ obtained by transforming GPC curves $G(RT)$ of the polymer is employed [26]:

$$\ln P(M) = \text{const} + \ln \frac{G(RT)}{M^2}.$$

The value of k_x is calculated by differentiating the function ln $P(M)$ with respect to the length of the chain i using the ratio

$$\lim_{i\to\infty} \frac{d\ln P}{di} = -\frac{k_x[\mathrm{X}]}{k_\mathrm{p}[\mathrm{M}]}. \qquad (2)$$

If the polymer is obtained under stationary conditions at a constant concentration of free nitroxide X, then a section of the dependence ln$P$ corresponding to the high molecular weight branch of the GPC curve is a straight line with the slope $(k_x[\mathrm{X}]/k_\mathrm{p}[\mathrm{M}])m$ (m is the molecular weight of the unit). Earlier, this method was used to determine a value of k_x = (1.5–2.0) × 10^6 L/(mol s) for the reaction of the PMMA radical with nitroxide TEMPO [24].

It turned out that, when replacing TEMPO with its analog containing two cyclohexyl substituents (N-1), the rate of reaction of nitroxide with the PMMA radical hardly changes. The value of k_x determined from the slope of the linear sections of the dependence ln$P(M) = f(M)$ (Fig. 3) is 1.0 × 10^6 L/(mol s) (Table 5). The measurement of this constant in the polymerization initiated by alkoxyamine A-1 and in the polymerization initiated by the AIBN–N-1 system leads to almost identical results.

Acyclic nitroxide DTBN is somewhat more active in the reaction with PMMA radicals which is obviously related to its smaller size.

On the contrary, upon transition to the five-membered sterically loaded imidazoline nitroxide N-2, the termination rate constant decreases. This is evidenced by a significantly larger slope of similar dependences ln$P(M)$ on M for PMMA obtained under different conditions in the presence of N-2 (Fig. 4). The value of constant k_x averaged over five experiments is an order of magnitude lower than that for nitroxide TEMPO.

Interestingly, the addition of as low as 10% styrene to MMA dramatically increases the rate of termination of growing radicals on nitroxides and the value of k_x grows to 4 × 10^6 L/(mol s) (Table 5). This behavior follows from the general concept of radical copolymerization operating by the reversible inhibition mechanism [27]; that is, when 5–10% styrene is added to MMA, the main kinetic characteristics of the process become close to those for styrene polymerization.

The second approach, which was used to find k_x, is the competitive inhibition method. It consists in the fact that polymerization is carried out in the presence of two nitroxides A and B, for one of which (reference) the value of constant k_{x1} for the rate of interaction with the monomer growing radical is known. The process is conducted at a low temperature to exclude the reverse reaction of polymer–nitroxide adduct decomposition and at low concentrations of inhibitors so that polymer radicals can grow before termination. By measuring the relative consumption rate of both inhibitors using the EPR method, the desired constant k_{x2} is determined through the relation

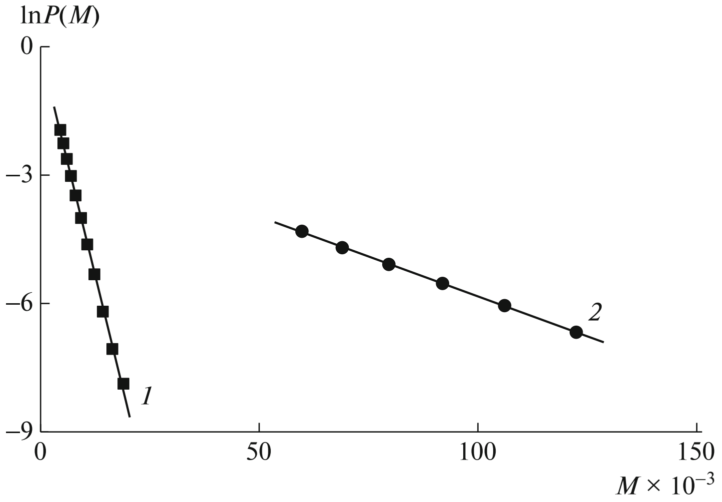


Fig. 3. Dependence of $\ln P(M)$ on M for PMMA obtained in (*1*) the MMA–A-1 system at 45°C and (*2*) the MMA–A-1–AIBN system at 80°C; the polymerization time is (*1*) 20 and (*2*) 45 min. [A-1] = 10 mmol/L; [AIBN] = 10 mmol/L.

