Nitroxyl radicals of the imidazoline series as agents of pseudoliving polymerization of styrene

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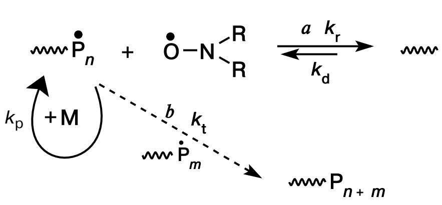
Radical polymerization of styrene in the presence of 2,2,4,5,5-pentamethyl-2,5-dihydroimidazol-1-oxyl, 2,2-diethyl-4,5,5-trimethyl-2,5-dihydroimidazol-1-oxyl, 2,2,5,5-tetramethyl-4-phenyl-2,5-dihydroimidazol-1-oxyl, 2,2,5-trimethyl-4,5-diphenyl-2,5-dihydroimidazol-1-oxyl, and 2-methyl-2,3-diphenyl-1,4-diazaspiro[4.5]deca-3-en-1-oxyl was studied. Effect of substituents in the nitroxyl radical and the nature of initiator on the features of "pseudoliving" polymerization and the molecular-weight characteristics of polystyrene synthesized were considered. Nitroxyl radicals of imidazoline series, like TEMPO and its derivatives, allow one to regulate polymerization of styrene and obtain polymers with relatively low values of polydispersity index.

Key words: controlled radical polymerization, imidazoline radicals, nitroxyl radicals, styrene.

Radical polymerization in the regime of "living" chains is one of the efficient methods for the synthesis of polymers with certain molecular weight and low polydispersity. Nitroxide mediated polymerization (NMP) is the most widespread version used for its performing.[1—6] The NMP mechanism is based on the reaction of propagation radicals ($\sim P_n^{\bullet}$) with stable nitroxyl radicals ($>N—O^{\bullet}$) to form alkoxyamines ($\sim P_n—O—N<$, Scheme 1, pathway *a*), that results in suppression of bimolecular termination of growing chains (see Scheme 1, pathway *b*).

Scheme 1



$\sim P_n^{\bullet}$ is a polymer radical, k_r, k_d, k_p, and k_t are the rate constants of recombination, dissociation, propagation, and termination of a chain, respectively, M is a monomer

Under certain temperature conditions, the inhibition process (see Scheme 1, pathway *a*) becomes reversible, leading to regeneration of propagation radicals. The equilibrium of the reversible inhibition reaction is determined by the ratio of the rate constants of radical recombination (k_r) and alkoxyamine dissociation (k_d) reactions. In turn, the constant ratio indicated considerably depends on the structure of a nitroxyl radical. It is known[1—6] that 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was one of the first nitroxyl radicals suggested for accomplishing "pseudoliving" radical polymerization at the temperatures of 120—140 °C. In the last years, a clear tendency is observed in the development of this concept consisting in the search for new sterically hindered radicals, which in contrast to the TEMPO derivatives allow one to carry out the "pseudoliving" polymerization under milder temperature conditions (<100 °C).[7—16] An approach consisting in the introduction of bulky substituents (for example, spiro structures[7—10] or silyloxyalkyl groups[11,12]) at α-position to the $>N—O^{\bullet}$ group in piperidine nitroxyls has proved very efficient, as well as in the synthesis of new sterically hindered nitroxyls, such as SG1,[13,14] 1,1-diadamantylnitroxyl,[15] and bisnitroxyl.[16] In addition, a number of research groups are developing an original method for

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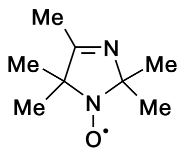
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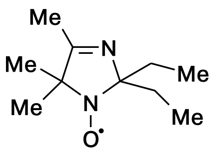
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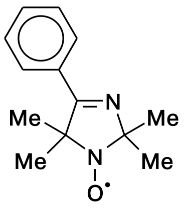
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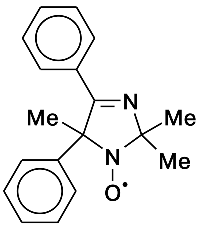
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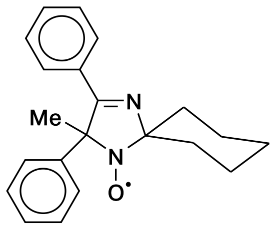
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carrying out polymerization in the regime of "living" chains, consisting in the generation of sterically hindered nitroxyl radicals directly during polymerization (*in situ*) by entrapment of bulky radicals of propagation or initiator with spin-traps.[17—23]

In a number of recent works,[24—26] imidazoline nitroxyls were suggested for the use in carrying out "pseudoliving" polymerization of styrene (ST). It was found that these compounds allow one to obtain polystyrene (PS) with relatively low values of polydispersity index (1.2—1.3) and required molecular weight (MW) in the temperature range 80—130 °C.

In order to further study specific features of controlled synthesis of macromolecules and search for new efficient regulators based on nitroxyl radicals, we studied polymerization of ST in the presence of nitroxyls of imidazoline series containing various sterically hindered groups at positions 2, 4, and 5: 2,2,4,5,5-pentamethyl-2,5-dihydroimidazol-1-oxyl (**1**), 2,2-diethyl-4,5,5-trimethyl-2,5-dihydroimidazol-1-oxyl (**2**), 2,2,5,5-tetramethyl-4-phenyl-2,5-dihydroimidazol-1-oxyl (**3**), 2,2,5-trimethyl-4,5-diphenyl-2,5-dihydroimidazol-1-oxyl (**4**), and 2-methyl-2,3-diphenyl-1,4-diazaspiro[4.5]deca-3-en-1-oxyl (**5**).

