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Synthesis of Self-Healing Polymers by Radical Controlled Polymerization

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Abstract

The formation of a complex of magnesium and 4-ethylterpiridyl-(N-*tert*-butyl-N-(1-diethylphosphone-2,2-dimethylpropyl))-nitroxide alkoxyamine (SG1-tpy) was investigated by means of NMR spectroscopy. The stoichiometry of the complex was determined by constructing the Job's plot. The homolysis rate constant of the alkoxyamine used was determined by means of EPR spectroscopy, and the activation energy was estimated. Polystyrene was obtained by radical controlled polymerization, and its molecular weight characteristics were studied by gel-permeation chromatography. When magnesium trifluoroacetate is added to the polymer solution, the molecular weight of the polymer increases, which indicates the formation of the complex. Polystyrene was also synthesized using the complex form of the initiator. It is shown that all the obtained polymers are narrowly dispersed, polydispersity is less than 1.5.

Keywords: radical controlled polymerization, self-healing polymers, complexation, alkoxyamines, EPR, NMR

INTRODUCTION

Self-healing polymers form a new class of materials that are able to recover their structure and properties after mechanical or some other damage [1, 2]. Self-healing may proceed autonomously, that is, without any external action, or non-autonomously, for example, under the action of ultraviolet radiation or magnetic field. At the molecular level, self-healing is implemented in polymers through the introduction of functional groups capable of reversible interactions. There are several mechanisms of self-healing, based on the recovery of specific interactions between molecules and atoms of a polymer:

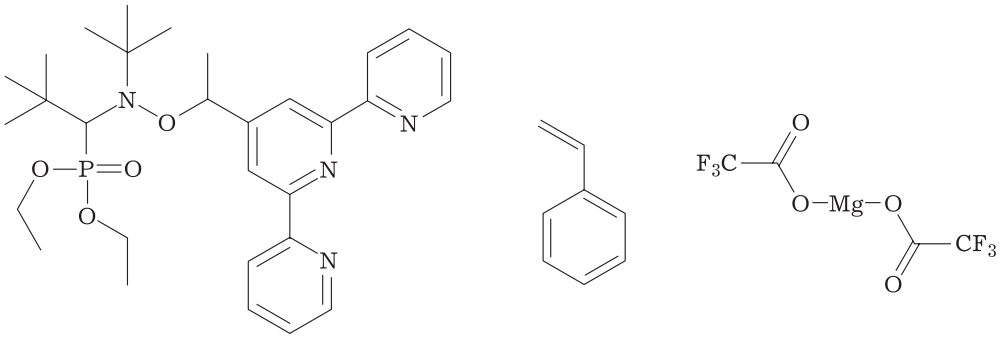
– recovery of covalent interactions, for example, through initiation of cycloaddition reactions [3–7], condensation between carbonyl and amino groups in molecules [8], or chain exchanges with disulphide, trithiocarbonate or siloxane bridges [9–13];

– recovery of hydrogen bonds between hydrophilic functional groups in the molecules [14–19];

– coordination of donor atoms in polymer molecules to metal atoms [20–22];

– implementation of stacking interaction by introducing short molecules containing aromatic fragments [23–25].

These self-healing mechanisms have been successfully tested in a number of works. However,



SG_1-tpy Styrene $Mg(tfa)_2$

Scheme 1. Objects of investigation.

in the majority of cases, only one of the above-listed self-healing mechanisms is involved. A combination of several mechanisms realized in one compound is of interest. For this purpose, it is possible to synthesize a copolymer in which different blocks would provide self-healing according to different mechanisms. At present, the most promising method of obtaining block-copolymers is radical controlled polymerization in the presence of nitroxide radicals [26–30]. At present, alkoxyamines are used as initiators for this type of polymerization. These compounds decompose reversibly under heating through homolysis of C–ON bond to form a stable nitroxide and alkyl radical that initiates polymerization. An optimal equilibrium alkoxyamine – radicals leads to the formation of polymers within a narrow fraction. To determine an optimal polymerization temperature, it is necessary to know the homolysis rate constant for alkoxyamine that is used as initiator [31]. The objects of investigation are presented in Scheme 1.