$$d[\mathrm{A}]/d[\mathrm{B}] = k_{x1}[\mathrm{A}]/k_{x2}[\mathrm{B}]. \qquad (3)$$

The applicability of this method to the nitroxide-mediated polymerization of MMA is limited by the choice of references with the known termination constant. Only TEMPO can serve as such a substance, since the reliable value of k_{x1} is available for this nitroxide. Nitroxide SG-1, for which the value of k_{x1} is also known, is not suitable here, since its activity is so low ($k_x \sim 10^4$ L/(mol s)) that it is not a competitor even for the irreversible quadratic termination reaction.

Table 5. Determination of constant k_x for the interaction of nitroxides with the PMMA radical

System	Concentration, mmol/L	T, °C	$k_x \times 10^{-6}$, L/(mol s)	$\langle k_x \rangle \times 10^{-6}$, L/(mol s)
A-1	10	45	1.2	1.0 ± 0.1
A-1–AIBN	10	80	0.95	–
N-1–AIBN	10	90	0.88	–
	–	–	0.89	–
A-1–TFA	10	80	0.28	0.27 ± 0.03
A-1	10	80	0.21	–
TFA	25	–	–	–
A-1	10	80	0.29	–
TFA	50	–	0.29	–
A-1	10	80	3.9	–
10% styrene	–	–	4.1	–
DTBN–AIBN	10	90	1.2	3.2 ± 1.7
DTBN	10	90	4.4	–
AIBN	12	–	4.0	–
A-2	3	80	0.19	0.16 ± 0.02
	10	80	0.15	–
	–	80	0.13	–
	30	–	0.14	–
A-2–AIBN	10	80	0.17	–
A-2–TFA	10	80	0.11	0.11
	–	–	0.11	–

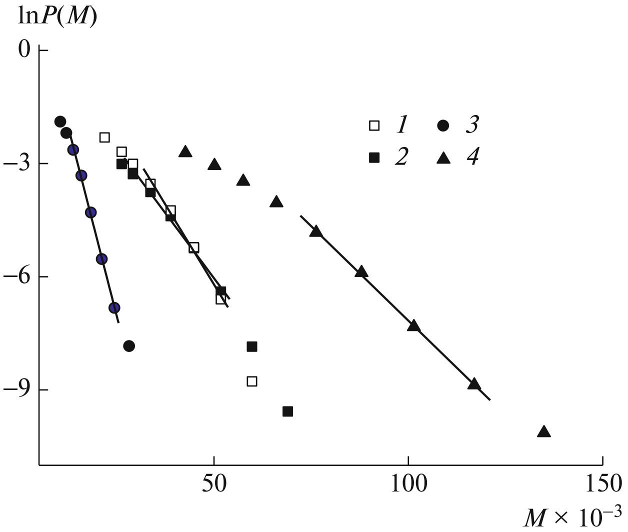


Fig. 4. Dependence of $\ln P(M)$ on M for PMMA obtained in the MMA–A-2 system at 80°C; the polymerization time is (*1*, *3*, *4*) 20 and (*2*) 13 min; [A-2] = (*1*, *2*) 10, (*3*) 30, and (*4*) 3 mmol/L.

Figure 5 shows evolution in the EPR spectra in the MMA–TEMPO–N-2–AIBN system during polymerization at 40°C. It can be seen that both nitroxides have the same spectral structure, namely, the triplet of singlets; however, a noticeable difference in the hyperfine splitting constants ($a_{N,TEMPO}$ = 15.4 Oe and $a_{N,N\text{-}2}$ = 14.0 Oe) makes it possible to determine the consumption of each nitroxide during the reaction from the low-field component of the spectrum. The obtained kinetic curves are shown in Fig. 6, and the calculated ratios of the termination constants are given in Table 6. Using the known value of $k_{x1} = 1.6 \times 10^6$ L/(mol s) [24], we find that for N-2 the average value is $k_{x2} = 5.0 \times 10^5$ L/(mol s). This means that the activity of N-2 as an inhibitor is half an order of magnitude lower than that of TEMPO.