Results and Discussion

It was found experimentally that the ratio of concentrations of an initiator, a nitroxyl, and a monomer plays a key role for the synthesis of polymers with a narrow molecular-weight distribution (MWD). For instance, when concentrations of an initiator and a nitroxyl are low with respect to a monomer (1 : 1.5 : 1000 and 1 : 1.5 : 500), PS with high polydispersity indexes, *viz.*, 1.6—3.0, are formed independent on the temperature conditions (Table 1). If the concentrations of an initiator and a nitroxyl is increased with respect to ST by the order of magnitude (1 : 1.5 : 100, see Table 1), PS with low enough polydispersity indexes (M_w/M_n) can be synthesized. However, a controlled process of polymerization of ST with such a ratio of reagents mainly occurred at temperatures ≥ 100 °C. In the low-temperature range, polymerization is completely

Table 1. Effect of synthetic conditions on molecular-weight characteristics of PS ($[ST]_0$ = 8.71 mol L^{-1})

Nitroxyl	T/°C	$[ST]_0 : [AIBN]_0 : [Nitroxyl]_0$	t/h	Conversion (%)	$M_n \cdot 10^{-3}$	M_w/M_n
1	100	1000 : 1 : 1.5	4	4	10.0	2.41
		500 : 1 : 1.5	10	7	7.9	2.16
	120	1000 : 1 : 1.5	3	10	8.0	1.99
		500 : 1 : 1.5	10	25	7.1	1.74
		100 : 1 : 1.5	10	10	3.7	1.43
2	70	100 : 1 : 1.5	75	27	4.0	1.60
	90	100 : 1 : 1.5	38	44	3.0	1.38
	120	100 : 1 : 1.5	31	71	4.5	1.38
3	80	1000 : 1 : 1.5	4	9	48.0	1.81
		100 : 1 : 1.5	30	0	—	—
	100	1000 : 1 : 1.5	4	4	10.0	2.41
	120	1000 : 1 : 1.5	3	35	21.0	1.82
		500 : 1 : 1.5	10	89	20.0	1.61
		100 : 1 : 1.5	10	19	2.3	1.28
4	100	1000 : 1 : 1.5	4	6	4.0	3.19
		500 : 1 : 1.5	10	8	8.9	3.68
	120	1000 : 1 : 1.5	3	21	8.1	2.27
		500 : 1 : 1.5	10	61	9.7	1.63
		100 : 1 : 1.5	10	14	2.0	1.37
5	120	100 : 1 : 0.5	10	75	10.4	2.00
		100 : 1 : 1.0	39	79	5.5	1.50
		100 : 1 : 1.5	81	82	5.0	1.23
		100 : 1 : 2.0	97	79	3.1	1.25

inhibited. Further increase in the concentration of nitroxyl (see Table 1) do not considerably improve the M_w/M_n, rather it retards the rate of polymerization. To sum up, from analysis of the experimental data on polymerization of ST in the presence of imidazoline nitroxyls it follows that the temperature of 120 °C and the high concentration of a nitroxyl with respect to a monomer (1.5 : 100) are the optimum conditions for the "pseudoliving" process.

It should be noted that polymerization of ST in the presence of these nitroxyls and peracyl or azonitrile initiators (benzoyl peroxide (BP) and azoisobutyric acid dinitrile (AIBN)) has some specific features. In all the cases, periods of induction were observed in the initial step (Fig. 1). When the peroxide initiator was used, the induction period ranged from ~4 to 10 h depending on the structure of the nitroxyl radical **1—5**. In the case of AIBN, induction periods were somewhat shorter and changed in the range from ~40 min to 6 h. Since the half-life periods for AIBN and BP at 120 °C are less than 1 and 3 min, respectively,[27,28] it can be stated that the initiators under conditions selected are completely consumed already within 30 min (≥ 10 half-life periods) after the process began. Thus, formation of PS after the time indicated (t_i) points to the direct involvement of alkoxyamines into its synthesis, which are formed in the polymerization system (*in situ*) due to recombination of nitroxyls with radicals of initiator and macroradicals emerging in the process of polymerization of ST self-initiation.

