Kinetics of the decay of nitroxyl radicals during polymerization of a complex of acrylamide with bismuth nitrate

N. P. Piven', V. S. Savost'yanov, S. D. Babenko, and A. N. Ponomarev*

*Branch of the Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation*

Kinetics of the decay of nitroxyl radicals during spontaneous polymerization of complexes of acrylamide (AAm) with Bi^{III} nitrate has been studied by ESR. From a comparison of the experimental and calculated kinetic curves, the initiation rate constant of polymerization has been determined. The approach proposed is suitable for determining the main kinetic characteristics of other polymerizable nonparamagnetic AAm complexes with metal nitrates.

Key words: acrylamide, bismuth nitrate, complex; polymerization; ESR spectroscopy; nitroxyl radicals.

In a series of recent papers,[1–6] a new type of polymerization of acrylamide (AAm) has been described, namely, the spontaneous polymerization of complexes of AAm with metal nitrates that occurs in a solution in the water of crystallization liberated as the monomer is triturated with metal nitrate hydrates. The rate of polymerization depends on the type of metal and on the concentration of components. Based on a study of the inhibiting action of radical inhibitors, a radical mechanism for the polymerization has been proposed. It was suggested that the nitrogen oxides arising during complex formation and hydrolysis may act as the initiating species. Calorimetric studies[4] showed that spontaneous polymerization occurs with an induction period, which is also typical of the NO_2-initiated polymerization of AAm in various solvents.[7–9] For the complex of AAm with chromium nitrate, the rate of initiation has been estimated.[4] A nitroxyl radical, 2,2,6,6-tetramethylpiperidin-1-oxyl, which is widely used as a spin label or probe in ESR spectroscopy, may act as an inhibitor of polymerization.[4] This fact allowed the authors to determine the rate of the initiation of the spontaneous polymerization of AAm complexes by ESR monitoring of the decay of nitroxyl radicals added to the mixture to be polymerized at the instant of its preparation.

The approach suggested is similar to the conventional inhibiting method.[10] However, when nitroxyl radicals are used as "indicators" of the polymerization of AAm complexes, a number of peculiarities should be taken into account. First, the reaction is initiated in an acid medium (which results from the hydrolysis of the salt in the water of crystallization liberated) in which nitroxyl radicals may disproportionate.[1,12] Second, as has been noted previously,[3] the dielectric losses associated with the presence of the water of crystallization, vary in the course of polymerization and, therefore, when the decay of nitroxyl radicals is recorded, the variation in the ESR signal caused by the change in the Q-factor of the resonator should be taken into account.

With due regard for the above considerations, we studied the kinetics of the decay of nitroxyl radicals during spontaneous polymerization of acrylamide complexes using the AAm—bismuth(III) nitrate complex as an example. This allowed us to obtain quantitative characteristics of the polymerization process by comparing the experimental and calculated dependences.

Experimental

Acrylamide purified by recrystallization from benzene and the crystal hydrate of bismuth nitrate of the "chemically pure" grade were used. The mixture for polymerization was prepared by triturating AAm and crystal hydrate powders at a molar ratio of 10:1; during this operation, the water of crystallization was liberated.[1–4] The resulting concentrated solution of the complex, which may undergo polymerization, was poured into glass tubes 4 mm in diameter immediately after preparation. To carry out continuous calibration of the ESR signal, which is necessary in view of the variation of the Q-factor of the resonator, a single crystal of DPPH sealed in a glass capillary was placed into the sample. The stable nitroxyl radical, 2,2,6,6-tetramethylpiperidin-1-oxyl, used as the inhibitor was added to the mixture to be polymerized during its preparation, so that its initial concentration in the sample did not exceed $5 \cdot 10^{-3}$ mol L^{-1}. ESR spectra were recorded on an SE/X-2544 spectrometer in the three-centimeter range of wavelengths at ambient temperature. The evolution of heat during polymerization was determined using a thermocouple with a sensitivity of 40 μV deg^{-1} placed in the tube with the sample.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1572—1575, September, 1994.

Results and Discussion

The polymerizing mixture free of nitroxyl radicals does not exhibit ESR signals. A sample with 2,2,6,6-tetramethylpiperidin-1-oxyl added exhibits a typical triplet signal corresponding to the ESR lines of nitroxyl radicals in a liquid.[13] A decrease in the concentration of radicals during polymerization results in changes in the integral intensity of the ESR spectrum. Since it is only necessary to know the concentration of nitroxyl radicals at the initial instant and the time variation of their relative concentration in the same sample to determine the initiation rate, the kinetic dependence required can be plotted on the basis of the variation in the intensity of any of the lines in the ESR spectrum.[13] The concentration of nitroxyl radicals in the sample must be relatively low lest an error arise in the determination of the intensity of ESR lines due to their concentration broadening.

