ISSN 1811-2382, Polymer Science, Series C, 2021, Vol. 63, No. 1, pp. 11–28. © Pleiades Publishing, Ltd., 2021.
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Kinetic Features of the Radical Polymerization of Methyl Methacrylate under Conditions of Nitroxide-Mediated Reversible Inhibition

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Received September 5, 2020; revised December 6, 2020; accepted January 28, 2021

Abstract—This review summarizes our and published data on the kinetics and mechanism of controlled radical polymerization of methacrylates mediated by nitroxide radicals. The reasons influencing the possibility or impossibility of the realization of radical polymerization of methyl methacrylate in the mode of reversible inhibition are analyzed. The main factors determining the specificity of the nitroxide-mediated polymerization of methacrylates are the interaction of nitroxides with growing radicals by the disproportionation mechanism, the Fischer hypereffect, a high rate of reinitiation, and an abnormally low rate of reversible termination.

DOI: 10.1134/S1811238221010069

INTRODUCTION

It is known that not all vinyl monomers are capable of participating in radical polymerization under conditions of nitroxide-mediated reversible inhibition. These include MMA and its derivatives. Periodically, information appears on the "first" implementation of the controlled polymerization of MMA mediated by nitroxides; however, in practice, the control area is usually limited to 30–50% monomer conversion [1–7]. Researchers put forward various hypotheses to explain this phenomenon. This was initially attributed to the absence of spontaneous polymerization in MMA [8, 9]. Later, it was generally accepted that the reason is the reaction of disproportionation of the growing radicals of MMA and its analogs and nitroxides [3, 10, 11]. However, it was found that there are a number of nitroxides for which the termination reaction with MMA radicals does not occur via the disproportionation mechanism. Nevertheless, the problem of controlled polymerization of methacrylic monomers under conditions of nitroxide-mediated reversible inhibition has not yet been solved.

In this work, we tried to generalize our new and published data on the kinetics and mechanism of MMA polymerization mediated by nitroxides. This made it possible to formulate the distinctive features of the process and propose other possible reasons for the inability of MMA to undergo controlled polymerization mediated by nitroxides. Below we will consider the main features of the kinetics and mechanism of methacrylate polymerization involving nitroxides.

REACTION OF DISPROPORTIONATION OF GROWING RADICALS WITH NITROXIDES

The first results on the polymerization of MMA involving nitroxide radicals were obtained in the late 1980s in our country and then in the late 1990s in Australia [12, 13]. It was shown that the bulk polymerization of MMA at 90°C mediated by TEMPO and other nitroxides of various nature

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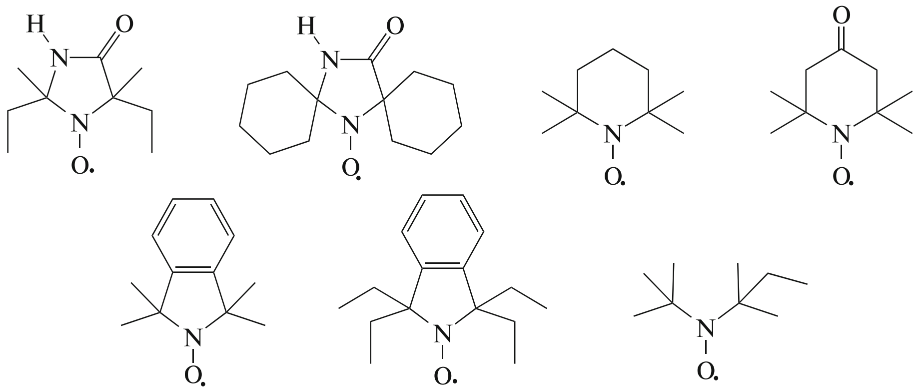
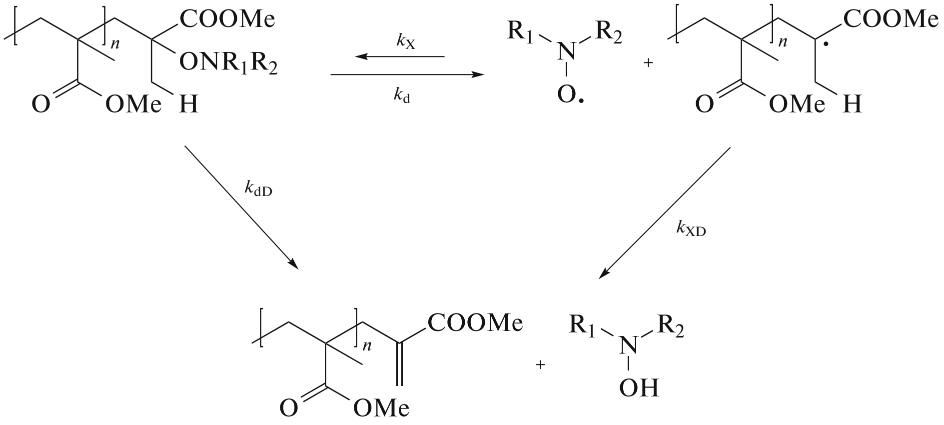


ends within 1 h and the monomer conversion does not exceed 10–40%. However, the number average molecular weight M_n of PMMA is close to the theoretical values typical of living processes. Thus, the controlled polymerization decayed over time. In this case, the purified polymers contained a double bond at the end of the chain. This was explained by the reaction of disproportionation of nitroxides with growing radicals which also leads to the formation of hydroxylamine.

The amount of terminal double bonds and hydroxylamine was determined using NMR spectroscopy and mass spectrometry. It was shown that, in poly(butyl methacrylate) obtained in the presence of TEMPO, the content of terminal double bonds is close to 100% [14]. This cannot be the result of the usual disproportionation reaction between two growing radicals (where this fraction cannot exceed 50% of the molecules) but only a consequence of the β hydrogen atom transfer from the growing radical to TEMPO.

It is believed that just this reaction is the main reason for the irreversible inhibition of MMA polymerization. Therefore, the main attempts to carry out the controlled synthesis of PMMA are aimed at searching new nitroxides that are not prone to disproportionation with methacrylate growing radicals.

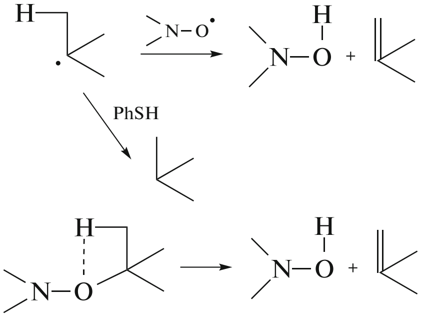
At the same time, two reactions can lead to the same products [11]:



In addition to disproportionation, intramolecular rearrangement is also possible at the stage of terminal group decomposition. The first one competes with the reaction of recombination of the growing radical and nitroxide and is characterized by a second-order rate constant k_{XD}, while the second one competes with the reinitiation reaction and is described by a first-order rate constant k_{dD}.

In practice, these two mechanisms are almost indistinguishable [15] and, in both cases, are described using the concept of a proportion of disproportionation $f_D = k_{XD}/(k_{XD} + k_X)$ or $f_D = k_{dD}/(k_d + k_{dD})$, respectively. It is believed that the intramolecular reaction of the H atom transfer in alkoxyamines is determined by the activation energy of homolytic dissociation but not by the nature of the nitroxide and not by the geometry of the transition state [16]. Such a reaction is very likely for alkoxyamines with a strong C–ON bond ($E_a > 125$ kJ/mol) and is unlikely for compounds with weak bonds ($E_a < 115$ kJ/mol).

To determine the disproportionation mechanism, an original approach was proposed at the Tomographic Center of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk). Alkoxyamine initiators, which are model compounds for the terminal group of PMMA-nitroxide, were decomposed thermally in the presence and absence of an active chain-transfer agent thiophenol [17]. If the reaction of disproportionation is an intramolecular process, then the presence of thiophenol will not affect its rate (Ib). But if this is the reaction between growing radicals and nitroxide (Ia), then the rate of formation of terminal double bonds in PMMA in the presence of thiophenol will sharply decrease, since the latter will become a competitor to nitroxide.



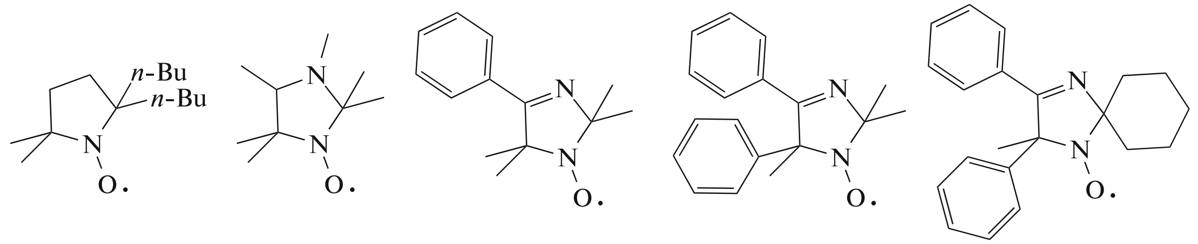
(Ia)

(Ib)

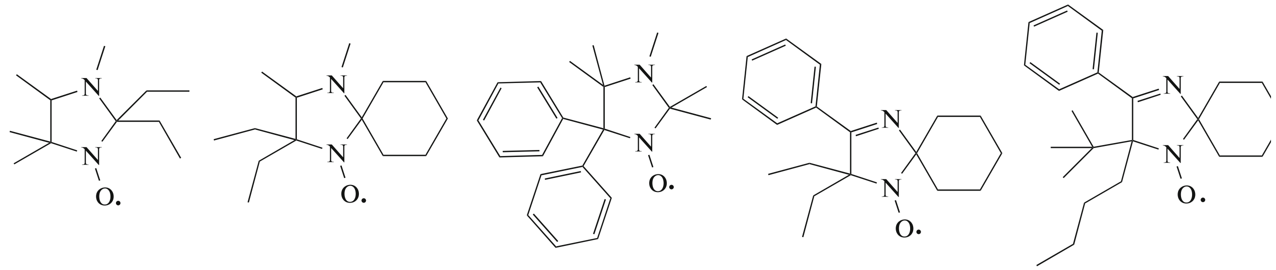
It was found that alkoxyamine 4-nitrophenyl-2-(2,2,6,6-tetramethylpiperidine-1-yloxy)-2-methylpropionate disproportionates exclusively according to the bimolecular mechanism with $f_D = 3.5\%$. The same reaction mechanism is assumed for the reaction of the

PMMA macroradical with TEMPO according to the data obtained for low molecular weight alkyl isobutyrate radicals [18].