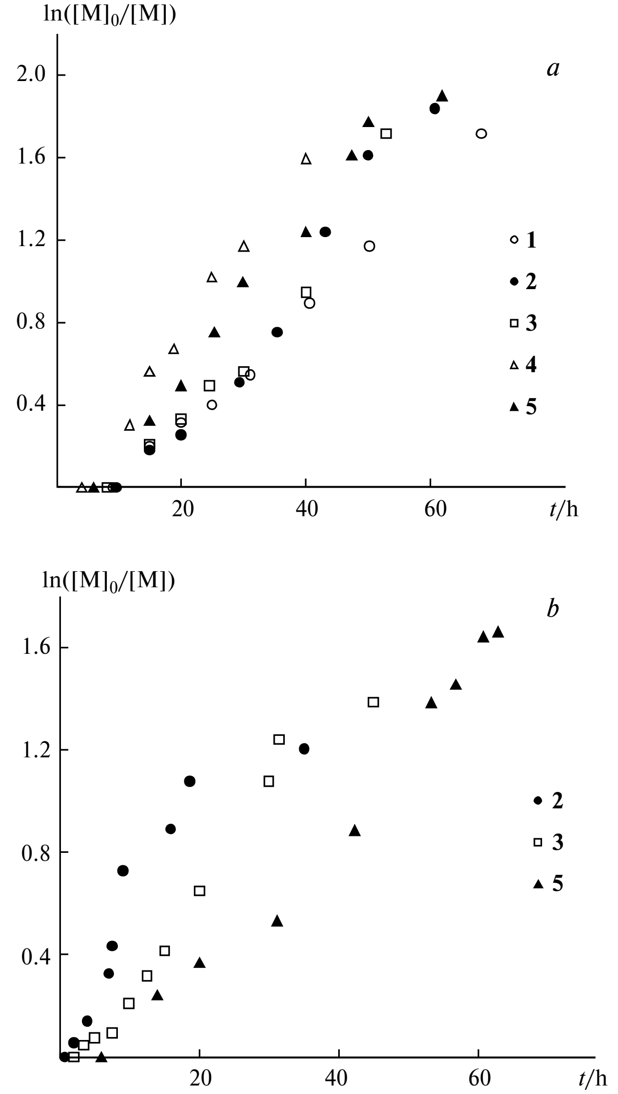


Fig. 1. Dependence of $\ln([M]_0/[M])$ from time on polymerization of styrene initiated with BP (*a*) and AIBN (*b*) at 120 °C in the presence of nitroxyls **1—5** (*a*) and **2**, **3**, **5** (*b*). The ratio of concentrations of polymerization system components: $[ST]_0 = 8.71$ mol L^{-1}, $[ST]_0 : [\text{Initiator}]_0 : [\text{Nitroxyl}]_0 = 100 : 1 : 1.5$.

The polymerization processes studied can be described by the first order kinetic equation in monomer (see Fig. 1). The dependences of $\ln([M]_0/[M])$ versus time given have a linear character to the high degrees of conversion (~70%), that points to the constant concentration of growing radicals and is an indirect evidence of "pseudoliving" character of polymerization of ST in the presence of nitroxyls of imidazoline series. When specific features of polymerization of ST in the presence of identical nitroxyl radicals and various initiators are compared, it is seen that the process of polymerization of ST in the presence of BP and nitroxyls **2** and **3** occurs at retarded rates and higher absolute values of induction period as compared to polymerization in the presence of AIBN. Polymerization of ST in the presence of **5** for both BP and AIBN proceeds virtually within the same period of time at comparable rates.

The experimental data obtained are an evidence that upon initiation with BP, the rate of polymerization of ST is weakly dependent on the structure of substituents in the imidazoline nitroxyls, though it somewhat decreases in the following order: **4** > **5** > **3** ≈ **2** ≈ **1**. In this case, comparison of the slopes corresponding to the lines of nitroxyls **1** and **3** (see Fig. 1, *a*) indicates that the introduction of a phenyl ring at position 4 has no effect on the rate of polymerization of ST. Thus, as in the case of TEMPO derivatives, "remote" sterical effect is not observed.[29,30] Polymerization of ST has the highest rate in the presence of nitroxyl radicals with bulky substituents at positions 2 and/or 5 of the imidazole ring (α-position with respect to the nitroxyl fragment).

For high concentrations of a nitroxyl radical, conversion of a monomer after t_i is described by the equation[5,31]

$$\ln[M]_0/[M] = (k_pK_{eq}2f[I]_0/[{>}NO^\bullet]_{ti})t, \qquad (1)$$

where $[M]_0$ and $[M]$ are the initial and current concentrations of a monomer, $[I]_0$ is the initial concentration of an initiator (AIBN or BP), f is the efficiency of initiation (0.5—0.6), $K_{eq} = k_d/k_r$, $[{>}NO^\bullet]_{ti}$ is the concentration of a nitroxyl radical.

A certain acceleration of polymerization when nitroxyls **4** and **5** are used can be due to the increase in the dissociation rate constants of alkoxyamines formed *in situ* (k_d, see Eq. (1)), as well as due to the decrease in the recombination rate constants of nitroxyls and propagation radicals (k_r, see Eq. (1)) because of the steric hindrance created by bulky groups. In fact, a number of works using alkoxyamines of various structure as an example demonstrate that an increase in the bulkiness of the groups at α-position with respect to the nitroxyl fragment leads to a considerable increase in the dissociation rate constants (k_d) of such alkoxyamines[12—14,24,32] and decrease in the recombination rate constant (k_r) of stable nitroxyl with a propagation macroradical.[11,12,32]

Retardation of polymerization rate in the presence of sterically hindered nitroxyl **5** as compared to **4** is apparently due to a number of reasons. In particular, this circumstance can be related to the so-called "levelled" steric effect.[33] This effect consists in the fact that the dissociation constants of alkoxyamines change nonmonotonously with the increase in the size of substituents of the nitroxyl fragment. For the substituents of a very large size, k_d do not virtually increase or can decrease. Another explanation for the effect observed can consist in the proceeding of side disintegration reactions of alkoxyamines, for example, intramolecular and intermolecular hydrogen transfer.[34]