In this work we report the results on the synthesis of the first block of copolymer exhibiting self-healing properties according to the metal-ligand interaction mechanism, because the chosen polymerization method allows obtaining polymer molecules containing functional end groups. To implement this mechanism, terpyridyl and diethylphosphite fragments of alkoxyamine 4-ethylterpyridyl-(N-*tert*-butyl-N-(1-diethylphosphon-2,2-dimethylpropyl))-nitroxide (SG_1-tpy), chosen as an initiator of polymerization. Magnesium cation was chosen as the chelating agent. Styrene is used as a model monomer in the present work. The concept of self-healing underlying the basic model of this investigation is presented in Fig. 1: magnesium cations that are present in the solution impregnating the damaged area coordinate the end functional groups of polymer molecules located on the surface and link them into a complex, thus providing partial recovery of the defect.

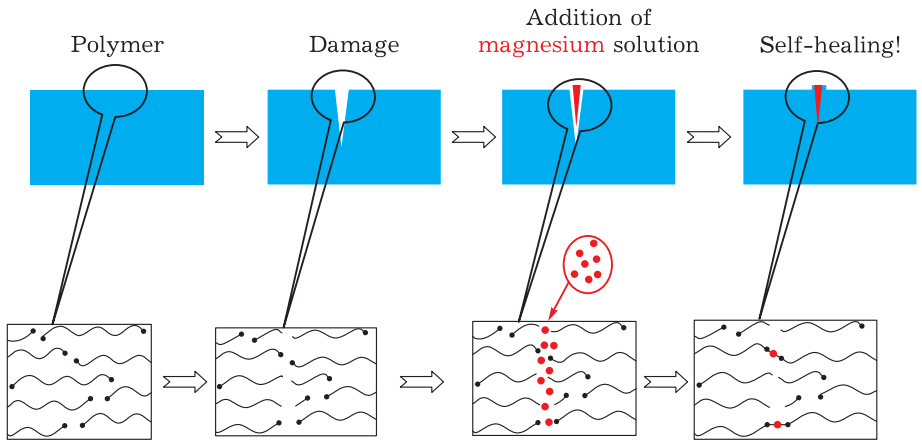


Fig. 1. Illustration of self-healing according to the mechanism of coordination bond formation between magnesium cations and the terminal functional groups of polystyrene.

EXPERIMENTAL

Materials

The following commercially available reagents were used in the work: acetone (Sigma Aldrich, 99.5 %), deuterated acetone (Sigma Aldrich, 99.9 %), deuterated chloroform (SOLVEX-D, 99.8 %), styrene (Sigma Aldrich, 99 %), tetrabutyl ammonium fluoride dehydrate (Sigma Aldrich, 98 %). Magnesium trifluoroacetate ($Mg(tfa)_2$) was provided by the Laboratory of Studying Nucleophilic and Radical Ion Reactions at NIOCh SB RAS (Novosibirsk).

Methods of investigation

The formation of a complex of alkoxyamine SG_1-tpy with magnesium ion is confirmed by means of NMR spectroscopy. To prepare 500 mL of the 10 mM solution of alkoxyamine in deuterated acetone, weighted portion of 2.8 mg (5 mmol) SG_1-tpy was prepared; magnesium trifluoroacetate 1.6 mg (5 mmol) was dissolved in 50 mL of deuterated acetone. The magnesium solution was gradually added to the solution of alkoxyamine (in the portions of 5, 10, 15, 25, 35 and 50 mL). Gradual decrease of the signal of alkoxyamine and increase of the signal of the complex were observed. All NMR spectra were recorded with a Bruker DRX500 spectrometer (Germany, 500 MHz).

