Brief Communications

Model investigation of the polymerization of acrylamide complexes with metal nitrates by ESR

N. P. Piven, V. S. Savostyanov, S. D. Babenko, and A. N. Ponomarev*

Branch of the Institute for Energy Problems of Chemical Physics, Russian Academy of Scienses,
142432 Chernogolovka, Moscow Region, Russian Federation

Modelling experiments have shown that the interaction between NO_2 and acrylamide (AA) and the AA complex with calcium nitrate leads to the formation of radical centers. Analogous paramagnetic centers are detected directly in AA complexes with calcium nitrate. The ESR spectrum differs from that of γ-irradiated AA and is caused by nitroxyl radicals appearing in the course of the consecutive transformations in the system. The data obtained support the earlier suggested mechanism of NO_2-initiated polymerization of acrylamide complexes with metal nitrates.

Key words: acrylamide; calcium nitrate; polymerization; ESR; nitroxyl radical.

Recently unusual monomers capable of polymerization have been discovered,[1] *i.e.*, acrylamide (AA) complexes with metal nitrates. The specific properties of these monomers make possible polymerization that proceeds readily at moderate temperatures without any initiator or activator. Thus, the AA complexes of some transition metal nitrates undergo polymerization in the frontal regime at atmospheric pressure and with low "ignition" temperatures.[2] The polymerization of AA complexes with the nitrates of many metals (transition as well as non-transition) occurs spontaneously at room temperature immediately after their synthesis.[3] It has been established that these are radical processes and it is suggested that nitrogen oxides are their initiators, since they can be present in systems containing metal nitrate.[4]

In fact, nitrogen oxides are capable of initiating AA polymerization in aqueous solutions or solutions in DMF or DMSO.[5–7] But it is known that NO, unlike NO_2, does not initiate this process in an aqueous medium. And so, since the crystallization water is liberated during the formation of AA complexes, one can suggest that free NO_2 radicals are the initiators of polymerization. Since this supposition has not yet been confirmed experimentally, in the present work the paramagnetic centers which are probably formed during the NO_2 initiated polymerization of AA and its complexes with metal nitrates are investigated by means of ESR.

Experimental

Vaseline oil in a glass ampule (d = 5 mm) was saturated with NO_2 (obtained by the thermal destruction of lead nitrate) up to a concentration of ~10^{16} cm^{-3}. Then the powder of AA or of its complex was added to the vaseline oil and mixed

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carefully. The AA used was purified by recrystallization from benzene, and the crystal-hydrates of the metal nitrates used, *i.e.*, $Ca(NO_3)_2{\cdot}4H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, and anhydrous $Pb(NO_3)_2$, were of "chemically pure" grade and gave no ESR signals. AA complexes with metal nitrates were prepared by mixing finely divided AA and the corresponding nitrate powders in a 4:1 molar ratio (see Refs. 1, 8, 9), which led to the liberation of the crystallization water followed by the dissolution of the polymerization-capable complex. In the case of Pb^{II} nitrate, a small amount of water was added to the mixture. The concentrated solution of the AA complex that formed was placed in ampules (d = 3÷5 mm). To obtain the solid phase AA complex with Ca^{II} nitrate, the product of the polymerization was dried, washed with ether, and evacuated.

To register the ESR spectra, the ampules with the samples were placed into the resonator of a 3 cm diapason E/X-2544 spectometer. All measurements were carried out at room temperature. To obtain the growing poly(acrylamide) (PAA) radical, AA was γ-irradiated in the evacuated ampule at −196 °C (irradiation dose 20 kJ kg^{-1}, dose power 1.4 J kg^{-1} s^{-1}, ^{60}Co source).

Results and Discussion

No ESR signals were registered during the spontaneous polymerization of any of the investigated AA complexes with metal nitrates. This was apparently due to the small concentrations of the radicals formed and the considerable deterioration of the quality of the resonator because of the presence of the liberated crystallization water in the system. Therefore an attempt was made to reveal the interaction of NO_2 with AA and its complexes in a model meduim with small dielectric losses. Vaseline oil was chosen to be this kind of medium since the needed concentration of NO_2 could be easily reached in it.