Initiation with AIBN shows no clear dependence of the rate of polymerization and induction period versus structure of a nitroxyl radical. For instance, from Fig. 1, *b* one can see that the rate of polymerization of ST decreases in the order **2** > **3** > **5**. An increase in steric hindrance created by substituents at C_α atoms of the nitroxyl group changes in another sequence. Considerable induction period and low rate of polymerization of ST in the presence of nitroxyl **5** containing bulky substituents are due to a number of factors. As it follows from Eq. (1), a degree of conversion will depend not only on the equilibrium constant, but also on the ratio of concentrations of initiating radicals and a nitroxyl. For AIBN, a "cage effect" becomes a considerable factor at 120 °C, which determines efficiency of initiator and, therefore, ability of radicals formed to react with nitroxyl radicals and further initiation of polymerization. In the case of the *in situ* synthesis of alkoxyamines from nitroxyl radicals **2**, **3**, and **5** and radical initiator, the current concentrations of the alkoxyamine formed and residual nitroxyl will depend on k_r and efficiency of the outcome of initial radicals from the "cage". It should be noted that the introduction of sterically hindered groups in the nitroxyl fragment of alkoxyamine to a greater extent affects not the dissociation rate constants of the corresponding alkoxyamines, but the decrease in the recombination rate constant of stable nitroxyl with propagation macroradical.[11,12] When nitroxyl **5** is used, for which the k_r value is lower virtually by the order of magnitude[32] than in the case of nitroxyls **2** and **3**, recombination of initial radicals of initiator in the "cage" with the formation of nonradical products is more likely. It is logically to suggest that polymerization of ST in the presence of alkoxyamines synthesized *in situ* from nitroxyl **5** proceeds under conditions of decreased concentrations of alkoxyamine and an excess of nitroxyl radicals. This leads to an increase in the induction period and

Table 2. Molecular-weight characteristics of PS synthesized at 120 °C in the presence of various initiators*

Initiator	Nitroxyl	Conversion (%)	$M_n \cdot 10^{-3}$	M_w/M_n
BP	**1**	18	2.2	1.27
		27	2.8	1.32
		42	4.1	1.39
		59	5.2	1.35
		82	7.4	1.40
	2	17	1.5	1.18
		40	3.7	1.25
		53	6.0	1.28
		73	8.0	1.27
		80	8.4	1.27
	3	19	2.0	1.23
		28	2.3	1.24
		39	3.2	1.25
		61	4.6	1.26
		82	5.9	1.24
	4	26	4.4	1.65
		43	5.2	1.61
		49	5.8	1.63
		64	6.5	1.63
		80	7.9	1.60
BP	**5**	28	3.3	1.38
		39	4.6	1.42
		53	5.6	1.43
		63	6.3	1.43
		83	7.8	1.40
AIBN	**2**	8	1.3	1.40
		28	1.7	1.39
		51	2.5	1.38
		66	4.1	1.38
		71	4.5	1.38
	3	19	2.2	1.27
		27	2.3	1.24
		48	2.8	1.28
		66	3.5	1.25
		75	3.7	1.25
	5	22	3.0	1.27
		31	3.3	1.23
		61	4.4	1.30
		75	4.7	1.23
		82	5.0	1.23

* $[ST]_0 = 8.71$ mol L^{-1}, the ratio $[ST]_0 : [Initiator]_0 : [Nitroxyl]_0 = 100 : 1 : 1.5$.

retardation of the process. Analogous decrease in the rate was observed in the works,[35,36] in which, together with alkoxyamines, related nitroxyl radicals were involved into polymerization. Such a change in kinetics of polymerization is due to the "persistent radical effect".[5]

The number average molecular weights of the polymers synthesized in the presence of either BP, or AIBN with the concentration of nitroxyls being 1.5 mol.% linearly increase with conversion of the monomer (Table 2). The polydispersity indexes of PS are low (see Table 2), with the correlation between polydispersity indexes of polystyrene and the rate of the synthesis of the latter being observed. Polymers formed at low rate are characterized by the lowest values of polydispersity indexes (1.2—1.3). An increase in the rate of polymerization leads to the increase in polydispersity indexes. This regularity is the most pronounced in the synthesis of PS in the presence of BP and sterically hindered nitroxyls **4** and **5** (see Table 2).

In addition, it should be noted another distinguishing feature of polymerization of ST in the presence of different initiators. The number average values of polystyrene MW synthesized in the presence of BP and nitroxyls **1—5** (Fig. 2, *a*) are in good agreement with the theoretically calculated values of M_n:

$$M_n^{calc} = M_{ST}([M]_0 - [M])/(2f[I])_0, \qquad (2)$$

where M_{ST} is the MW of a monomer unit of styrene.

In all the cases, the dependences given are extrapolated to zero, that points that polymerization of ST in the presence of selected nitroxyls has "pseudoliving" character and good enough correlation with the "ideal" conditions for controlled process.

In the case of synthesis of PS with involvement of nitroxyls **2**, **3**, and **5** and AIBN, experimental M_n values do not correlate with those calculated using formula (2) (see Fig. 2, *b*). Two regions can be selected on the graph: theoretical values of number average MW of 2000 g mol^{-1} and higher. In the diagram region of low MW, the M_n values found experimentally are higher as compared to theoretical. In the case of nitroxyl **3**, in the region to 2000 g mol^{-1} the MW of PS decreases with conversion of the monomer. In the region of MW higher 2000 g mol^{-1} for all the nitroxyls studied, dependences of M_n from conversion are approximated by straight lines. However, the MW values found experimentally are lower than those predicted theoretically (Fig. 2, *b*), that is reflected in the lower slopes of functional curves. The effect observed is due to the higher concentration of growing radicals during polymerization of ST initiated by AIBN with involvement of dihydroimidazole nitroxyls, due to a considerable contribution of the thermal component. This is also reflected in higher rate of polymerization and has been discussed above.