To construct the Job's plot for the purpose of determining the stoichiometry of the complex, the solutions of alkoxyamine SG_1-tpy and magnesium trifluoroacetate with the total concentration of components 10 mM and the volume 1000 mL were prepared. For this purpose, the solutions of alkoxyamine and magnesium trifluoroacetate, each 40 mM, were mixed in different proportions so that the molar fraction of alkoxyamine in the solutions varied from 0.1 to 0.9. The solution of alkoxyamine was prepared by dissolving a portion of 22.2 mg in 1 mL of deuterated acetone; the solution of magnesium trifluoroacetate was prepared by dissolving 12.9 mg of the substance in deuterated acetone. After mixing, the solutions were diluted by adding deuterated acetone to the necessary volume (500 mL).

The magnesium complex of alkoxyamine SG_1-tpy was obtained by mixing 1 mL of the acetone solution of 29 mg (90 mmol) of magnesium trifluoroacetate and 1 mL of the acetone solution of 100 mg (180 mmol) of alkoxyamine. After evaporation of the solution, white precipitate was formed. It was washed with chloroform several times to remove the excess ligand. Only one signal is observed in the ^{31}P NMR spectrum of the washed precipitate, and this signal corresponds to the complex, which allows us to speak of the quantitative yield. To record ^{31}P NMR (with H_3PO_4 as the internal standard), we used a standard one-dimensional pulse sequence with complete suppression of proton signals. To record the ^1H NMR spectra (deuterated acetone, δ_H 2.3 ppm), a standard one-dimensional pulse sequence was used. The results of elemental analysis for $Mg_3C_{72}H_{84}N_8O_{20}P_2F_{18}$ complex with magnesium/alkoxyamine ratio = 3 : 2 are, wt. %: calculated, C 46.48, H 4.66, N 6.02; found, C 46.40, H 4.65, N 6.52.

To determine the homolysis rate constant for alkoxyamine SG_1-tpy, 15 solutions with the concentration $2.5 \cdot 10^{-4}$ M and the volume 100 mL each were prepared. The ampoules with the solutions were heated in a thermostat at 110 °C, put out in turn after different time intervals, and EPR spectra were recorded. The rate constant of homolysis of the magnesium complex of alkoxyamine SG_1-tpy was also carried out by means of EPR spectroscopy. A solution of the complex with the concentration $2.5 \cdot 10^{-4}$ M and nitroxide TEMPO, 10^{-3} M, 100 mL in volume, was degassed, and then EPR spectra were recorded in the thermostated sensor of Adani Spinscan spectrometer (Belarus). The parameters of EPR spectra recording were: microwave power 200 mW, modulation amplitude 1 G, scanning width 120 G, frequency 9.3 GHz.

Styrene polymerization was carried out at a temperature of 115 °C, with the ratio initiator/monomer = 1 : 400. The mass of alkoxyamine portion was 14 mg (25 mmol), styrene volume 1.1 mL (10 mmol). In the case of polymerization using the magnesium complex of alkoxyamine as initiator, its weighted portion was 47 mg (25 mmol). Monomer conversion was determined as the ratio of NMR signals of styrene and polystyrene in the sample, $CDCl_3$ was used as a solvent (500 mL of the solvent for sample volume about 50 mL). The molecular mass and polydispersity were determined by means of gel permeation chromatography (GPC) with the help of Agilent LC 1200 chromatograph (USA) with a refractometric detector. The polymers were analyzed using a PL-gel Mixed C column (Polymer Laboratories), calibrated with standard polystyrene samples (Polymer Laboratories). Tetrahydrofuran was used as an eluent with the flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Test of the possibility of magnesium complexation with alkoxyamine SG_1-tpy