The values of k_x for N-1 and DTBN cannot be determined by this method, since their EPR spectra and the TEMPO spectrum practically coincide.

Two important conclusions follow from the above results: the first, the activity of imidazoline nitroxides is an order of magnitude lower than that of piperidine ones and, second, a comparison of constants k_x for the reaction of N-2 with the PMMA radical and its low molecular weight analog $k_x = 1 \times 10^8$ L/(mol s) [3] shows that they differ by two and a half orders of magnitude. For the TEMPO nitroxide, as presented above, this difference is also two and a half orders of magnitude. Thus, a sharp drop in the reactivity of polymethacrylate radicals in reaction with nitroxides is a general rule.

Constant of Equilibrium Between Dormant and Growing Chains

From the above reinitiation and termination rate constants, it follows that the constant of equilibrium between growing and dormant PMMA chains $K = k_d/k_x$ should decrease during the N-2 mediated polymerization of MMA from 2×10^{-8} to 5×10^{-9} L/(mol s). Determination of the equilibrium constant by the direct experiment, i.e., by determining the equilibrium concentrations of nitroxide N, macroradical P, and

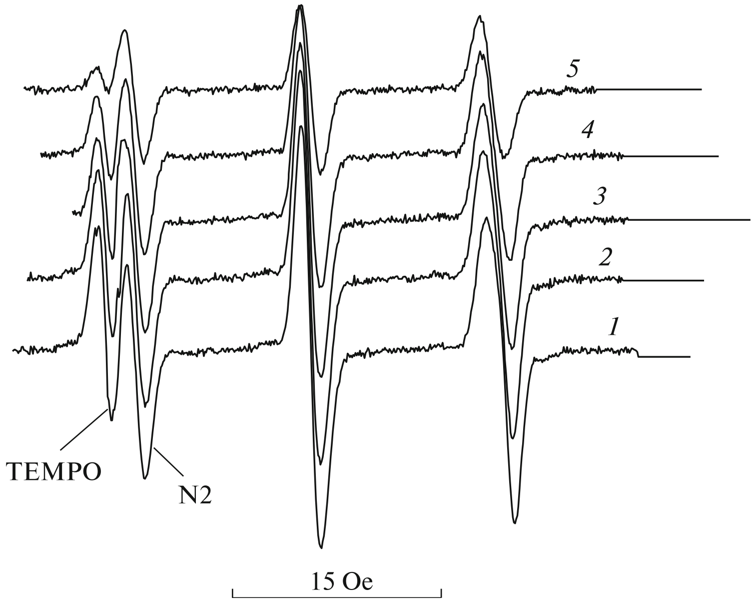


Fig. 5. Changes in the EPR spectra in the MMA–TEMPO–N-2–AIBN system during the polymerization of MMA at 40°C; the recording time is (*1*) 2, (*2*) 5, (*3*) 8, (*4*) 11, and (*5*) 17 min.