The fact found experimentally is explained by the low rate of alkoxyamines decomposition formed *in situ* in the presence of AIBN in the first moment of time. This effect has been predicted theoretically and substantiated earlier.[5,37] To make allowance for the rate of decomposition of initial adducts, a number of correction factors were suggested[5,37] to introduce into the denominator of Eq. (2):

$$M_n^{calc} = M_{ST}([M]_0 - [M])/\{[I]_0[1 - \exp(-k_d t)]\}, \qquad (3)$$

$$M_n^{calc} = M_{ST}([M]_0 - [M])/\{[I]_0[1 - \exp(-k_d t)] + R_i t\}, \qquad (4)$$

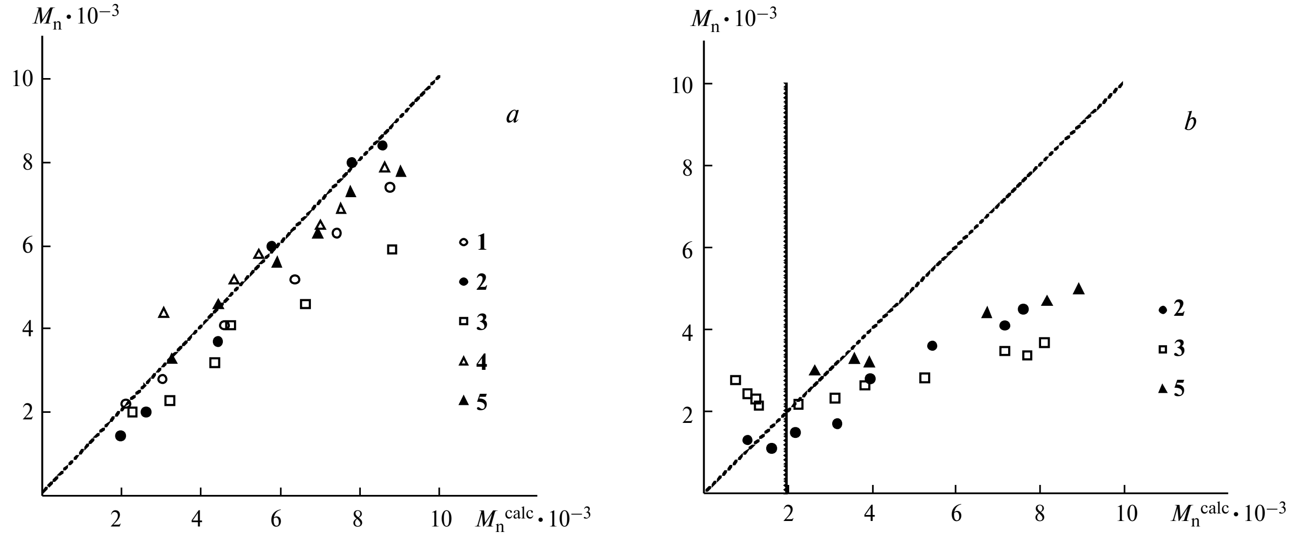


Fig. 2. Correlation of experimental M_n values of PS with theoretically calculated M_n^{calc} values at different degrees of conversion of the PS monomer synthesized in the presence of BP (*a*) and AIBN (*b*) at 120 °C and nitroxyls **1—5** (*a*) and **2**, **3**, **5** (*b*). The ratio of concentrations of polymerization system components: $[ST]_0 = 8.71$ mol L^{-1}, $[ST]_0 : [Initiator]_0 : [Nitroxyl]_0 = 100 : 1 : 1.5$.

where k_d is the rate constant of dissociation of alkoxyamines, R_i is the rate of thermal self-initiated polymerization of styrene, t is the time.

For the theoretical calculations of MW by Eqs (3) and (4), the dissociation rate constant value (k_d)[32] for nitroxyl **3** of $4.4 \cdot 10^{-5}$ s^{-1} and R_i (see Ref. 38) of $6 \cdot 10^{-7}$ mol L^{-1} s^{-1} were used. To determine [M], known values of k_p (see Ref. 38) and k_t,[37] equal to 2026 and 10^8 L mol^{-1} s^{-1}, respectively, were used, as well as a recombination rate constant for nitroxyl **3** k_r equal to $1.6 \cdot 10^8$ L mol^{-1} s^{-1} (see Ref. 32). It is seen from the data given in Fig. 3 that the dependence of M_n from the monomer conversion calculated by Eq. (2) is linear within all the range of conversions (curve *1*). If a correction coefficient, making allowance for the alkoxyamines dissociation rate constant (see Eq. (3)), is introduced, the M_n values calculated theoretically decrease with the increase in conversion to 20% (see Fig. 3, curve *2*). Introduction into the denominator of a term responsible for the thermal self-initiated polymerization of styrene (R_i), whose value is constant only for the initial degrees of the monomer conversion (see Eq. (4)), leads to yet greater decrease in the calculated values in the region of initial conversions (see Fig. 3, curve *3*). The M_n values obtained experimentally (curve *4*) for the low conversions better correlate with values calculated using Eqs (3) and (4). Analogous regularities have been noted earlier.[39]

A reason for the differences in both the polymerization rates and molecular-weight characteristics of polymers obtained in the presence of nitroxyls **1**—**5** and different initiators (BP or AIBN) consists in different reactivity of the initial radicals formed upon decomposition of initiator. For instance, kinetic analysis performed for the formation of alkoxyamines showed[40] that in the case of organic peroxides and azonitriles, alkoxyamines of different structures can be formed. When alkoxyamines containing several monomeric units are derived from BP, the MM of polymers and the rates of their synthesis are completely predictable. A clear correlation is present between characteristics and structure of a nitroxyl radical. The presence of "anomalies" indicated previously in the case of AIBN is explained by the difference in the rates of alkoxyamine decomposition and a possibility to proceed for the side nonradical decomposition reactions of initial adducts of cyanoisopropyl and nitroxyl radicals, for example, intramolecular hydrogen transfer.[34]