For alkoxyamines based on five-membered cyclic nitroxides, the disproportionation mechanism depends on the nature of substituents in the 2 and 5 positions of the nitroxide [18]. Below are the structures of nitroxides based on imidazoline, imidazolidine, and pyrrolidine which are characterized by intermolecular and intramolecular disproportionation



and only intermolecular disproportionation



The intramolecular mechanism requires a cyclic transition state with a good overlap of the nitrogen orbital n_σ and the antibonding orbital σ* of the C–H bond. This is possible in the case of less sterically hindered compounds, for example, nitroxide with four methyl groups in positions 2 and 5. The temperature dependence of this reaction obeys the Arrhenius equation for k_{dD} with the pre-exponential factor $A = 5.2 \times 10^{15}$ s^{-1} and a high activation energy ($E_a \sim 140$ kJ/mol). On the contrary, for imidazoline nitroxides with bulky 2 and 5 substituents, the reaction of intermolecular disproportionation is typical.

Usually the proportion of disproportionation in vinyl polymerization mediated by nitroxides is small and this side process is neglected. For example, in the TEMPO-mediated polymerization of styrene, it is only 0.4–0.6% [19, 20] and, in the case of nitroxide SG1, it tends to zero in general. However, it rises sharply during the polymerization of methacrylates.

The theoretical calculation [15] predicts complete inhibition of polymerization even if the proportion of disproportionation is only a few percent. The maximum achievable conversion $q_{\max}$ is related to the probability of disproportionation by the equation

$$q_{\max} \approx 1 - \exp\left\{-\frac{3}{2}k_p\left(\frac{[\mathrm{RX}]_0}{3f_D^2 k_d(k_X + k_{XD})k_t}\right)^{1/3}\right\}, \qquad (1)$$

where $[\mathrm{RX}]_0$ is the initial concentration of the alkoxyamine initiator, and k_p, k_d, k_X, k_t, and k_{XD} are the rate constants of propagation, reinitiation, termination on nitroxides, square-law termination, and disproportionation of the growing radical and nitroxide, respectively.

Thus, under typical conditions of nitroxide-mediated polymerization with a set of elementary constants $k_d = 4.5 \times 10^{-3}$ s^{-1}, $k_t = 10^8$ (mol/L)$^{-1}$s^{-1}, $k_X = 2.2 \times 10^7$ (mol/L)$^{-1}$s^{-1}, and $k_p = 5 \times 10^3$ (mol/L)$^{-1}$ s^{-1} at $[\mathrm{RX}]_0 = 0.1$ mol/L, the maximum conversion of the monomer is 93, 81, and 59% at f_D = 1, 2, and 5%, respectively. This prohibition cannot be circumvented even if the propagation constant or the initiator concentration is increased. With an increase in the propagation constant by four times ($k_p = 2 \times 10^4$ (mol/L)$^{-1}$ s^{-1}), polymerization to deep conversions becomes possible only if the probability of disproportionation is less than 7%. If, in this case, the concentration of the initiator is simultaneously increased by an order of magnitude, then the probability of disproportionation should also be less than 22%.

Hence, for the realization of the living growth of PMMA chains in the entire range of monomer conversions, such nitroxides and/or such reaction conditions are required that would provide a disproportionation probability of less than 1%.

From Eq. (1), it is not difficult to obtain [15] a simplified formula for solving the inverse problem of estimating the proportion of disproportionation over the time of cessation of polymerization $t_p \approx 2/f_D k_d$. This is how f_D = 20% was estimated for the TEMPO-mediated polymerization of MMA at 120°C [15]. According to other indirect data, it is equal to 10% [21]. Using

Table 1. Molecular weight characteristics of PMMA obtained by the AIBN-initiated polymerization of MMA mediated by 4-hydroxy-TEMPO and di-*tert*-butyl nitroxide (DTBN) in bulk ([4-hydroxy-TEMPO] = [DTBN] = [AIBN] = 0.01 mol/L)

Nitroxide	T, °C	Time, min	Conversion,%	$M_n \times 10^{-3}$	$Đ$
4-Hydroxy-TEMPO	120	3	8	10.1	1.6
		10	12	12.5	2.7
		160	17	11.8	2.7
4-Hydroxy-TEMPO	90	35	5	8.3	2.1
		55	19	16.1	2.4
		120	49	20.7	3.7
DTBN	90	40	2	1.0	2.3
		60	31	7.8	2.3
		80	60	21.3	2.4

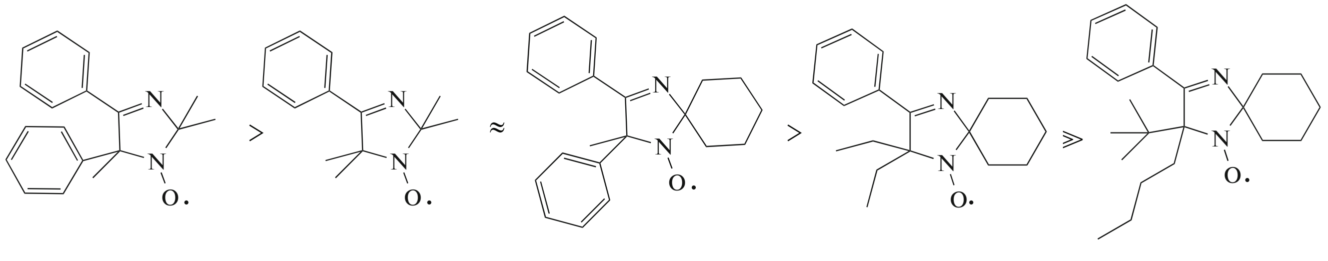
The conversion indicated in the tables was determined by the gravimetric method. As a rule, it is slightly higher than the conversion determined by the calorimetric method, which is associated with instrumental losses during heating of the sample.

this approach we estimated the value of f_D as 11 and 9% at 90 and 80°C, respectively. The direct measurement of the disproportionation probability according to NMR data gives $f_D < 2\%$ at 60°C [13]. It follows that the probability of disproportionation decreases significantly with decreasing temperature.

This circumstance allowed us to increase the PMMA yield up to 60% at 80°C. Moreover, under such conditions, the molecular weight of the polymer can be increased with an increase in the monomer conversion (Table 1). The same features are characteristic of the polymerization of MMA involving di-*tert*-butyl nitroxide. However, even under these conditions, polymerization decays and does not reach the complete conversion of the monomer into polymer (Fig. 1).

Obviously, the nature of substituents in the 2 and 6 positions of the piperidine nitroxide should affect the probability of disproportionation. However, there are very few corresponding experimental data. According to our data, the TEMPO analog with 2,6-cyclohexyl substituents disproportionates even faster than TEMPO: the complete conversion of nitroxide to hydroxylamine (and, accordingly, the termination of polymerization) occurs at 80°C in just 15 min. The MMA conversion does not exceed 4%.

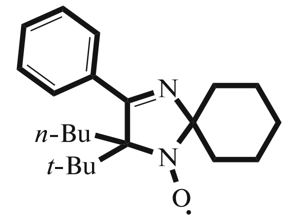
The effect of the nature of substituents in imidazoline nitroxides on disproportionation with low molecular weight radicals, model for the MMA growing radical, *tert*-butyl isobutyrate and nitrophenyl isobutyrate, was described [2, 3, 17, 18, 22–24]. The disproportionate probability decreased from 23 to 0.3% in the following sequence:

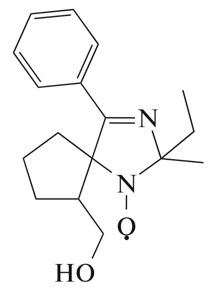


As can be seen, the rule that the probability of disproportination decreases with an increase in the size of substituents at positions 2 and 5 is fulfilled.

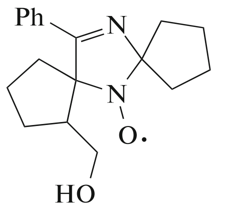
The nature of the alkyl substituent in alkyl methacrylate, according to the authors of [18], does not significantly affect the disproportionation rate. Nevertheless, as the authors themselves showed, when passing from *tert*-butyl isobutyrate radical to *p*-nitrophenyl isobutyrate, the probability of disproportionation with TEMPO increases by 1.5 times (from 2.2 to 3.5%).