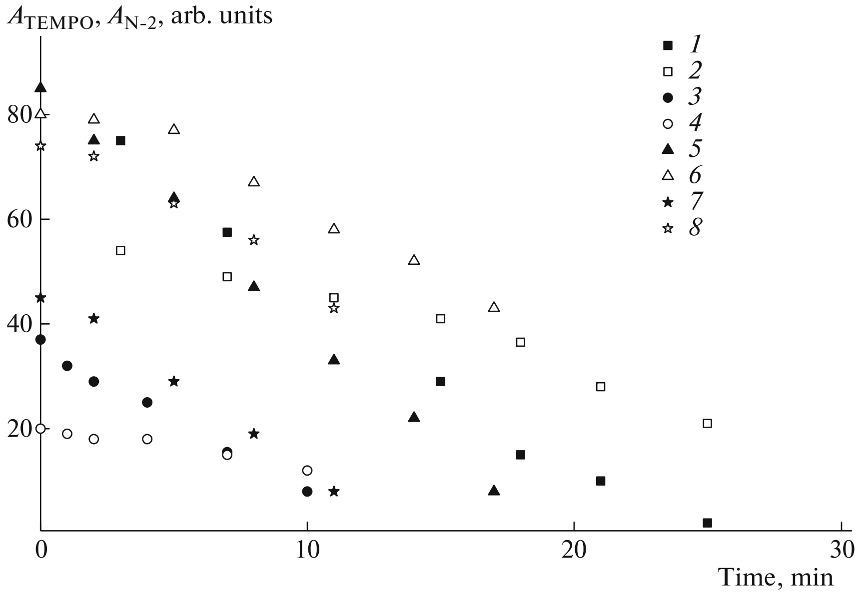


Fig. 6. Dependence of the amplitude of signal A due to (*1*, *3*, *5*, *7*) TEMPO and (*2*, *4*, *6*, *8*) N-2 nitroxides during the polymerization of MMA at 40°C in the TEMPO–N-2–AIBN systems. [TEMPO] = (*1*, *2*) 0.055, (*3*, *4*, *7*, *8*) 0.16, and (*5*, *6*) 0.22 mmol/L; [AIBN] = (*1*, *2*) 100 and (*3*–*8*) 500 mmol/L; [N-2] = (*1*, *2*) 0.0025, (*3*, *4*) 0.0075, and (*5*–*8*) 0.22 mmol/L.

adducts A from EPR and calorimetry data $K = [\text{N}][\text{P}]/[\text{A}]$, gives close values (Table 7).

Clearly, during polymerization mediated by nitroxide N-1 the equilibrium constant turns out to be one to two orders of magnitude lower than that in the case of N-2, which agrees with the constants of elementary events of reinitiation and chain termination found above.

A good agreement between the values of reinitiation, nitroxide termination, and equilibrium constants determined by different methods confirms the validity of these results.

Effect of Accelerating Additives on the Nitroxide-Mediated Polymerization of MMA

To prevent the decay of the nitroxide-mediated polymerization of MMA, i.e., shift the equilibrium toward the formation of growing chains, a number of accelerating additives are used [4]. The most effective among them are highly polar compounds (malononitrile, trifluoroacetic anhydride, metal salts) and radical initiators, which decompose much more slowly than basic alkoxyamine. The nature of the action of the former is not completely clear. Radical initiators, which supply additional active radicals to the system, bind free nitroxide and, thereby, shift the equilibrium toward dissociation.

In the present work, we studied how the addition of TFA and AIBN affects the quantitative parameters of MMA polymerization mediated by N-1 and N-2 nitroxides.

It is known that polar compounds decrease the value of k_x since they facilitate the transfer of spin density to the nitrogen atom in the nitroxide, decreasing its activity [28]. This effect was previously described in the reactions of nitroxides with polymer radicals in polar solvents [29]. We observed the same effect with small additions of TFA to the polymerization product containing nitroxides N-1 and N-2.

Figure 7 shows the dependences of $\ln P(M)$ on M for PMMA obtained in the presence of nitroxide N-1 and TFA in an amount from equivalent to a fivefold excess with respect to the nitroxide. It turned out that

Table 6. The ratio of rate constants for the interaction of methyl methacrylate growing radicals with TEMPO (k_{x1}) and N-2 (k_{x2}) in the system monomer–TEMPO–N-2–AIBN, $T = 40$°C

[TEMPO], mmol/L	[N-2], mmol/L	[AIBN], mmol/L	k_{x1}/k_{x2}
0.055	0.025	100	3.5 ± 0.2
0.16	0.075	500	3.5 ± 0.6
0.16	0.22	500	3.3 ± 0.6
0.22	0.22	500	3.0 ± 0.3

Table 7. Equilibrium concentrations of growing radicals and nitroxides and the equilibrium constant