A possibility to carry out postpolymerization is an irrefutable evidence of polymerization in controlled regime using the nitroxyls selected. The process was carried out at 120 °C in the presence of macroinitiators obtained using nitroxyls **1**—**5**. Postpolymerization resulted in the formation of a polymer with the MW higher than the starting polymer (Table 3). In all the cases (when peracyl and azonitrile initiators were used), the curves of the MWD of postpolymers are unimodal, and their mode is displayed to the region of higher MW as compared to the starting samples (Fig. 4). In this case, the MWD curves of initiating polymers and postpolymers have nonoverlapped regions, *i.e.*, the low-molecular-weight fractions of initiating polymers are absent in postpolymers. Polydispersity indexes of postpolymers obtained in the presence of nitroxyls **1**—**3** are low enough (1.2—1.4) and comparable with the macroinitiator polydispersity indexes (see Table 3). This is an evidence that the length of all the chains included in the initiating polymers is increased due to the addition of new monomeric units. When postpolymeriza-

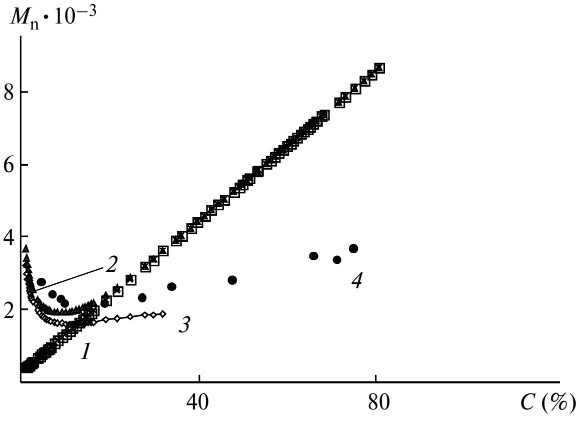


Fig. 3. Dependence of experimental and theoretically calculated M_n of PS from conversion (*C*) of the monomer: *1*, *2*, *3* are the M_n values calculated using Eqs (2), (3), and (4), respectively; *4* is the experimental M_n of PS synthesized in the presence of nitroxyl **3**, the ratio concentrations of polymerization system components: $[ST]_0 = 8.71$ mol L^{-1}, $[ST]_0 : [Initiator]_0 : [Nitroxyl]_0 = 100 : 1 : 1.5$.

Table 3. Molecular-weight characteristics of PS-macroinitiators (indicated with an asterisk) and postpolymers synthesized at 120 °C

Initiator	Nitroxyl	t/h	Conversion (%)	$M_n \cdot 10^{-3}$	M_w/M_n
BP	**1**	50*	69*	6.3*	1.35*
		14	45	10.4	1.43
	2	50*	73*	7.9*	1.26*
		14	47	11.0	1.30
	3	30*	43*	4.1*	1.27*
		14	62	7.5	1.31
	4	30*	69*	6.9*	1.63*
		14	41	11.7	1.72
	5	30*	63*	6.3*	1.43*
		14	43	8.1	1.42
AIBN	**2**	17*	51*	2.5*	1.38*
		16	67	7.4	1.23
	3	20*	48*	2.8*	1.28*
		50	98	6.7	1.43
	5	70*	73*	4.8*	1.25*
		38	81	5.2	1.75