The formation of magnesium complex with alkoxyamine SG_1-tpy is confirmed by means of ^{31}P and ^{1}H NMR spectroscopy (Fig. 2). One can see in the ^{31}P NMR spectra that the intensity of the signal of free alkoxyamine decreases after the addition of magnesium solution to alkoxyamine under investigation, while the signal of the complex increases. The formation of the coordination bond of magnesium ion with the electron donor groups of alkoxyamine will act as the mechanism of polymer self-healing. One can see in the ^{1}H NMR spectra (Fig. 3 and 4) that not only chemical shifts of the protons of terpyridyl group change but also the chemical shifts of the protons of diethylphosphite group. This may be evidence of the complicated structure of the complex in which magnesium cations form coordination bonds with both functional groups.

Evaluation of the stoichiometry of the formed complex by constructing the Job's plot

Evaluation of the stoichiometry of the complex was carried out by means of ^{31}P NMR titration, followed by constructing the Job's plot (Fig. 5) [32, 33]. The plot depicts the dependence of the molar fraction of complex on the molar fraction of alkoxyamine. The molar fraction of alkoxyamine is the number of moles of alkoxyamine in the initial mixture, divided by the total number of moles of alkoxyamine and magnesium. The molar fraction of the formed complex was calculated as a ratio of the integral of its signal in ^{31}P NMR spectra to the total integral of the signals of complex and free alkoxyamine. To construct this plot, the total concentration of alkoxyamine and magnesium in all samples was con-

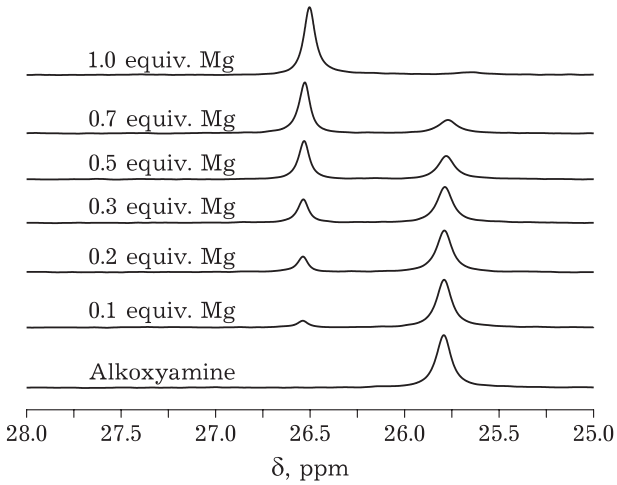


Fig. 2. Formation of the complex of magnesium with alkoxyamine SG_1-tpy, illustrated with ^{31}P NMR spectroscopy.