Alkoxyamine	Alkoxyamine concentration, mmol/L	Time, min	[N], mmol/L	$[R] \times 10^8$, mol/L	$K \times 10^8$, L/mol
A-2	30	17	3.1	13	1.3
		30	3.3	8.3	0.91
		45	3.4	5.0	0.57
		60	3.4	3.2	0.37
		70	3.3	2.3	0.26
	20	20	2.5	8.8	1.1
		40	3.6	4.1	0.73
		60	3.2	2.0	0.32
	10	20	1.5	7.7	1.1
		30	1.6	6.2	1.0
		40	1.7	4.6	0.77
		60	1.9	2.5	0.42
		70	1.7	1.8	0.32
	9	20	1.4	6.6	1.1
		30	1.6	4.8	0.82
		40	1.7	3.4	0.62
		50	1.7	2.2	0.42
		60	1.7	1.5	0.29
	5	25	1.1	5.0	1.1
		45	1.1	2.6	0.56
		65	1.3	1.4	0.35
	3	20	0.57	5.5	1.04
		25	0.64	4.3	0.92
		45	0.66	2.0	0.44
		65	0.76	1.0	0.24
A-2–AIBN	0.01–0.01	20	0.56	11.8	0.53
		25	0.42	11.5	0.38
		35	0.27	10.7	0.23
		45	0.22	10.5	0.18
A-1	30	25	2.5	1.0	0.084
		50	2.6	0.20	0.018
		70	2.3	0.071	0.0057
		100	2.2	0.020	0.0015
	10	25	3.4	0.58	0.18
		40	4.1	0.11	0.045
		75	2.6	0.012	0.0036
	3	25	0.35	0.29	0.033
		55	0.28	0.033	0.0031
A-1–AIBN	10–5	30	0.17	9.7	0.16
		40	0.061	7.1	0.044
		60	0.029	3.7	0.011
		80	0.019	1.8	0.0035

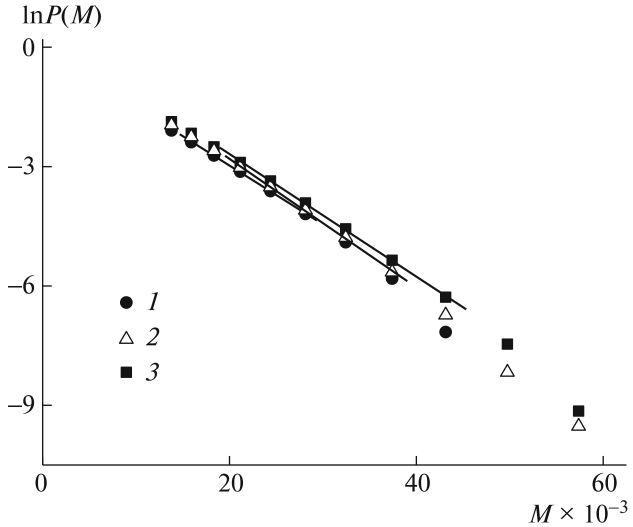


Fig. 7. Dependence of ln$P(M)$ on M for PMMA obtained in the MMA–A1–TFA system at 80°C; the polymerization time is (*1*) 17, (*2*) 20, and (*3*) 10 min. [A-1] = 10 mmol/L; [TFA] = (*1*) 10 and (*2*, *3*) 50 mmol/L.

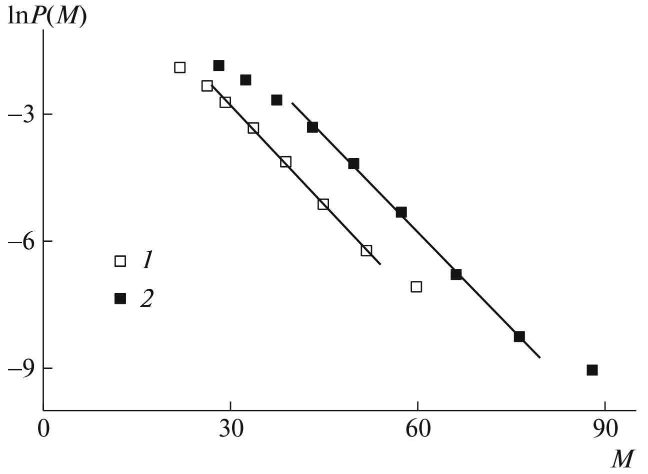


Fig. 8. Dependences of ln$P(M)$ on M for PMMA obtained in the MMA–A-2–TFA system at 80°C; the polymerization time is (*1*) 20 and (*2*) 30 min. [A-2] = 10 mmol/L; [TFA] = 10 mmol/L.

the addition of TFA reduces the activity of N-1 by a factor of 3 to 4 (Table 8). Moreover, the termination rate constant is practically independent of the amount of the additive.