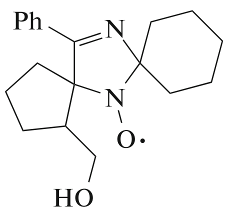
In recent years, new nitroxides have been synthesized which hardly disproportionate with low molecular weight radicals ($f_D \le 1\%$) imitating MMA growing radicals. These are the following [3, 23]:

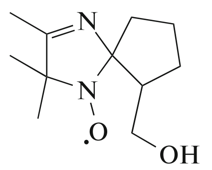




N2







Just they are considered now as potential agents for the controlled synthesis of PMMA [24].

However, it should be borne in mind that, even in the case when the decomposition products of the alkoxyamine initiator themselves cannot disproportionate in an inert medium, such a possibility appears as soon as MMA growing radicals are formed in the system. For example, nitroxide N2 does not really disproportionate with the ethyl isobutyrate radical in benzene and chlorobenzene. However, when the inert reaction medium is replaced with the MMA monomer, already 5 min after the start of polymerization, the system contains 3% hydroxylamine, and after 20 min, its concentration increases to ~15% and does not change further [25].

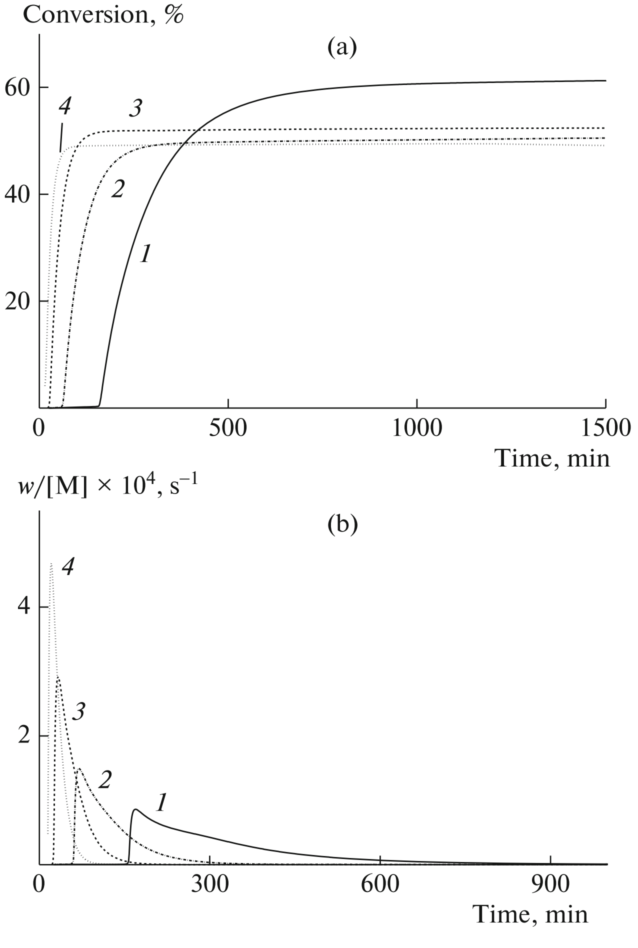
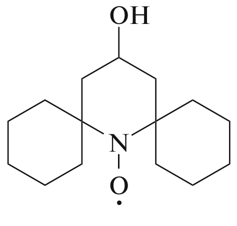


Fig. 1. (a) Integral and (b) differential kinetic curves of MMA polymerization. [MMA] = 9.4, [4-hydroxy-TEMPO] = 0.01, and [AIBN] = 0.01 mol/L. T = (*1*) 80, (*2*) 84, (*3*) 90, and (*4*) 96°C. Color drawings can be viewed in the electronic version.

A similar result was observed when studying the behavior of nitroxide



N1

In an inert medium, the probability of disproportionation was low. However, in the monomer medium, already in 15 min, all the nitroxide was converted to hydroxylamine [25].

This means that high molecular weight radicals disproportionate much better than their low molecular weight counterparts.

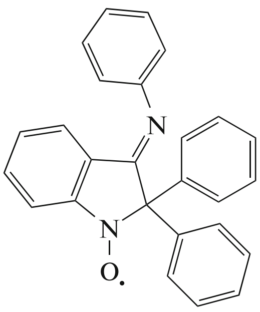
The same pattern is typical of unsubstituted TEMPO. It was mentioned above that its proportion of disproportionation during the polymerization of MMA is 20%. However, if PMMA radicals are replaced with their low molecular weight analogs it decreases to 3–4% [17, 26].

The data on the disproportionation of PMMA radicals with nitroxide SG1 are very contradictory. Previously, it was believed that such a reaction does not occur at all since PMMA does not contain terminal double bonds [1, 27]. The kinetic modeling of this process under the assumption of bimolecular disproportionation gives $k_{XD} = 1.7 \times 10^3$ (mol/L)$^{-1}$ s^{-1} which corresponds to $f_D = 8.5\%$. [28]. A direct experiment on the model reaction between the methyl isobutyrate radical and SG1 gave the same value [16]. However, in [29], the proportion of disproportionation products in PMMA obtained with SG1 ranged from 64 to 100%. Finally, the authors of [30] assume a different intramolecular disproportionation mechanism, the products of which are PMMA with the terminal double bond and SG1 N-oxide. It was suggested that these disagreements are caused by the presence of residual oxygen in the polymer [2]. Indeed, in less degassed solutions, that is, under conditions of conventional degassing by evacuation with an oil pump or bubbling with an inert gas, the alkene content in the reaction products is 25% versus 90% for products degassed in a high vacuum.

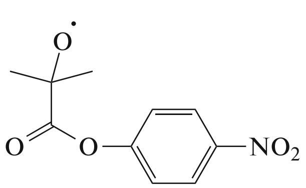
Note that a sharp increase in the proportion of disproportionation is observed for nitroxide SG1 as well when passing from the reaction with the low molecular weight radical to the reaction with a poly(methyl methacrylate) radical [2].

Thus, in all the systems described, the disproportionation reaction in the monomer proceeds much faster than that in an inert solvent. In other words, the probability of disproportionation for a high molecular weight growing radical is significantly higher than that for a low molecular weight one.

In recent years, there have been high expectations of DPAIO nitroxide in the nitroxide-mediated polymerization of MMA.

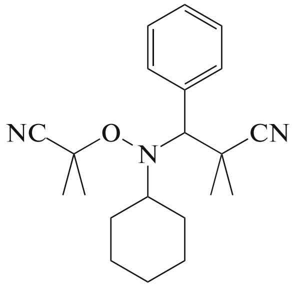


In its presence, the controlled polymerization of MMA can be carried out up to a conversion of 60% [4]. This is due to the fact that the disproportionation reaction with MMA radicals is not typical of this nitroxide. Indeed, it was shown experimentally that such a reaction between DPAIO and the radical



is absent [17]. For the PMMA radical, as far as we know, there is no such information yet. Note that the radical polymerization of MMA also decays in the presence of this nitroxide [4].

Interesting data were obtained quite recently for the polymerization of MMA with an alkoxyamine initiator, which the authors called Dispolreg 007 [31, 32]



Unlike SG1 and DPAIO, the nitroxide of this compound contains two H atoms in α positions with respect to the N–O group, which, according to the authors, prevents disproportionation. Indeed, the value of f_D during MMA polymerization initiated by Dispolreg 007 at 90°C is only 0.2% and the proportion of disproportionation products in the final polymer does not exceed 1%. The polymer yield reaches 90%. Note that M_n hardly increases during polymerization but is close to theoretical at a conversion of 100%.

Thus, disproportionation is an important but not the only reason that prevents the implementation of the reversible inhibition mechanism in MMA polymerization.

INGOLD–FISCHER PERSISTENT RADICAL HYPEREFFECT

It is well known that the polymerization of vinyl monomers occurs against the background of a high concentration of free nitroxide (several orders of magnitude higher than the concentration of growing radicals). This is a consequence of the realization of the persistent radical effect, the Ingold–Fischer effect [33–35].

The nature of this effect can be easily understood from the simplest scheme of polymerization initiated by the alkoxyamine initiator RX. The decay of RX yields nitroxide X• and an alkyl radical R· starting chain growth

$$RX^{\bullet} \to R^{\bullet} + X^{\bullet},$$

$$R^{\bullet} + nM \to P_n^{\bullet}.$$

For primary growing radical $P_n^{\bullet}$, the recombination reaction with both nitroxide and another growing radical is equally probable

$$P_n^{\bullet} + X^{\bullet} \to P_nX \quad \text{and} \quad P_n^{\bullet} + P_m^{\bullet} \to \text{loss}.$$

In the latter case, each event of square-law termination of macroradicals leads to the formation of a dead chain and two free nitroxide radicals X·. That is why, at the beginning of polymerization, there is an intense accumulation of nitroxide radicals in the system.