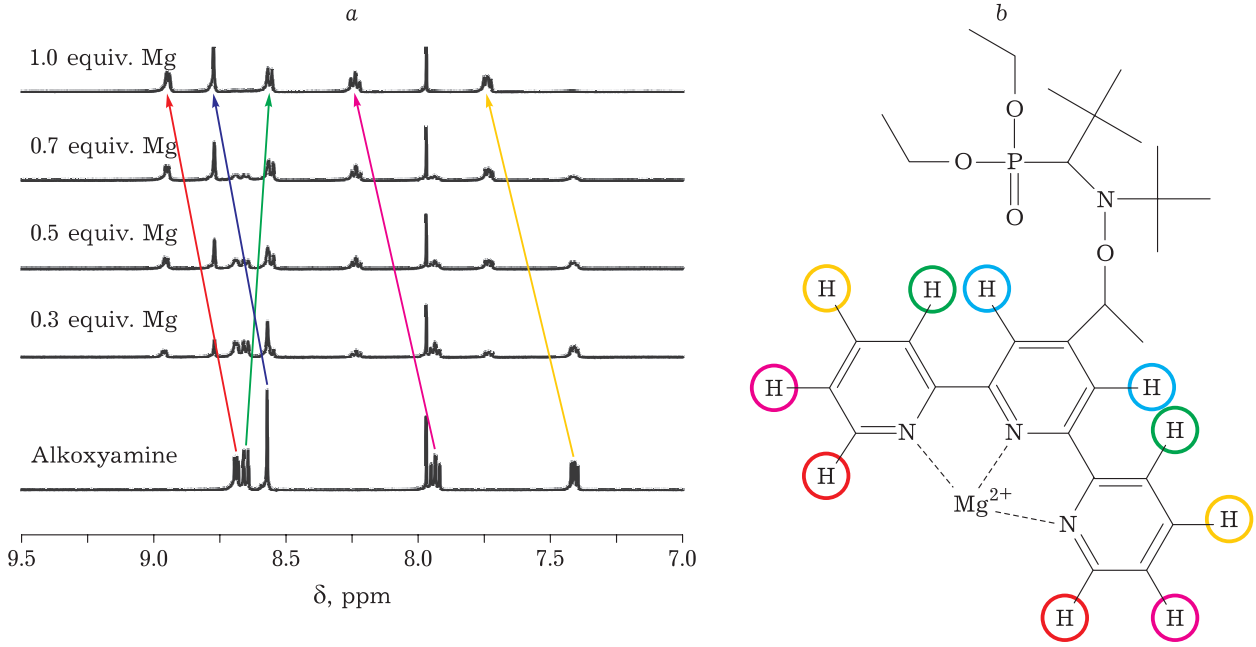


Fig. 3. Shift of the signals from protons of terpyridyl group in ^{1}H NMR spectra after the addition of magnesium solutioni to alkoxyamine SG_1-tpy (*a*); the structure of the assumed fragment of complex (*b*).

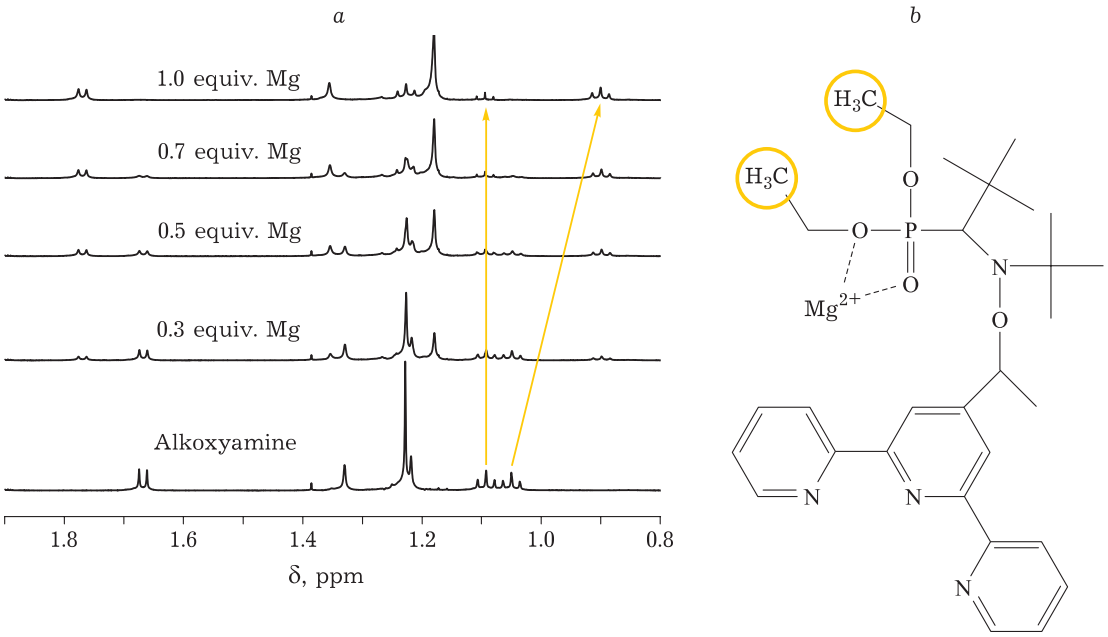


Fig. 4. Shift of the signals from the protons of diethylphosphite group in ^{1}H NMR spectra after the addition of magnesium solution to alkoxyamine SG_1-tpy (*a*); the structure of the assumed fragment of complex (*b*).