In the experiments performed, we found that the rate of the decay of nitroxyl radicals depends essentially on the $[\mathrm{AAm}]/[\mathrm{Bi(NO_3)_3 \cdot 5H_2O}]$ molar ratio. When the initial concentration of the initiator in the sample ($[\mathrm{I}]_0$) is equal to $5 \cdot 10^{-3}$ mol $\mathrm{L^{-1}}$ and the $[\mathrm{AAm}]/[\mathrm{Bi(NO_3)_3 \cdot 5H_2O}]$ molar ratio is 3, the radicals almost entirely disappear within the first three minutes of the measurement, which is probably due to the high concentration of nitrogen dioxide formed during the preparation of the sample and to its interaction with the radicals. The chosen ratios between the concentrations of AAm, metal nitrate, and the inhibitor make it possible to monitor the beginning of polymerization on the basis of the kinetics of the decay of the nitroxyl radicals.

Figure 1 shows typical kinetic curves of the decay of nitroxyl radicals during the spontaneous polymerization of the AAm complexes. Some spread in the data for identically prepared samples (*cf.* curves *1* and *2*) should be noted. Though we did not study in detail the causes for this irreproducibility, we believe that it may reflect the effect of the temperature and humidity of the environment.

The plots obtained contain three sections of the variation of the concentration of the radicals. At the outset the concentration of the inhibitor sharply decreases, then follows a flattened section associated with a lower rate of the decay of the radicals, and then the rate of their decay noticeably increases. The presence of these sections may apparently be explained in the following way. The first of them corresponds to disproportionation of the radicals in the acid medium and their interaction with nitrogen dioxide. The subsequent decay of the radicals is due to their interaction with the radicals of the growing polymer chain. The presence of an unmonitored impurity retards the polymerization and results in the induction period observed, which accounts for the second section. Dissolved oxygen, whose inhibiting action has been noted in a number of papers,[4,9] may act as the impurity that determines the duration of the induction period. The increase in the rate of the decay of the radicals is explained by exhaustion of this unmonitored impurity.

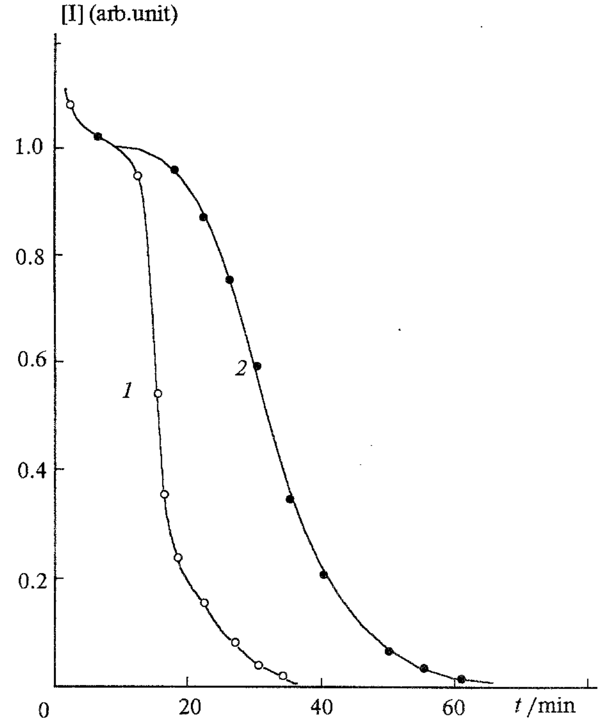

Fig. 1. The variation of the concentration of nitroxyl radicals during spontaneous polymerization of a mixture of AAm and bismuth(III) nitrate at ~20 °C for two samples (*1* and *2*) prepared in the same manner, $[\mathrm{AAm}]/[\mathrm{Bi(NO_3)_3 \cdot 5H_2O}]$ = 10:1.

The estimation of the correlation time based on the relationship between the width and intensity of the ESR lines for nitroxyl radicals[13] shows that it does not exceed 10^{-9} s over the whole range of inhibitor concentrations, *i.e.*, it may be considered that the decay of the radicals occurs in a viscous homogeneous medium. The interaction of nitroxyl radicals with AAm can be ignored, since the rate constant of this process is approximately 10 orders of magnitude smaller than the rate constant of their interaction with the radicals of the growing polymer chain.[14] Thus, the kinetics of the decay of nitroxyl radicals (without regard for their initial decay) can be described by a system of simple differential equations:[10]