This usually occurs at the initial short period (from 10 min to 2–3 h), and then the concentration of nitroxides hardly changes. In terms of relative value,

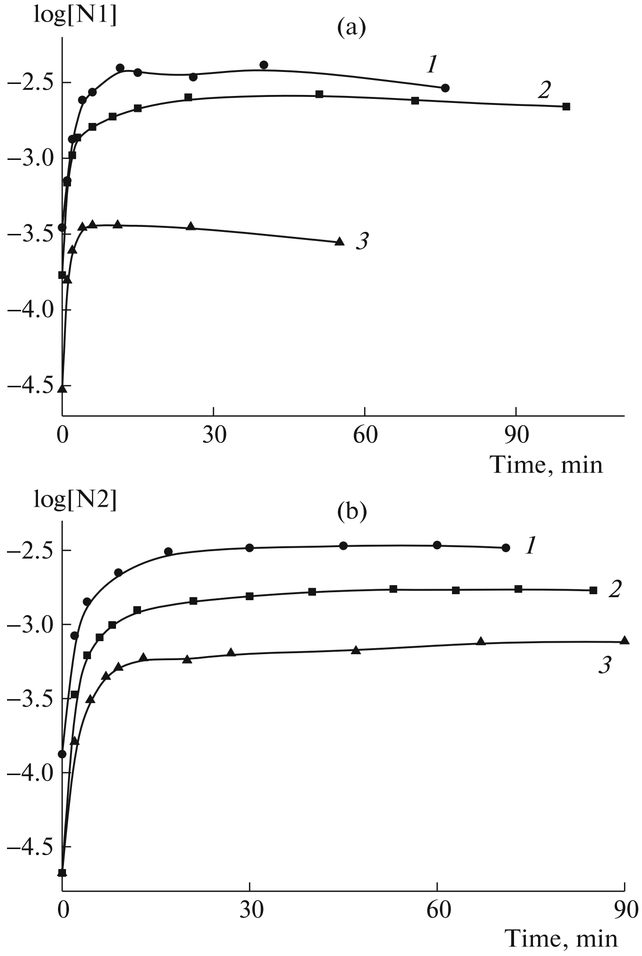
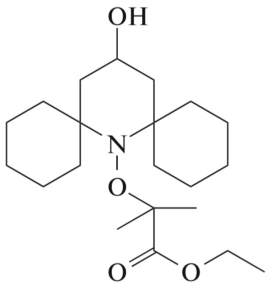


Fig. 2. Time dependences of the concentration of (a) N1 and (b) N2 for MMA polymerization. [A1] = [A2] = (*1*) 0.03, (*2*) 0.01, and (*3*) 0.003 mol/L; $T = 80$°C. Here and below, the data obtained for bulk polymerization in vacuum are presented.

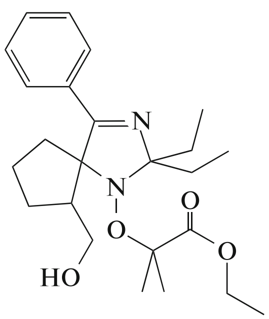
the fraction of released nitroxide is from 0.1 to 1% of the initial initiator. On the hand, this concentration is not enough to stop the process; on the other hand, it is quite sufficient for an almost complete suppression of further irreversible loss of macroradicals. In this case, the mode of reversible inhibition is realized which is characterized by the establishment of an equilibrium between the reaction of reinitiation and the reversible termination of growing chains on nitroxides. Although it is not possible to completely suppress the square-law termination and other side reactions, the fraction of living macromolecules remains predominant up to limiting conversions. Such a picture is observed for the polymerization of styrene mediated by TEMPO, SG1, imidazoline, indoline, and other nitroxides. In the polymerization of alkyl acrylates and other acrylic derivatives, the concentration of free nitroxide accumulated according to the Fischer effect is lower and insufficient to suppress the square-law termination of macroradicals. Therefore, an additional amount of free nitroxides is initially added to these systems.

A distinctive feature of MMA polymerization is the Fischer hypereffect. According to our studies, in a short initial period, the concentration of free nitroxide reaches 5–20% of the concentration of the initial initiator.

Let us consider this feature for the polymerization of MMA initiated by alkoxyamines using the example of initiators A1 and A2 based on nitroxides N1 and N2:



A1



A2

On the kinetic curves of change in the concentration of nitroxide, as in the polymerization of styrene [33], two regions can be distinguished (Fig. 2). In the first region, an increase in nitroxide concentration is observed, which is associated with the square-law termination of primary radicals. In the second region, the TEMPO concentration reaches a constant value. The higher the initial concentration of the initiator, the more free nitroxide is released.

For the piperidine initiator A1, the fraction of nitroxide in the second region is 10–20% of the initial concentration of A1 (Fig. 2a). In this case, accumulation occurs in a short initial period of 10–15 min. Almost the same regularity is characteristic of the imidazoline initiator A2 (Fig. 2b).

For the polymerization of MMA proceeding in the presence of binary systems radical initiator–nitroxide, the effect of accumulation of stable radicals is somewhat different from that considered above.

On the kinetic curves of change in nitroxide concentration of (Fig. 3), an additional short initial region of a sharp drop appears, which is due to the rapid decomposition of the initiator and the capture of primary radicals by nitroxides. Then, the same regions of growth and reaching the limiting inhibitor concentration are observed as in the polymerization of MMA initiated by alkoxyamines. The role of the latter is played by adducts of primary growing radicals with nitroxides formed in situ.

In these systems, the concentration of free nitroxide is also fairly high. For example, in the polymerization of MMA carried out in the presence of the AIBN–TEMPO system at 120°C, it is 1.5 orders of magnitude higher than that for styrene under the same conditions (Fig. 3a).

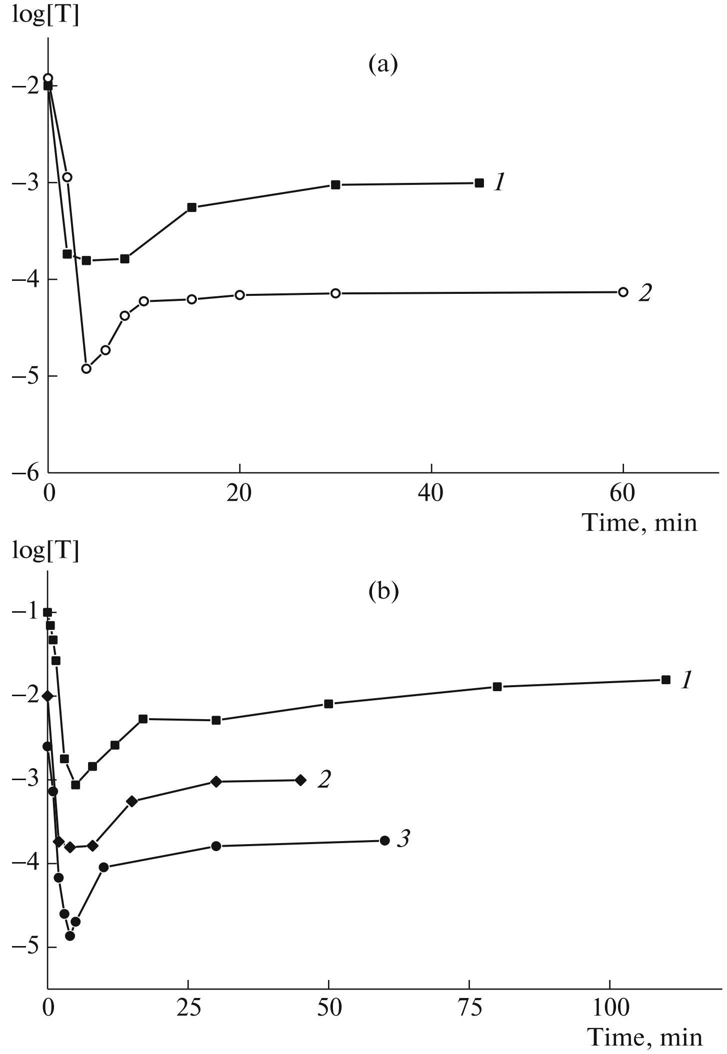


Fig. 3. Time dependences of TEMPO concentration for the polymerization of (a, b) MMA and (a) styrene at 120°C. a: (*1*) MMA and (*2*) styrene; [AIBN] = 0.01 mol/L and $[\mathrm{TEMPO}]_0$ = (*1*) 0.01 and (*2*) 0.012 mol/L; b: [AIBN] = $[\mathrm{TEMPO}]_0$ = (*1*) 0.1, (*2*) 0.01, and (*3*) 0.0025 mol/L.

A decrease in the initial concentration of TEMPO while maintaining the molar ratio of AIBN–TEMPO leads to a decrease in its fraction in the stationary region. As in the case of styrene polymerization [37], dilution of the monomer with a solvent causes a sharp increase in the steady-state concentration of TEMPO (Table 2).

From a comparison of the curves of the change in the concentration of nitroxide (Figs. 2, 3b) with the kinetic data [25, 36], it follows that the polymerization of MMA both initiated by alkoxyamines and with binary systems radical initiator–nitroxide is possible only in the initial period when the concentration of free nitroxide is small. This corresponds to the first region on the curves in Fig. 2 and the "pit" on the curves in Fig. 3b. On the stationary region, polymerization is almost completely stopped. This is the fundamental difference between the polymerization of styrene and MMA mediated by nitroxides. If for styrene stationary conditions are the main stage of polymerization, in which living chains grow in the reversible inhibition mode, then for MMA this is a dead region, in which owing to the high concentration of free nitroxide the equilibrium between the growing and dormant chains shifts to the side of the latter and polymerization decays until it stops completely. Note that, at an initial concentration of AIBN and TEMPO of 0.1 mol/L, when the concentration of free TEMPO does not fall below 10^{-3} mol/L, the polymerization is inhibited completely.