The fall of the reversible termination constant in the presence of TFA causes an increase in the equilibrium constant. This leads to the fact that the rate of MMA polymerization increases and the polymer yield grows from 3–5 to 25%.

The effect of TFA on the activity of nitroxide N-2 is less pronounced. The value of k_x found from the slope of similar dependences (Fig. 8) is only 1.5 times lower than that in the absence of the additive (Table 8). The introduction of TFA does not affect the equilibrium concentrations of growing radicals and nitroxide, and, consequently, the equilibrium constant.

On the contrary, the addition of AIBN, although it leads to a noticeable increase in the equilibrium concentration of growing radicals and a decrease in the concentration of free nitroxide, causes a decrease in the equilibrium constant. This is characteristic of polymerization involving both N-1 and N-2 nitroxides. Obviously, this result is related to a decrease in the number of living chains due to an increase in the probability of quadratic termination. When 0.5–1.0 of AIBN equivalent is added, K drops by two to three times in both systems.

Such an amount of added AIBN does not affect the rate of chain termination. This is evidenced by the same values of the termination constant both in the presence of AIBN and in its absence. This can be due to two reasons: either the main termination of the macroradicals occurs via the reaction with nitroxides rather than with each other, or the rates of reversible and quadratic terminations are close.

However, the addition of AIBN affects the reinitiation constant. A comparison of the rates of decomposition of samples PMMA–N-2 (1) and PMMA–N-2 (2a) (Table 2) suggests that it decreases by two times. This fact is in good agreement with the general decrease in the equilibrium constant owing to the accumulation of dead macromolecules in the latter.

Thus, the addition of AIBN and TFA leads to increase in the equilibrium concentration of growing radicals and decrease in the concentration of nitroxide. This circumstance reduces the “decaying” character of the polymerization but does not prevent it.

CONCLUSIONS

The study was aimed at identifying the features of elementary events in the polymerization of MMA mediated by various nitroxides. The observed patterns help to understand the “stubborn resistance” of MMA to polymerize by the nitroxide-mediated reversible inhibition mechanism and overcome this “resistance.”

PMMA–nitroxide adducts are quite active as initiators (an order of magnitude more active than the corresponding PS–nitroxide adducts and two orders of magnitude more active than polyacrylate–nitroxide adducts). The nature of nitroxide does not play a fundamental role in this process. The reinitiation reaction also occurs successfully in the case of TEMPO, its derivatives, and imidazoline nitroxides. From this point of view, there are no obstacles to the implementation of the reversible inhibition mechanism. On the contrary, the reaction should be carried out at lower temperatures in order to reduce the rate of reinitiation

Table 8. The equilibrium concentration of growing radicals and nitroxides and the equilibrium constant; [A] = 10 mmol/L; $T = 80°C$

Alkoxyamine	Additive	Concentration, mmol/L	Time, min	[N], mmol/L	$[R] \times 10^8$, mol/L	$K \times 10^8$, L/mol
A-1	–	–	25	3.4	0.58	0.18
	TFA	10	"	0.64	10.8	0.69
	TFA	50	"	0.57	12.9	0.73
	AIBN	5	"	0.06	10.9	0.06
	–	–	30	3.6	0.33	0.12
	TFA	10	"	0.57	6.6	0.37
	TFA	50	"	0.57	7.8	0.44
	AIBN	5	"	0.06	9.38	0.06
	–	–	35	3.7	0.19	0.05
	TFA	10	"	0.51	3.9	0.20
	TFA	50	"	0.57	5.3	0.30
	AIBN	5	"	0.06	8.6	0.05
A-2	–	–	20	1.50	7.7	1.1
	TFA	10	"	1.57	7.2	1.1
	AIBN	10	"	0.56	11.8	0.51
	–	–	30	1.6	6.2	1.0
	TFA	10	"	1.6	5.9	0.93
	AIBN	10	"	0.35	8.5	0.30
	–	–	40	1.7	4.6	0.77
	TFA	10	"	1.6	4.6	0.72
	AIBN	10	"	0.25	8.2	0.21

so that the likelihood of the quadratic termination of the resulting macroradicals can be reduced.