$$\frac{\mathrm{d[i]}}{\mathrm{d}\tau} = -[\mathrm{i}][\mathrm{r}]\,, \tag{1}$$

$$\frac{\mathrm{d[r]}}{\mathrm{d}\tau} = A - A[\mathrm{r}]^2 - B[\mathrm{i}][\mathrm{r}] - CD[\mathrm{o}][\mathrm{r}]\,, \tag{2}$$

$$\frac{\mathrm{d[o]}}{\mathrm{d}\tau} = -C[\mathrm{o}][\mathrm{r}]\,, \tag{3}$$

with the following initial conditions:

$$[i_0] = 1, \qquad (4)$$

$$[r_0] = 0, \qquad (5)$$

$$[o_0] = 1. \qquad (6)$$

Relationships (1)—(6) are written in the reduced form, where $[i] = [I]/[I]_0$ is the relative concentration of the inhibitor, *viz.* nitroxyl radicals; $[r] = [R]/[R_{00}]$ is the relative concentration of the growing chain radicals, $[R]_{00}$ is their quasi-steady-state concentration, $[R]_{00} = (v/2k)^{1/2}$ (v is the rate of chain generation); $[o] = [O]/[O_0]$ is the relative concentration of the unmonitored impurity; $A = k/k_1$, $B = [I]_0/[R_{00}]$, $C = k_2/k_1$, $D = [O_0]/[R_{00}]$; k, k_1, and k_2 are the bimolecular constants of the decay of the chain radicals as they interact with each other (disproportionation and recombination), with nitroxyl radicals, and with the inhibiting impurity, respectively; $\tau = k_1[R_{00}]t$, where t is the current time of the process.

Figure 2 presents the kinetic curve (*1*) of the decay of nitroxyl radicals calculated from Eqs. (1)—(6) at $A = 1050$, $B = 900$, $C = 18$, $D = 1600$; these magnitudes of the parameters give the best fit with the experimental curve (*2*). Two sections can be clearly seen on the calculated and experimental plots. The flattened section with characteristic time t_i corresponds to the decay of the radicals when polymerization is inhibited by the unmonitored impurity[10] and is determined by Eq. (7)

$$t_i = [o_0]/v, \qquad (7)$$

which makes it possible to calculate the rate of initiation (v). The second section corresponds to the decay of the nitroxyl radicals under the conditions of competition with the decay of the chain radicals in their recombination. Since the nitroxyl radicals inhibit polymerization, the active process of the formation of polymer chains begins only when their concentration decreases noticeably. This is confirmed by the heat evolution observed (see Fig. 2, curve *3*). The good agreement between the calculated and experimental data allows one to evaluate the basic kinetic parameters of the polymerization. One should keep in mind that the plots obtained may be characterized by three parameters: the duration and slope of the flattened section of the curve and the characteristic time of the decrease in the concentration of the radicals in the second section. Thus, using three differential equations with four variable parameters, one cannot completely describe the process, *i.e.*, determine unambiguously all of the rate constants. From the magnitudes of the parameters found, which correspond to the coincidence of the experimental and calculated dependences (see Fig. 2), we obtain relationship (8) for the rate of initiation of polymerization

$$v = [I]_0(A/B)(\tau/t), \qquad (8)$$

then we obtain the value $v = 2 \cdot 10^{-6}$ mol L^{-1} s^{-1} ($[I]_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}) and the ratios between the rate constants are $k/k_1 = 1000$ and $k_2/k_1 = 18$.

The analysis carried out indicates that the above-noted distinction between the kinetics of the decay of nitroxyl radicals for two samples prepared in like manner (see Fig. 1) can be related to different rates of initiation of the polymerization. In fact, mathematical processing of the experimental plots shown in Fig. 1 implies that the kinetic curve with a steeper slope corresponds to a rate of initiation (v) approximately one order of magnitude greater and a simultaneous 4—5-fold increase in the concentration of the unmonitored impurity ($[O_0]$). The other parameters were not varied in the calculation. The k/k_1 ratio found agrees with the literature data on the rate constants of the interaction of nitroxyl radicals with alkyl radicals and the recombination of the chain radicals: $k_1 = 10^4$ L mol^{-1} s^{-1} (see Ref. 14), $k = 10^7$ L mol^{-1} s^{-1} (see Ref. 15).

The resulting initiation rate constant was greater than that reported previously[4] for chromium nitrate; this may be associated with the fact that it depends on the purity of the crystal hydrate used and the conditions of its hydrolysis.