Thus, in all the studied systems (with piperidine and imidazoline nitroxides, in bulk and solution polymerization, in initiation with alkoxyamines, and in the presence of AIBN–nitroxide binary systems),

Table 2. The fraction of TEMPO released during MMA polymerization ($T = 120°C$)

[AIBN], mol/L	$[X^\bullet]_0$, mol/L	Fraction of released TEMPO, %
0.10	0.10	15
0.010	0.010	12
0.012	0.010	10
0.0025	0.0025	8
2×10^{-4}	2.4×10^{-4}	4 [36]
7×10^{-5}	8×10^{-5}	4 [36]
0.036*	0.030*	33*

* Polymerization in 50% benzene solution.

the MMA polymerization is characterized by the hypereffect of accumulation of stable radicals. The reason for this phenomenon will be discussed below.

The degree of its manifestation in the polymerization of MMA can be reduced by lowering the reaction temperature. As seen in Fig. 4, with a decrease in temperature to 80–90°C, the concentration of free TEMPO decreases to 10^{-4}–10^{-5} mol/L. Under such conditions, as noted above, the polymerization of MMA proceeds up to a conversion of 50–60%. In this case, not only the probability of disproportionation decreases, but also the effect of accumulation of stable radicals degenerates. However, even in this case, the polymerization of MMA mediated by TEMPO decays over time.

The experiments show that there is one more reason, along with disproportionation, due to which MMA cannot polymerize by the mechanism of reversible inhibition: the equilibrium between the dormant and growing chains is shifted toward the former under the action of a high concentration of free nitroxide accumulating in the system. For nitroxides that are not prone to disproportionation, such as N2, just this factor is the main reason for the decay of polymerization.

It should be noted that for the first time the assumption about the decay of MMA polymerization due to the accumulation of nitroxides during polymerization was made in 1998 on the basis of kinetic modeling [13]. However, the calculations were performed using constants of elementary events far from reality, unknown at that time.

HIGH INITIATION RATE AND ABNORMALLY LOW TERMINATION RATE

Naturally, the question arises: What is the reason for such a pronounced effect of accumulation of stable radicals? In our opinion, this is the result of a large difference between the rate constants of reversible and irreversible termination and a high value of the reinitiation rate. The rate of accumulation of nitroxides will depend on the ratio of the rates of these reactions.

It is obvious that the degree of manifestation of the Fischer effect will increase with the increase in the difference in the rates of irreversible and reversible termination. What is less obvious is that it will increase with an increase in the rate of reinitiation. The physical meaning of this phenomenon is an increase in the probability of square-law termination of a large number of primary radicals at the beginning of polymerization. This reason, as the main one hindering the implementation of the living mechanism of nitroxide-mediated polymerization of MMA, was mentioned in [33].

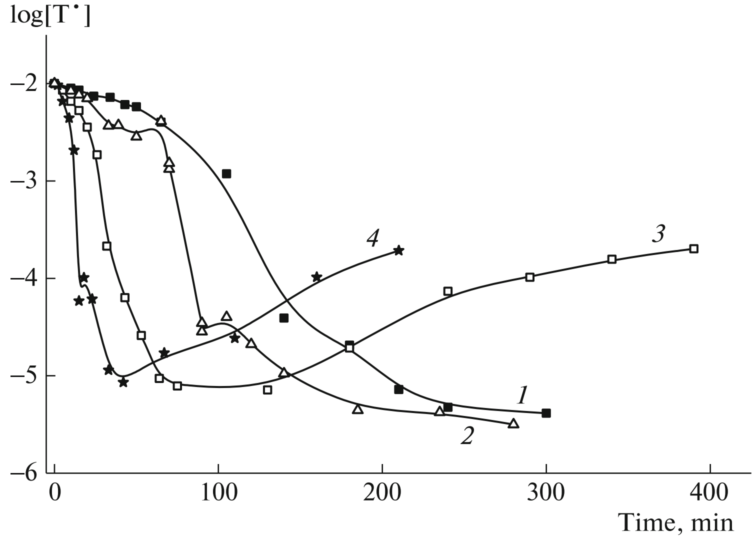


Fig. 4. Time dependence of the concentration of 4-hydroxy-TEMPO for the polymerization of MMA in bulk at (*1*) 80, (*2*) 84, (*3*) 90, and (*4*) 96°C in the presence of 0.01 mol/L of AIBN and 0.01 mol/L of 4-hydroxy-TEMPO.

Table 3. Comparison of the constants of elementary events for the reactions of nitroxides with the growing radicals of styrene and MMA

Nitroxide	Growing radical	$k_d \times 10^3$ s^{-1}/T, °C	$k_X \times 10^{-6}$ M^{-1} s^{-1}	$k_t^* \times 10^{-6}$ M^{-1} s^{-1}
TEMPO	MMA	3/93 [36]	1.6 [36]	60
	Styrene	0.2/100 [37, 38]	15 [33]	30
SG1	MMA	2400/120 [39]	0.014 [1]	–
	Styrene	3.4/120 [40]	0.26 [27]	–
	Styrene	11/120 [41]	0.5 [42]	–
	Styrene		0.6 [40]	–

* Average data [43].

According to the simplest Fischer model, the concentration of nitroxide X is proportional to the ratio [34, 35]

$$[X] \sim (k_t k_d^2 / k_X^2)^{1/3}. \quad (2)$$

While for the polymerization of styrene and alkyl acrylates mediated by nitroxides the values of both termination constants are approximately equal [33], for MMA, the value of k_X is one or two orders of magnitude lower than k_t [25]. Moreover, the value of k_d for nitroxide adducts of PMMA is one to two orders of magnitude higher than that for the adducts of PS [25]. This feature was considered in detail in our work using the example of imidazoline nitroxides [25]; therefore, here we will restrict ourselves to only comparing these constants for other known systems (Table 3).

Using the table values, we find that the parameter $(k_t k_d^2 / k_X^2)^{1/3}$ increases on going from a polystyrene radical to a poly(methyl methacrylate) radical by a factor of 30 and 500 for nitroxides TEMPO and SG1, respectively. All the factors should lead to an increase in the concentration of free nitroxide by tens to hundreds of times, which is observed in the experiment.

DEPENDENCE OF POLYMERIZATION RATE ON INITIATOR CONCENTRATION

According to the Fischer model [34, 35], the polymerization of vinyl monomers at the stage of accumulation of nitroxides is characterized by the order of the reaction rate n with respect to the concentration of alkoxyamine initiator equal to 1/3. Our data give the values of $n = 0.37$ and 0.53 for the initial rate of MMA polymerization initiated by A2 and A1, respectively (Fig. 5). In the first case, the kinetics of polymerization obeys the indicated law. In the second case, the order with respect to the initiator is indicative of the predominant square-law termination of growing radicals in comparison with the reversible one. Unfortunately, we failed to find information on the order

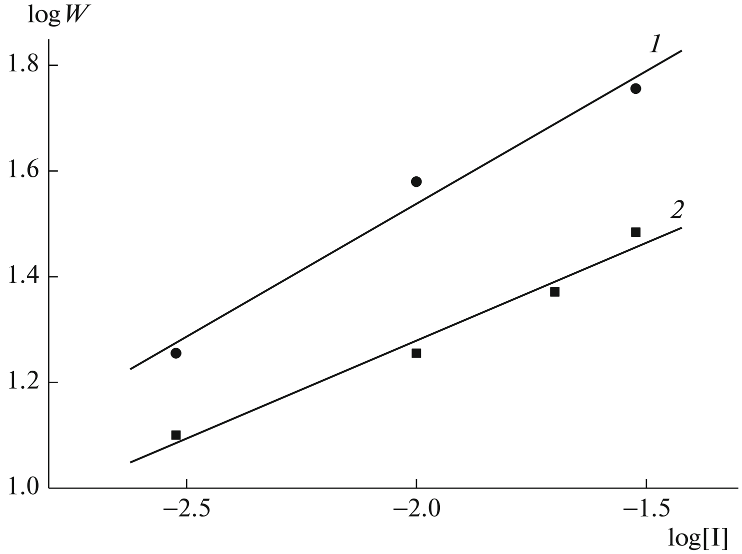


Fig. 5. Dependence of the initial rate of polymerization of MMA with participation of (*1*) A1 and (*2*) A2 on initiator concentration in logarithmic coordinates. T = (*1*) 100 and (*2*) 80°C.

with respect to initiator for other cases of MMA polymerization mediated by nitroxides.