stant. Under these conditions, the maximum of complex concentration is to be observed at the stoichiometric reagents ratio. In the plot, this maximum corresponds to the molar fraction of alkoxyamine equal to 0.4, which points to the stoichiometric ratio of magnesium and alkoxyamine 3 : 2. So, this result provides evidence of the possible self-healing of the polymers containing the same electron donor grounds as terminal ones, according to the metal-ligand coordination mechanism.

Determination of homolysis rate constant and activation energy for alkoxyamine under investigation and the magnesium complex

Homolysis rate constant (k_d) for the initiator at the C–O bond was determined by means of EPR spectroscopy (Fig. 6), the measured value was $(2.0\pm0.1)\cdot10^{-3}$ s^{-1} at 110 °C. On the basis of the determined constant, the activation energy of homolysis (E_a) was evaluated using the average pre-exponential factor ($A = 2.4\cdot10^{14}$ s^{-1}) [34], the value of E_a was 125 kJ/mol.

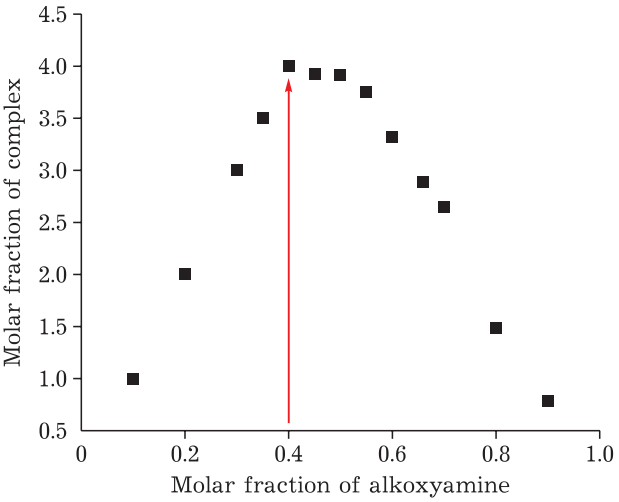


Fig. 5. The Job's plot of magnesium complexation with alkoxyamine SG_1-tpy.

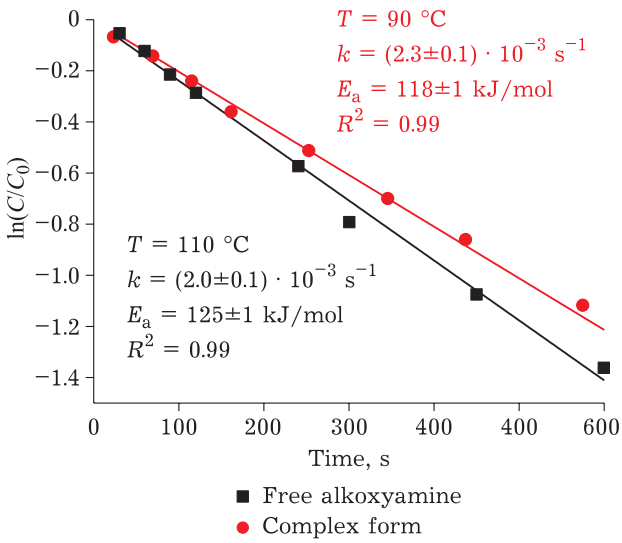


Fig. 6. Kinetics of alkoxyamine SG_1-tpy homolysis in the free and complexed forms. C, C_0 – alkoxyamine concentrations.