The constant of equilibrium between growing and dormant chains is in the range of 10^{-8}–10^{-10} mol/L, which also satisfies requirements for the living mechanism of polymerization.

However, in the case of both TEMPO derivatives and imidazoline radicals, the polymerization proceeds in the decaying mode and the effective equilibrium constant decreases by several times. Moreover, in the first case, decay leads to the transformation of growing chains into a dead polymer almost immediately.

The main obstacle to the implementation of the reversible inhibition mechanism in MMA polymerization is the disproportionation of growing radicals and nitroxides, in each act of which a dead chain and hydroxylamine are formed. That is why there is a constant search for new alkoxyamine initiators that would not produce disproportionation products. Among them are, for example, imidazoline alkoxyamines. The data obtained show that these initiators are also characterized by the decay of MMA polymerization. Therefore, the lack of disproportionation of initiator radicals is a necessary but not sufficient condition. After primary radicals are converted to MMA growing radicals, they begin to go into the disproportionation reaction even with imidazoline nitroxides. But this side reaction is significantly less likely for them than for TEMPO derivatives. Therefore, imidazoline nitroxides can significantly increase the yield of PMMA and improve the control of its molecular weight characteristics.

The low probability of disproportionation of imidazoline radicals with MMA growing radicals is apparently explained by their general low activity as inhibitors of MMA polymerization when compared with TEMPO derivatives. The rate constant for the interaction of PMMA radicals with the former ones is an order of magnitude lower than with the latter ones and two orders of magnitude lower than the constant of their quadratic termination. This means that, during the polymerization of MMA mediated by imidazoline nitroxides, the probability of quadratic termination of growing chains is very high, at least at the beginning of polymerization, until a sufficient amount of free nitroxides is accumulated in the system.[1]

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[1] Note that the nitroxide SG-1, the termination constant of which is one order of magnitude lower and equal to 10^4 L/(mol s), does not suppress the quadratic termination of PMMA radicals.

Thus, the disproportionation reaction makes it possible to understand why it is impossible to implement the regime of reversible inhibition of MMA polymerization in the case of TEMPO derivatives. But it cannot explain the decay of MMA polymerization mediated by imidazoline nitroxides. According to our data, only 15% of growing chains become dead because of disproportionation. This would reduce the effective equilibrium constant during the process by only 15%; however, it drops by three to four times. Such a drop is not associated with any change in the rate of reinitiation with increasing the degree of polymerization of the PMMA–nitroxide adduct, as follows from Tables 1 and 2. It is also not associated with the accumulation of dead molecules in PMMA due to quadratic termination, since the fraction of such molecules does not exceed 10–15% (estimated as the ratio of the concentration of free nitroxide at the end of polymerization to the concentration of the initial alkoxyamine). The reason for this phenomenon is not yet clear and requires further research.

Our experiments show that, if the decay of nitroxide-mediated polymerization of MMA cannot be avoided, then it can be substantially limited. The introduction of TFA or AIBN additives shifts the balance between the growing and dormant chains toward the former. The final answer to the possibility of controlled nitroxide-mediated polymerization of MMA can be given by mathematical modeling of the kinetics of the process and the MWD of products using the values of the constants of elementary reactions, including those presented in this work.

ACKNOWLEDGMENTS

We are grateful to E.S. Garina for the GPC analysis of the polymers and D.A. Parkhomenko for his help in determining the initiation constant.

FUNDING

This study was supported by the Russian Foundation for Basic Research (project no. 18-03-00707).

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