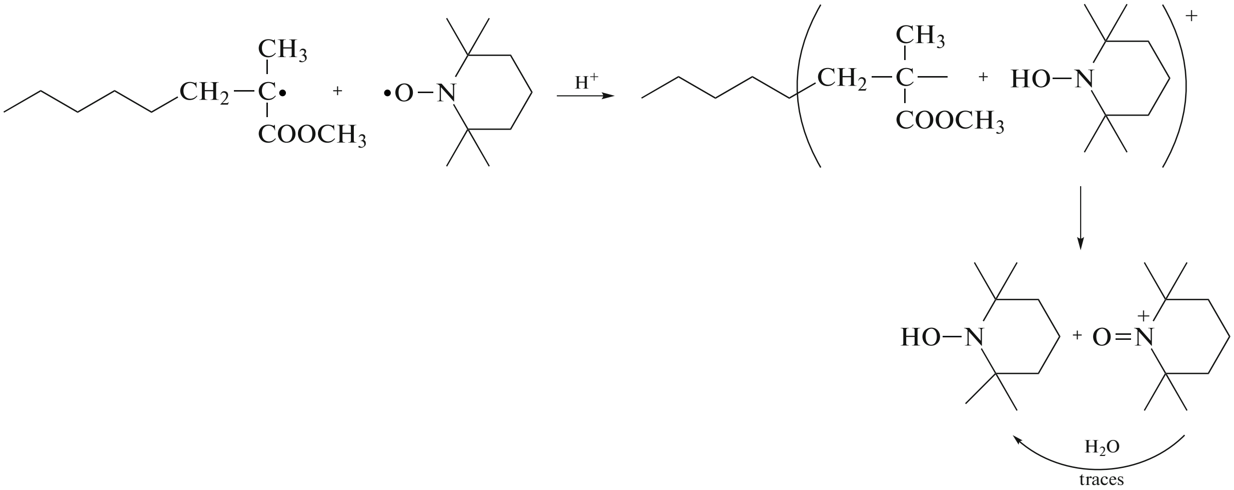
INFLUENCE OF VARIOUS FACTORS ON THE KINETICS OF MMA POLYMERIZATION MEDIATED BY NITROXIDES

It follows from the above that the absence of the disproportionation reaction between MMA growing radicals and nitroxides is a necessary but not sufficient condition for the process to proceed in the reversible inhibition mode. In addition, free nitroxide should not accumulate in such amounts that completely suppress polymerization owing to the shift of equilibrium toward dormant chains. Currently, there are two approaches to shift the equilibrium toward dissociation, copolymerization with a more active monomer and lowering the background concentration of nitroxide.

The first approach is based on the fact that even a small addition (sometimes only a few percent) of an active monomer (e.g., styrene) can direct the process by the mechanism of reversible inhibition because living nitroxide adducts with the terminal radical of the active monomer will be predominantly formed. This method was first described in [44], substantiated in [45], and discussed in detail in the review [11]. Here we will focus on the second approach, which involves reducing the background concentration of nitroxide. It was mentioned above that this can be reached by lowering the polymerization temperature. The same result can be achieved using special additives. These include strong acids, polar compounds, and radical initiators.

Weak acids have no noticeable effect on nitroxide-mediated polymerization. This is convincingly evidenced by the fact that the mechanism of polymerization of acrylic acid does not differ from the mechanism of polymerization of alkyl acrylates [46, 47]. On the contrary, strong organic and mineral acids significantly increase the rate of such polymerization. This approach was first applied in 1996 by the example of using camphor sulfonic acid in the polymerization of MMA mediated by TEMPO [48]. Upon addition of an acid equivalent relative to nitroxide, the PMMA yield increased from 16 to 40%, the value of M_n grew from 2×10^4 to 4×10^4, but at the same time the MWD broadened (the value of $Đ$ changed from 1.5 to 2.5). The "accelerating" effect was explained by the protonation of the nitroxide group in the polymer adduct, which, according to the authors, facilitated dissociation of the C—ON bond.

Unusual results were reported [49, 50] for the TEMPO-mediated polymerization of MMA carried out in the presence of sulfuric acid. With the addition of a sevenfold excess of acid with respect to the alkoxyamine initiator based on TEMPO and 4-oxo-TEMPO, the polymerization of MMA proceeded according to the mechanism of reversible inhibition at both 70 and 130°C. The MMA conversion in both cases reached 90%, and the dispersion of PMMA at limiting conversions was 1.04–1.15. Finally, not only the kinetic dependence $\ln([M]_0/[M]) = f(t)$ but also the dependence of conversion on the polymerization time was linear up to the limiting conversions. According to the authors, the role of sulfuric acid is that it "removes" free TEMPO from the polymer, converting it into hydroxylamine, thereby avoiding disproportionation between the growing radical and nitroxide:



This mechanism of TEMPO hydrolysis was ascertained experimentally by boiling TEMPO in sulfuric acid [51].

According to our data, sulfuric acid performs a double function: firstly, it instantly "binds" a part of the nitroxide close to equivalent, and, secondly, it

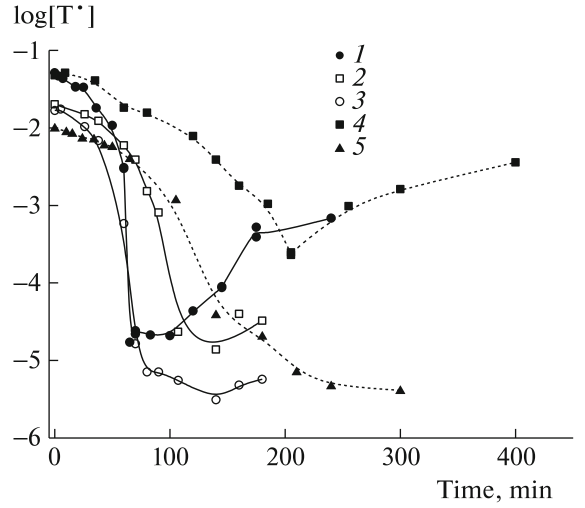


Fig. 6. Dependence of TEMPO concentration for the AIBN-initiated polymerization of MMA in the presence of H_2SO_4 at 80°C. (*1*) $[T^{\bullet}]$ = [AIBN] = 0.1 and $[H_2SO_4]$ = 0.7 mol/L, (*2*) $[T^{\bullet}]$ = [AIBN] = 0.05 and $[H_2SO_4]$ = 0.035 mol/L, (*3*) $[T^{\bullet}]$ = [AIBN] = 0.05 and $[H_2SO_4]$ = 0.05 mol/L, (*4*) $[T^{\bullet}]$ = [AIBN] = 0.05 mol/L (without acid), and (*5*) $[T^{\bullet}]$ = [AIBN] = 0.01 mol/L (without acid).

continues to react with free TEMPO during polymerization, which contributes to a significant decrease in its concentration. The addition of sulfuric acid in an amount of 70 and 100% of the initial concentration of TEMPO leads to a decrease in its background concentration during MMA polymerization by 2 and 2.5 orders of magnitude, respectively (Fig. 6). Naturally, this causes a sharp increase in the polymerization rate (Fig. 7). However, in these cases, the polymerization also proceeds in the decaying mode and the limiting conversion does not exceed 60%.

With a multiple (sevenfold or higher) excess of sulfuric acid, the protonated form of TEMPO arises as a red oil that is incompatible with MMA and does not take part in polymerization. In this case, the monomer is polymerized according to the usual mechanism with a typical pronounced gel effect (Fig. 7, curve *1*).

It should be noted that the approach involving the introduction of small additions of sulfuric acid allowed us to carry out the controlled copolymerization of MMA with poly(ethylene glycol) methacrylate. As seen in Fig. 8a, the copolymerization rate and copolymer yield increase with increasing acid content. The reason for this effect, as in the homopolymerization of MMA, is a decrease in the concentration of the free inhibitor against the background of which polymerization proceeds (Fig. 8b). Despite the fact that copolymerization proceeds in the decaying mode, the molecular weight of the copolymers increases linearly with conversion at a low value of the polydispersity coefficient (Table 4).

Note that this additive has an adverse effect on the polymerization of MMA mediated by N2. Polymerization proceeds during the first few minutes, reaches a conversion of 8–10%, and then is inhibited.

Among the highly polar compounds, malononitrile [52] and trifluoroacetic anhydride (**TFA**) are used most effectively in the nitroxide-mediated polymerization of MMA [53]. The nature of their effect is not completely clear. Interestingly, acetic anhydride, which is widely used to increase the rate of styrene polymerization mediated by TEMPO [54–56], was inefficient in the polymerization of MMA. It has almost no effect on the concentration of nitroxide in the polymerization of MMA initiated by A1 (Table 5). On the contrary, TFA makes it possible to obtain narrowly dispersed and high molecular weight PMMA in the presence of TEMPO [53]. With an equivalent addition of TFA, the PMMA yield increases to 50%, and the dispersion decreases to 1.17; with a 2.5-fold excess of TFA, these values are 96% and 1.14, respec-

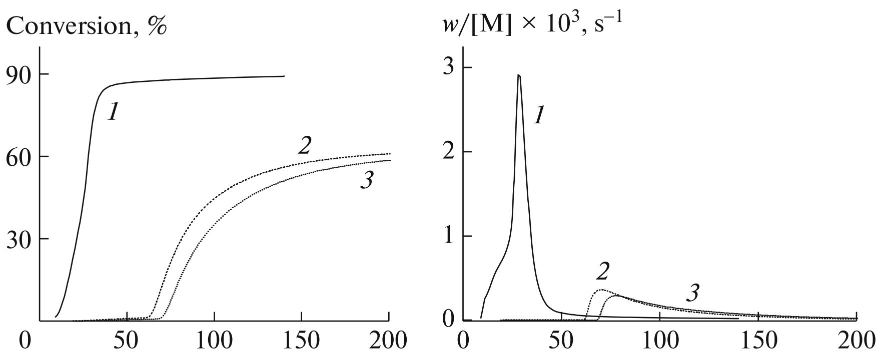


Fig. 7. (a) Integral and (b) differential kinetic curves of MMA polymerization in the presence of the system TEMPO–AIBN–H_2SO_4 at 80°C. [TEMPO] = [AIBN] = (*1*, *2*) 0.1 and (*3*) 0.05 mol/L and $[H_2SO_4]$ = (*1*) 0.7, (*2*) 0.07, and (*3*) 0.035 mol/L.