Homolysis rate constant k_d was also determined for the magnesium complex of alkoxyamine under investigation (see Fig. 6), which is equal to $(2.3\pm0.1)\cdot10^{-3}$ s^{-1} at 90 °C. The calculated activation energy is 118 kJ/mol. The difference between E_a values for free alkoxyamine SG_1-tpy and its complex form was 7 kJ/mol, which is typical for experiments of this kind and confirms the formation of complex [35].

Styrene polymerization. Test of self-healing properties

Styrene polymerization with alkoxyamine SG_1-tpy as initiator was carried out at 115 °C, with the monomer/initiator ratio 400:1. A linear increase in the molecular mass of the polymer with an increase in conversion was observed, which is one of the main criteria of successful radical controlled polymerization. Polydispersity index remained within the range of 1.2–1.4 (Fig. 7). A linear dependence of $\ln(C_m/C_{m0})$ on time, where C_m is monomer concentration, points to insignificant contribution from the reactions of irreversible chain termination by recombination of the growing radicals with the formation of unreactive chains.

At the next stage, the obtained polymer was titrated with magnesium solution (Fig. 8). One can see in the chromatograms obtained by means of GPC that after the addition of magnesium into the system, the peak corresponding to the mass of the polymer complex increases, and the shoulder of the peak related to free polystyrene disappears, which provides evidence of the formation of complex and is in fact self-healing phenomenon.

We also used previously synthesized complex of alkoxyamine with magnesium to carry out polymerization (see Fig. 7). The monomer/initiator ratio was the same for this experiment, but the mass of the obtained complex at the same degrees of monomer conversion increased by a factor of more than 2, which, on the one hand, provides one more confirmation of complex formation, on the other hand, suggests coordination of at least two polymer chains to magnesium cation (see Fig. 7, *a*).

CONCLUSION

Thus, a polymer containing terpyridyl and diethylphosphite terminal groups and exhibiting self-healing according to the complexation me-