The approach suggested can be applied to the determination of the basic kinetic characteristics of other

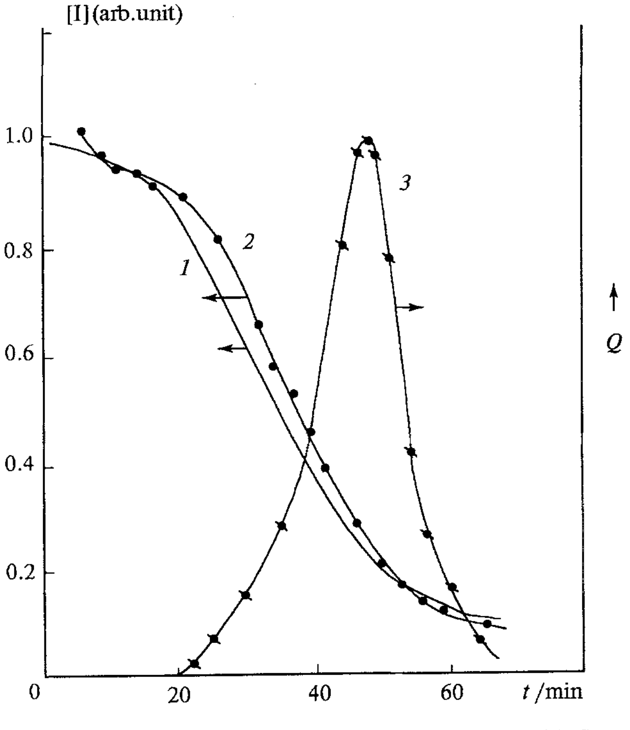

Fig. 2. The kinetics of the decay of nitroxyl radicals (*1*, *2*) and heat evolution (*3*) during polymerization of the complex of AAm with bismuth(III) nitrate: calculated from Eqs. (1)—(6) at $A = 1050$, $B = 900$, $C = 18$, $D = 1600$ (*1*); obtained experimentally at $[AAm]/[Bi(NO_3)_3 \cdot 5H_2O] = 10{:}1$ (*2*).

polymerizable nonparamagnetic complexes of metal nitrates.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No93-03-4162).

References

1. V. S. Savost'yanov, V. I. Ponomarev, B. S. Selenova, A. D. Pomogailo, A. G. Starikov, and L. O. Atovmyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 762 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 674 (Engl. Transl.)].
2. V. S. Savost'yanov, B. S. Selenova, A. D. Pomogailo, D. A. Kritskaya, and A. N. Ponomarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 768 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 680 (Engl. Transl.)].
3. V. S. Savost'yanov, V. N. Vasilets, O. V. Ermakov, E. A. Sokolov, D. A. Kritskaya, A. D. Pomogailo, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 762 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1615 (Engl. Transl.)].
4. V. S. Savost'yanov, V. V. Pilyugin, D. A. Kritskaya, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1070 [*Russ. Chem. Bull.*, 1993, **42**, 1023 (Engl. Transl.)].
5. D. A. Kritskaya, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1410 [*Russ. Chem. Bull.*, 1993, **42**, 1344 (Engl. Transl.)].
6. D. A. Kritskaya, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1414 [*Russ. Chem. Bull.*, 1993, **42**, 1348 (Engl. Transl.)].
7. S. N. Bhadani and Y. K. Prasad, *Macromol. Chem.*, 1980, **181**, 1089.
8. M. K. Mishra and S. N. Bhadani, *J. Polym. Sci.: Polym. Lett.*, 1984, **22**, 491.
9. M. K. Mishra and S. N. Bhadani, *J. Appl. Polym. Sci.*, 1985, **30**, 723.
10. N. M. Emanuel' and A. L. Buchachenko, *Khimicheskaya fizika molekulyarnogo razrusheniya i stabilizatsii polimerov* [*Chemical Physics of Molecular Destruction and Stabilization of Polymers*], Nauka, Moscow, 1988 (in Russian).
11. V. A. Golubev, Yu. N. Kozlov, A. N. Petrov, and A. P. Purmal, *Prog. React. Kinet.*, 1991, **16**, 36.
12. V. A. Golubev, V. D. Sen', I. V. Kulyk, and A. L. Aleksandrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2235 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24**, No. 10 (Engl. Transl.)].
13. A. N. Kuznetsov, *Metod spinovogo zonda* [*The Spin Probe Method*], Nauka, Moscow, 1976 (in Russian).
14. A. L. Buchachenko and A. M. Vasserman, *Stabil'nye radikaly* [*Stable Radicals*], Khimiya, Moscow, 1973 (in Russian).
15. Yu. S. Lipatov, A. E. Nesterov, T. M. Gritsenko, and R. A. Veselovskii, *Spravochnik po khimii polimerov* [*Handbook on the Chemistry of Polymers*], Naukova dumka, Kiev, 1971 (in Russian).

Received March 10, 1994;
in revised form May 20, 1994