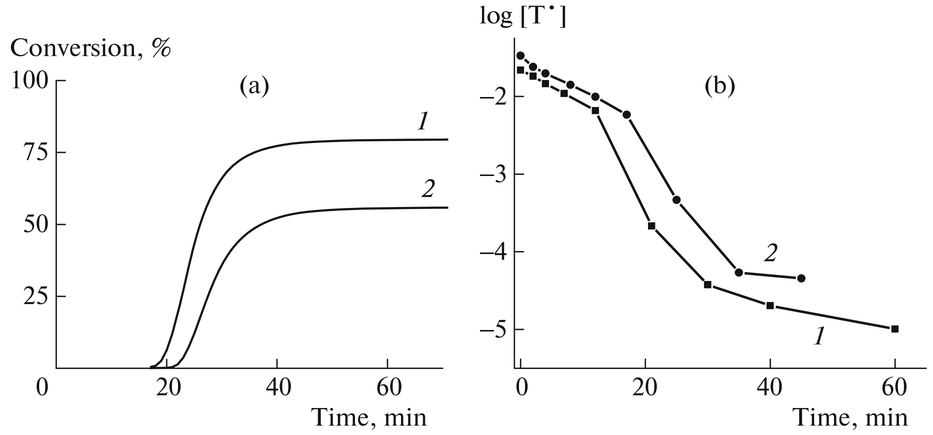


Fig. 8. (a) Kinetic curves and (b) changes in TEMPO concentration for the copolymerization of MMA–PEGMA (10 wt %) in presence of the system AIBN–TEMPO–H_2SO_4 at 90°C. [TEMPO] = [AIBN] = 0.1 mol/L and [H_2SO_4] = (*1*) 0.07 and (*2*) 0.035 mol/L.

tively. However, the process cannot be called controllable, since M_n increases linearly only up to a conversion of 60% and the MW values are an order of magnitude higher than theoretical ones.

According to our data, the effect of TFA on the polymerization of MMA involving A1 is less pronounced. When an equivalent to a fivefold excess of TFA is added, the nitroxide concentration decreases by an order of magnitude (Fig. 9). As a result, the polymer yield increases to 20% (Fig. 10). The molecular weight of the polymer does not increase so noticeably (Table 5). TFA in essence "does not work" in the case of imidazoline nitroxides: the degree of conversion hardly changes (Fig. 11a), and the nitroxide concentration remains at the same level (Fig. 11b). The MW values are comparable with the results obtained during polymerization without the addition of TFA (Table 6). The reason for this phenomenon has not yet been explained.

Table 4. Yield and molecular weight characteristics of the PMMA–PEGMA copolymers ([AIBN] = [TEMPO] = 0.05 mol/L and [H_2SO_4] = 0.035 mol/L; $T = 80$°C)

Fraction of PEGMA, wt %	Time, min	Conversion, %	$M_n \times 10^{-3}$	*Đ*
10	105	22	33.7	1.2
	125	40	44.6	1.3
	150	59	52.4	1.4
	250	88	67.7	1.4
30	115	11	28.5	1.2
	122	22	41.7	1.4
	250	53	71.4	2.5

The effect of polar additives on the polymerization of MMA mediated by aromatic *p*-dimethoxydiphenyl nitroxide was studied in detail [57]. In the sequence diethyl malonate < acetylacetone < malononitrile, the polymerization rate increases by an order of magnitude. It increases in proportion to the amount of additive in the range from an equivalent to a threefold (with respect to the initiator) excess, and then it stops changing. In all systems, there is the linear growth of M_n of the polymer to a conversion of 70% and the dispersion is 1.3–1.5. Interestingly, the effect of malononitrile is based not on a decrease in the background concentration of free nitroxide during polymerization, but on a twofold increase in the rate constant of reinitiation. Note that camphor sulfonic acid has no significant effect on the polymerization of MMA mediated by this nitroxide.

To accelerate the polymerization of MMA mediated by nitroxides, we tried to use metal salts, such as $ZnCl_2$ or iron ammonium sulfate, but polymerization remained uncontrolled [50].

The rate of nitroxide-mediated polymerization of MMA may be increased and the process switched to the reversible inhibition mode by adding a high-temperature initiator. The latter supplies additional active radicals to the system, "binds" the free nitroxide, and thereby shifts the equilibrium toward dissociation. In this case, the term "high-temperature initiator" in relation to AIBN is not entirely successful. It implies that the rate of additional initiation with its help is much less than the rate of reinitiation. For the polymerization of MMA initiated by A1 or A2, such an initiator can be AIBN, the half-life of which is an order of magnitude longer than that of the named alkoxyamines.

To reach a noticeable effect on the polymerization of MMA initiated by alkoxyamine A1, it is necessary to add AIBN at a molar ratio of (0.5–1.0) : 1 with respect

Table 5. Yield and molecular weight characteristics of PMMA obtained with the participation of 0.01 mol/L of adduct A1 at 80°C

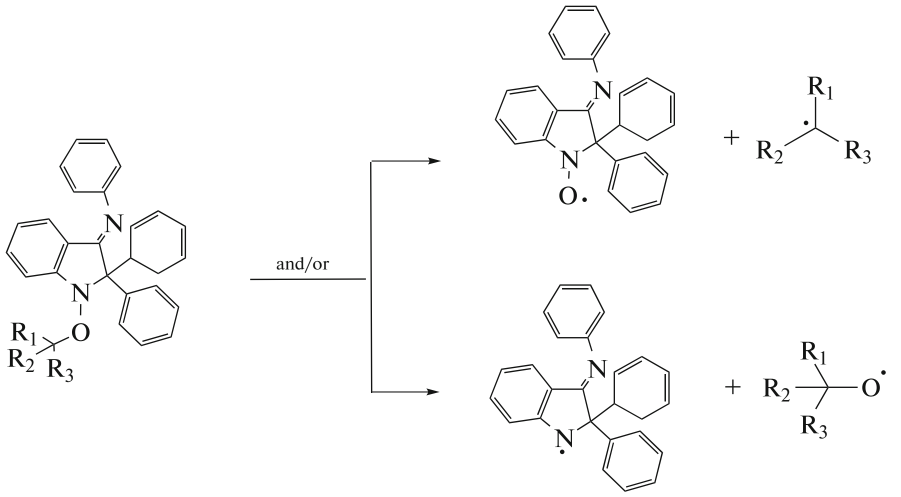
Additive	Additive concentration, mol/L	Time, min	Conversion, %	$M_n \times 10^{-3}$	$Đ$
–	–	500	7	5.5	1.6
AA	0.010	500	6	3.5	1.9
TFA	0.010	500	20	7.4	1.6
AIBN	0.005	500	36	18.7	2.6
AIBN	0.010	500	54	16.2	3.0

to A1. This makes it possible to lower the concentration of free nitroxide by more than an order of magnitude and, accordingly, to increase the degree of conversion by more than 10 times (Figs. 9, 10). The more initiator in the system, the better the polymerization proceeds. Comparison with the system without additive shows that the M_n of the polymer increases by almost two times, but the dispersion also increases (Table 5). The latter is obviously associated with the constant supply of additional radicals to the system initiating the nucleation of new chains.

The same regularities are characteristic of the polymerization of MMA initiated by A2. AIBN significantly lowers the concentration of nitroxide, which makes it possible to bring the monomer conversion to 86% (Fig. 11), that is, to the limiting value. The molecular weight of the polymer increases by a factor of 5 during polymerization (Table 6).

It is important that the dependence of the molecular weight of PMMA on conversion does not change upon the addition of TFA and AIBN. Although the experimental points lie below the theoretical straight line, they are close to those observed in the absence of additives at the same conversions (Fig. 12). This means that the additives do not affect the growth mechanism of the molecular weight of macromolecules but only prolong this process to higher conversions. Thus, the addition of AIBN and TFA increases the rate of MMA polymerization but does not completely prevent “decay.”

The polymerization of MMA mediated by DPAIO can also be assigned to the category of processes “with the addition of high-temperature initiators.” The specificity of this nitroxide is that, in the course of polymerization, its partial destruction occurs to generate an active O-centered radical [4, 58, 59].



In other words, the nitroxide itself plays the role of a high-temperature initiator. As a consequence, two positive effects are realized: firstly, the concentration of the free inhibitor decreases, and, secondly, new active growing radicals are supplied, which prevents the decay of MMA polymerization. The negative effect of this “destruction,” naturally, is the broadening of the MWD of the product. Under typical conditions, the polymerization of MMA mediated by DPAIO at 130°C runs until a conversion of 60%. In this case, the M_n of the polymer grows linearly and reaches (40–70) × 10^3 and the dispersion of PMMA is 1.4–2.4.

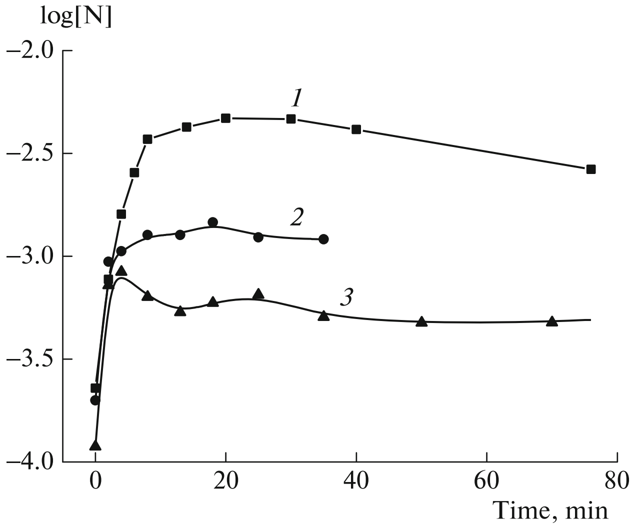


Fig. 9. Time dependence of the concentration of nitroxide radicals for the polymerization of MMA in bulk in the presence of 0.01 M of adduct A1 at 80°C (*1*) without additives and using 0.01 mol/L of (*2*) TFA and (*3*) AIBN.