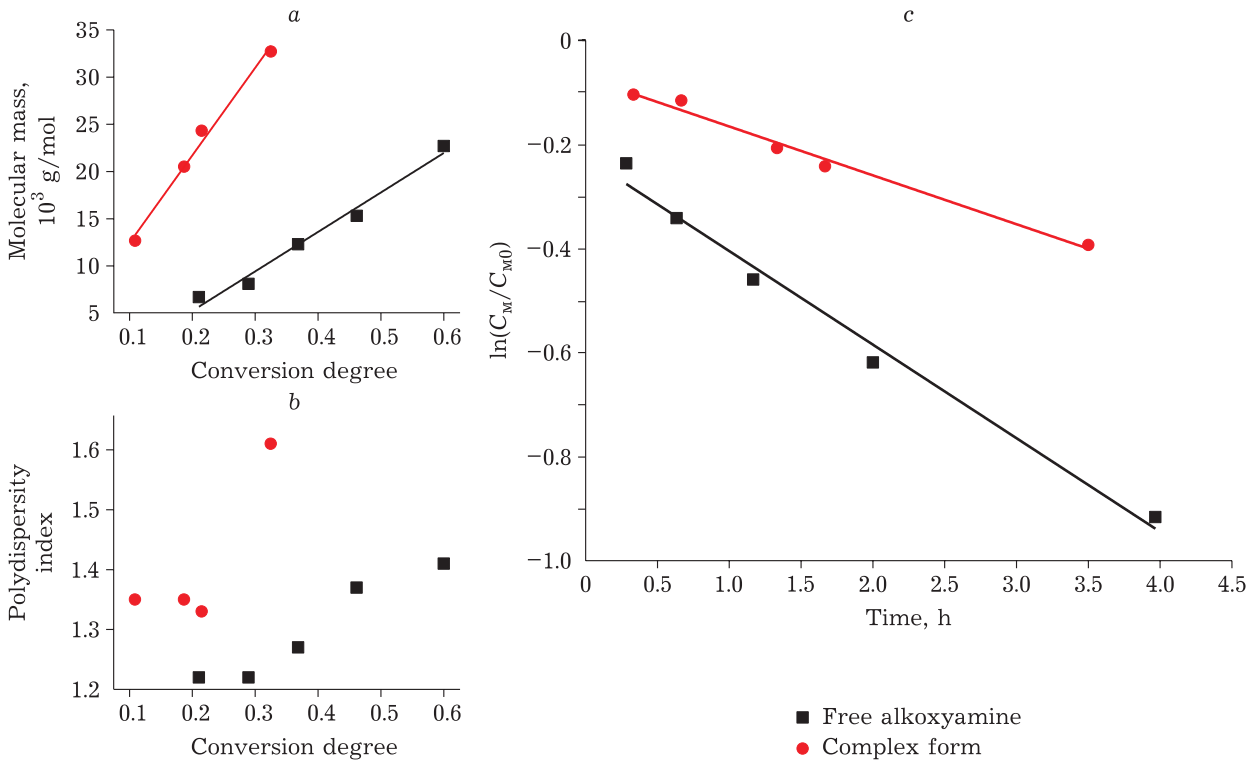


Fig. 7. Styrene polymerization in the controlled mode using the free and complex forms of lakoxyamine SG_1-tpy as initiator: *a* – linear increase in the molecular mass with monomer conversion (R^2 = 0.97); *b* – molecular mass distribution depending on conversion degree; *c* – linear dependence of $\ln(C_m/C_{m0})$ on time (R^2 = 0.98), where C_m, C_{m0} are monomer concentrations.

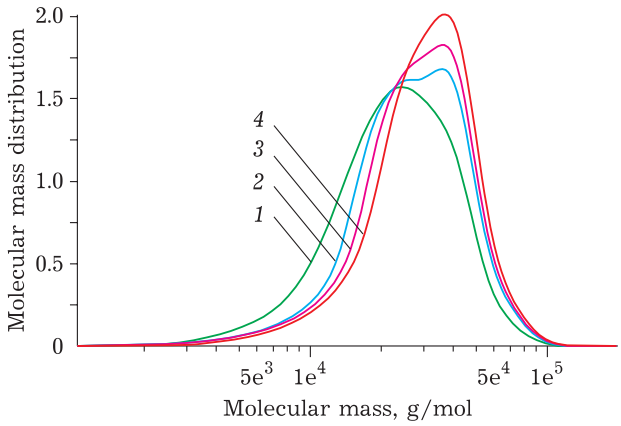


Fig. 8. Polystyrene titration with the solution of magnesium trifluoroacetate ($Mg(tfa)_2$): polymer, $M_n = 1.82 \cdot 10^4$ g/mol (*1*); polymer + 1 equiv. $Mg(tfa)_2$, $M_p = 2.16 \cdot 10^4$ g/mol (*2*); polymer + 2 equiv. $Mg(tfa)_2$, $M_p = 2.23 \cdot 10^4$ g/mol (*3*); polymer + 10 equiv. $Mg(tfa)_2$, $M_p = 2.52 \cdot 10^4$ g/mol (*4*). M_n – molecular mass of the polymer before the addition of magnesium cations into the system; M_p – molecular mass of the polymer complex formed after the addition of magnesium solution.

chanism was obtained by means of radical controlled polymerization. It is shown by means of NMR spectroscopy that complex is formed both at the terpyridyl group and at the diethylphosphite one. Evaluation of the stoichiometry of the complex by constructing the Job's plot gave the ratio 3 : 2, which points to the possibility to coordinate two alkoxyamine molecules to one magnesium cation. It is demonstrated that at the same monomer conversion degrees, the mass of the polymer obtained using the magnesium complex of alkoxyamine SG_1-tpy is more than twice as large as the mass of the polymer obtained using free alkoxyamine as polymerization initiator. The addition of magnesium trifluoroacetate solution to the polymer solution causes an increase in its molecular mass, which evidences in favour of complex formation, that is, self-healing according to coordination mechanism.

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