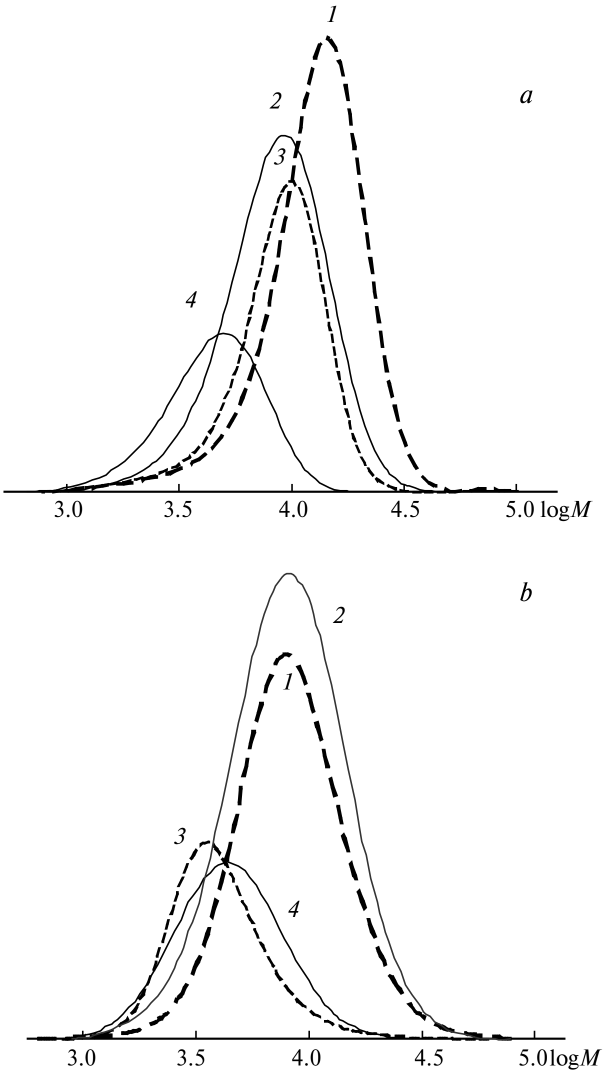


Fig. 4. The MWD curves of PS postpolymer samples (*1*, *2*) synthesized at 120 °C. Macroinitiators (curves *3*, *4*) were obtained in the presence of BP (*a*) and AIBN (*b*) at the following ratio of component concentrations: $[\mathrm{ST}]_0$ = 8.71 mol L^{-1}, $[\mathrm{ST}]_0$: $[\mathrm{Initiator}]_0$: $[\mathrm{Nitroxyl}]_0$ = 100 : 1 : 1.5; *1*, *3* — in the presence of nitroxyl **2**, *2*, *4* — in the presence of nitroxyl **3**. Conversions (%): *a* — 73 (*3*), 47 (*1*), 43 (*4*), 62 (*2*); *b* — 51 (*3*), 67 (*1*), 50 (*4*), 98 (*2*). The curves are normalized on conversion.

tion was performed with involvement of macroinitiators based on compounds **4** and **5**, the samples with somewhat higher values of $M_\mathrm{w}/M_\mathrm{n}$ (~1.7) than for the starting polymers were obtained (see Table 3). It is possible, that this is due to the "dead" polymer formed in the starting PS during the synthesis because of termination of alkoxyamines by mono- and bimolecular reactions.[34]

On the whole, the data obtained are an unambiguous evidence that polymerization of ST in the presence of nitroxyls of imidazoline series follows the "pseudoliving" mechanism. It was showed that spatial groups at α-position with respect to the nitroxyl fragment have considerable effect on the kinetic regularities of polymerization of ST and molecular-weight characteristics of polymers synthesized. These specific features are seen the most clear when a peroxide initiator was used.

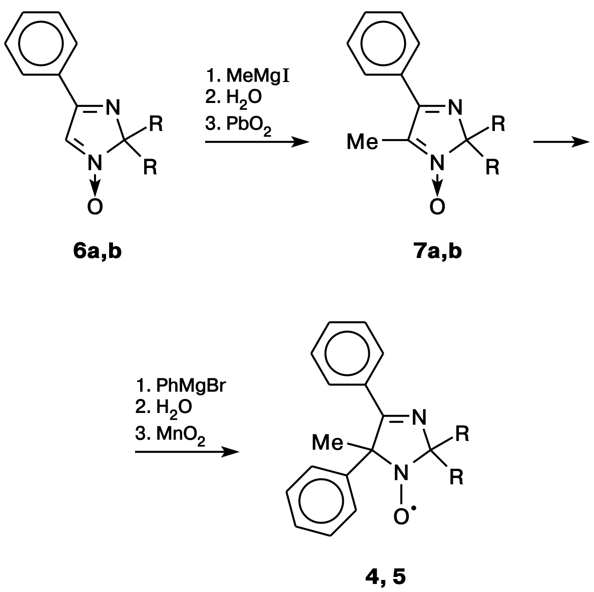
Experimental

Initiators BP and AIBN were recrystallized from hexane and ethanol, respectively. Solvents were purified according to the standard procedures,[41,42] ST was purified off from hydroquinone by repeated washing with 5% aqueous alkali until the monomer became colorless, then was washed off from residual alkali with DI water until the aqueous layer was neutral, and dried with calcium dichloride. The dried monomer was distilled under reduced pressure. Physico-chemical constants agree with the literature data.[43]

Synthesis of nitroxyl radicals. All the nitroxyl radicals synthesized were characterized by IR spectroscopy on a Bruker Vector 22 FTIR spectrometer (in KBr pellets with the concentration 0.6%, the pellet was 1 mm thick), UV spectroscopy on a HP Agilent 8453 spectrometer (EtOH with concentration 10^{-4} mol L^{-1}), NMR spectroscopy on a Bruker AV300 spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz) or Bruker AM-400 spectrometer (^{1}H, 400.136 MHz; ^{13}C, 100.6 MHz) in $\mathrm{CDCl_3}$, and elemental (C, H) analysis.

Nitroxyl radicals **1**—**3** were synthesized according to the procedures published earlier.[44—46] Nitroxyl radicals **4** and **5** were obtained according to the general Scheme 2 from 2,2-dimethyl-4-phenyl-2-hydroimidazole 1-oxide (**6a**) and 3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (**6b**), whose synthesis is described in the work.[47]

Scheme 2



6, **7:** R = Me (**a**); R + R = $(\mathrm{CH_2})_5$ (**b**)

Synthesis of 5-methyl-4-phenyl-2*H*-imidazole-1-oxides 7a,b. A solution of methylmagnesium iodide in anhydrous diethyl ether, obtained from magnesium turnings (0.72 g, 30 mmol) and methyl iodide (1.25 mL, 20 mmol) in anhydrous diethyl ether (30—40 mL), was added dropwise to a solution of nitrone **6a,b** (10 mmol) in minimum dry benzene so that the ether simmered. The reaction mixture was stirred for 1 h until the starting compound disappeared according to the TLC data (Silufol UV 254, chloroform). Then, water was added thoroughly dropwise until a viscous inorganic phase was formed. The organic solution was decanted. The inorganic mass was washed with diethyl ether ((2—3)S10 mL). A combined organic solution was dried with magnesium sulfate, then, lead dioxide (15 g) was added to the solution, which was vigorously stirred for 2—3 h. The oxidant was filtered off and 2—3 times washed with a mixture of chloroform with ethanol (4 : 1), the solvents were evaporated under reduced pressure. The residue was recrystallized from hexane. Compounds **7a,b** obtained correspond to the authentic samples.[48]