It should be noted that all the regularities and effects described above refer to the polymerization of MMA involving low molecular weight nitroxides. In addition to them, to control the process, it was proposed to use macronitroxides which were obtained in situ from spin traps (nitrons) [60–63]. As a result, it was possible to lower the polymerization temperature to 40–50°C and increase the PMMA yield to 80%; there was the linear growth of M_n with conversion [60–62]. However, the molecular weight of the polymer was more than an order of magnitude higher than that predicted by theory and the width of the molecular weight distribution was of the same order of magnitude as that in the case of low molecular weight nitroxides. Unfortunately, we were unable to find information on the change in the concentration of nitroxides, the presence of disproportionation, and the values of the constants of elementary events in the case of MMA polymerization mediated by macronitroxides.

CONCLUSIONS

In conclusion, let us give examples of the successful controlled polymerization of MMA mediated by nitroxides over the past five years, that is, since the publication of the last review [11].

Aromatic nitroxides began to be used for the first time for these purposes [57]. As noted above, polymerization in their presence ends at the initial conversions, as for most nitroxides. However, the use of various “accelerating” additives makes it possible to accomplish the controlled polymerization of MMA up to a conversion of 70% and to synthesize PMMA with a molecular weight of up to 60 × 10^3 and dispersion of ~1.3–1.4.

The search continues for new nitroxides which would make it possible to simultaneously carry out the controlled polymerization of MMA and other monomers. It is reported that block copolymers PS–*block*–poly(butyl methacrylate) and PMMA–*block*–PS can be synthesized in the presence of Dispolreg 007 [32]. However, the value of $Đ$ ~ 2 for the copolymers is

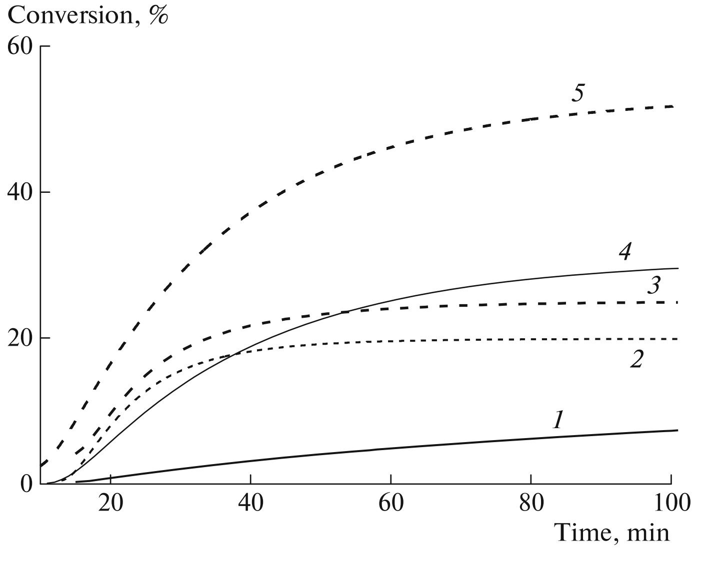


Fig. 10. Time dependences of conversion for the polymerization of MMA in bulk in the presence of 0.01 M of adduct A1 at 80°C (*1*) without additives and using (*2*) 0.01 and (*3*) 0.05 mol/L of TFA and (*4*) 0.005 and (*5*) 0.01 mol/L of AIBN.

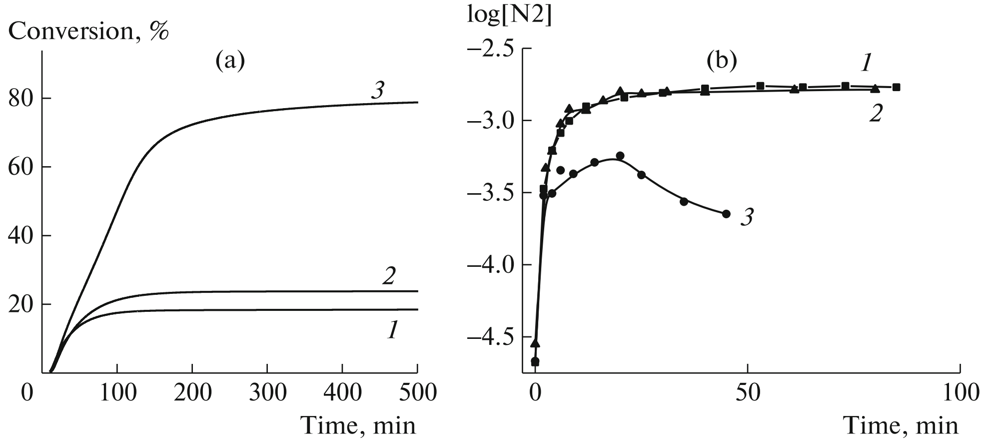


Fig. 11. Dependences of (a) conversion and (b) nitroxide concentration for the polymerization of MMA in bulk in the presence of 0.01 M of A2 adduct at 80°C (*1*) without additives and using 0.01 mol/L of (*2*) TFA and (*3*) AIBN.

clearly higher than that for controlled polymerization. The random copolymers of MMA with butyl acrylate obtained with the same nitroxide are characterized by a high yield (more than 80%), MW coinciding with that calculated according to the law of living chains, and Đ ~ 1.5–1.6 [10].

One of the effective tools for improving control in the nitroxide-mediated polymerization of MMA is to lower the reaction temperature, which allows one to minimize the contribution of side reactions. Therefore, the most interesting works concern photopolymerization. For example, a photoactive alkoxyamine based on the quinoline derivative of TEMPO was synthesized, which allowed the polymerization of MMA at room temperature. Although from the point of view of MW control this nitroxide did not meet expectations, it was effective in the stereo control of macromolecules: in its presence, the fraction of syndio triads in PMMA increased from 46 to 60% [64].

Table 6. Molecular weight characteristics of PMMA obtained by the polymerization of MMA in bulk with the participation of A2 and additives TFA and AIBN (additive concentration, 0.01 mol/L; $T = 80°C$)

Additive	Time, min	Conversion, %	$M_n \times 10^{-3}$	Đ
TFA	5.5	5	6.8	1.5
	12	8	7.3	1.6
	20	10	7.7	1.8
	30	15	12.2	1.5
	500	33	12.4	2.1
AIBN	9	20	8.4	2.6
	17	27	10.5	2.3
	29	32	20.4	1.5
	64	45	27.8	1.6
	500	86	40.8	1.8

Finally, the “copolymerization direction” continues to develop. Traditionally, styrene is used as an active comonomer to improve the control of polymerization of MMA. Recently, 4-vinylpyridine and a number of halogenated styrenes have been successfully used for this purpose [65, 66]. A small amount (5–11%) of the aforementioned comonomers is sufficient to transfer the uncontrolled polymerization of MMA mediated by SG1 into the reversible inhibition mode. This approach remains the main one for the design of MMA-based copolymers of various structures through polymerization mediated by SG1 [67–71].

Summarizing all the accumulated data on the polymerization of MMA mediated by nitroxides, we can draw some conclusions that are useful from the practical point of view. The “additive method” is currently the main method for the controlled synthesis of PMMA and its copolymers by nitroxide-mediated polymerization.

Ongoing attempts to search for new nitroxides that are incapable of disproportionation with MMA growing radicals may be unsuccessful, since the absence of disproportionation is not the only reason for the disruption of the living polymerization mechanism. In our opinion, the main efforts should be directed at the search for such agents of controlled synthesis that would allow polymerization of MMA at low temperatures close to room temperature. It is under these con-

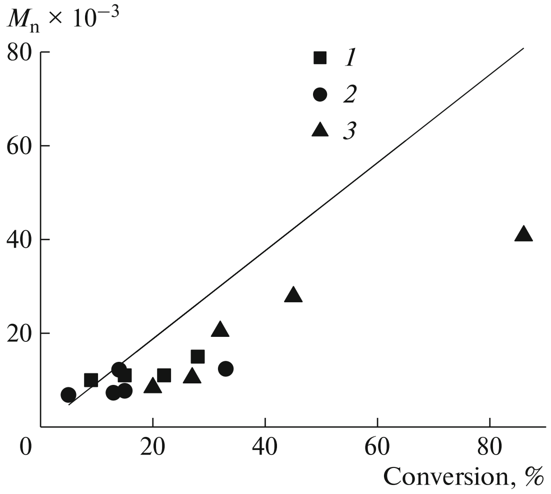


Fig. 12. Dependence of the M_n of polymer on conversion for the polymerization of MMA in the presence of A2 (*1*) without additives and using (*2*) TFA and (*3*) AIBN. Straight line is the theoretical dependence. The synthesis conditions are given in Table 6.

ditions that not only the contribution of disproportionation decreases but also the Fischer effect is reduced to a minimum.

FUNDING

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

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