2,2,5-Trimethyl-4-phenyl-2*H*-imidazole-1-oxide (7a). The yield was 1.9 g (96%), colorless crystals, m.p. 87—89 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.52 (s, 6 H, 2 Me); 2.25 (s, 3 H, Me); 7.43 (m, 3 H, *m*-H, *p*-H, Ph); 7.70 (m, 2 H, *o*-H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 10.68 (Me, C(5)); 24.06, 24.15 (2 Me, C(2)); 99.03 (C(2)); 127.59 (*o*-C, Ph); 128.70 (*m*-C, Ph); 130.89 (*p*-C, Ph); 132.18 (*ipso*-C, Ph); 135.56 (C(5)); 166.38 (C(4)).

2-Methyl-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide (7b). The yield was 2.3 g (93%), colorless crystals, m.p. 75—77 °C. ^{1}H NMR (300 MHz; $CDCl_3$), δ: 1.35 (m, 3 H, CH_2, $(CH_2)_5$); 1.85 (m, 5 H, CH_2, $(CH_2)_5$); 2.12 (m, 2 H, CH_2, $(CH_2)_5$); 2.28 (s, 3 H, Me); 7.43 (m, 3 H, *p*-H, Ph); 7.75 (m, 2 H, *o*-H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 10.46 (Me); 22.94 (2 CH_2, $(CH_2)_5$); 24.51 (CH_2, $(CH_2)_5$); 34.63 (2 CH_2, $(CH_2)_5$); 101.56 (C(5)); 127.54 (*o*-C, Ph); 128.53 (*m*-C, Ph); 130.53 (*p*-C, Ph); 132.36 (*ipso*-C, Ph); 135.71 (C(2)); 166.20 (C(3)).

Synthesis of nitroxyl radicals 4 and 5. A solution of phenylmagnesium bromide, obtained from magnesium (1.5 g, 63 mmol) and bromobenzene (4.0 mL, 38 mmol) in anhydrous diethyl ether (30 mL) was added dropwise to a solution of methylnitrone **7a,b** (9.5 mmol) in minimum dry benzene. The reaction mixture was stirred for another 1 h, then, water was added thoroughly dropwise until a viscous inorganic phase was formed. The organic solution was decanted. The inorganic mass was washed with diethyl ether (2×10 mL). A combined organic solution was dried with magnesium sulfate, then, manganese dioxide (15 g) was added to the solution, which was vigorously stirred for 2—3 h. The oxidant was filtered off and 2—3 times washed with a mixture of chloroform with ethanol (4 : 1), the solvents were evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel, using the chloroform—hexane (1 : 1) solvent mixture as an eluent. Product **4** was recrystallized from hexane, whereas **5** from the mixture ethyl acetate—hexane (1 : 8).

2,2,5-Trimethyl-4,5-diphenyl-2,5-dihydroimidazol-1-oxyl (4). The yield was 1.1 g (42%), yellow crystals, m.p. 128—132 °C. Found (%): C, 77.72; H, 6.82; N, 10.12. $C_{18}H_{19}N_2O^{\bullet}$. Calculated (%): C, 77.39; H, 6.86; N, 10.03. IR, ν/cm^{-1}: 3065, 3032 (H—C=, Ph); 2982, 2932 (Me); 1599, 1572 (C=N, C=C). UV, λ_{max}/nm: 248 (logε = 4.20).

2-Methyl-2,3-diphenyl-1,4-diazaspiro[4.5]deca-3-en-1-oxyl (5). The yield was 1.1 g (37%), yellow crystals, m.p. 161—163 °C. Found (%): C, 78.80; H, 7.29; N, 8.76. $C_{21}H_{23}N_2O^{\bullet}$. Calculated (%): C, 78.96; H, 7.26; N, 8.77. IR, ν/cm^{-1}: 3067, 3031 (H—C=, Ph); 2997, 2977, 2938, 2923, 2857 (CH_3, CH_2); 1597, 1570 (C=N, C=C). UV, λ_{max}/nm: 249 (logε = 4.61).

Polymerization. Initiators and nitroxyl radicals were accurately weighted and dissolved in the monomer. The solutions were dozed into glass tubes and degassed under reduced pressure by triple refreezing in the liquid nitrogen. The tubes were kept in a thermostat at a certain temperature (T±1 °C) for a given time, followed by isolation of a polymer. Polystyrene was purified off from organic impurities by double reprecipitation from a chloroform solution into isopropanol and dried *in vacuo* at 50 °C until the mass was constant. The polymer yield (conversion of the monomer) was determined gravimetrically.

To perform postpolymerization, the reprecipitated polymer obtained in the presence of imidazoline nitroxyls was dissolved in the monomer in concentration 50 wt.%. Preparation of tubes, polymerization, isolation of postpolymers, and calculation of conversions were carried out similarly to the procedures described previously.

Analysis of polymers. Analysis of molecular-mass characteristics of polymers[49] was carried out on a KNAUER liquid chromatograph equipped with a cascade of Phenomenex columns (300 mm×7.8 mm, phenogel, 10 μm) with pores of 10^5 and 10^3 Å in diameter and two detectors (refractometric and UV). Tetrahydrofuran was an eluent, the column temperature was 25.0±0.1 °C. Calibration of the column was carried out using polystyrene standards with molecular mass from $2.9 \cdot 10^3$ to $1.2 \cdot 10^6$ Da.

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