Nitrogen dioxide is a stable σ-electron radical and its stucture and ESR spectrum have been studied quite thouroughly.[10] The ESR spectrum of NO_2 in vaseline oil (a single line with a width of 15 mT and g-factor equal to 2.00) registered by us is presented in Fig. 1, *a* and corresponds to the commonly known spectrum. AA powder in vaseline oil which does not contain NO_2 gives no ESR signal, whereas the sample of the AA complex with Ca^{II} nitrate gives a weak triplet (Fig. 1, *b*). When the interaction of this complex with the NO_2 dissolved in vaseline oil occurs, the intensity of this line increases substantially (Fig. 1, *c*) and the wide NO_2 band actually dissappears. Afterwards, the signal intensity of the triplet decreases. When non-coordinated AA reacts with the dissolved NO_2, a similar triplet appears against the background of the wide NO_2 band, and the intensity of the former diminishes, while the intensity of the latter eventually increases.

It should be noted that the ESR spectrum of the radical discovered is an anisotropic triplet, that is, it differs from the symmetrical triplet belonging to the growing PAA radical (**1**) formed in γ-irradiated AA at room temperature (Fig. 2, *a*) as a result of the addition of an AA molecule to the initiating radical.[11]

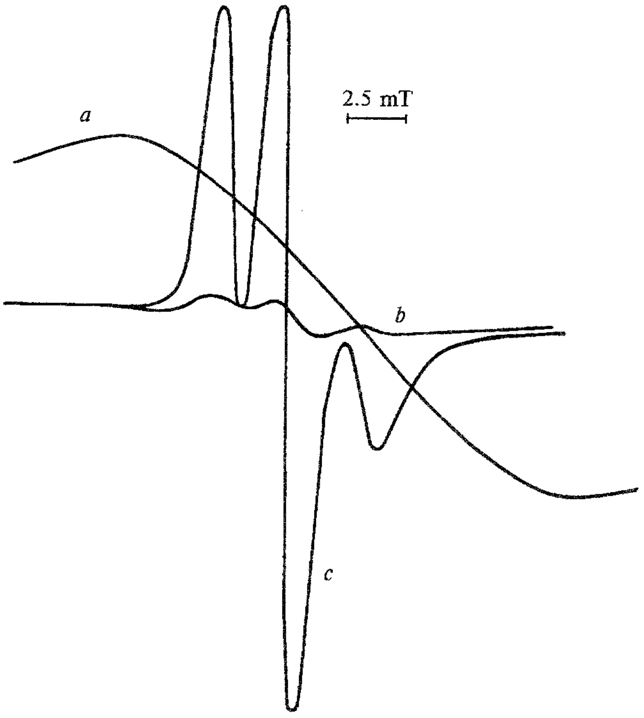


Fig. 1. ESR spectra of the radical forms in vaseline oil at 20 °C: NO_2(*a*); AA complex with Ca^{II} nitrate (*b*); product of the interaction between AA-Ca^{II} nitrate complex and NO_2 (*c*).

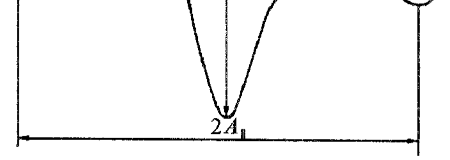
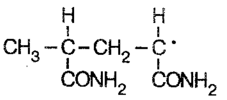
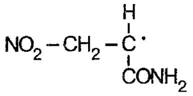


Fig. 2. ESR spectra of γ-irradiated AA (*a*) and of the product of the interaction between the AA-Ca^{II} nitrate complex and NO_2 in vaseline oil (*b*).


$$CH_3-\underset{CONH_2}{\overset{H}{C}}-CH_2-\underset{CONH_2}{\overset{H}{C}}{\cdot}$$

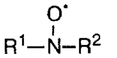
1

The addition of nitrogen dioxide to the double bond of the monomer[5] must lead to another structure (**2**).



$$NO_2-CH_2-\overset{H}{\underset{CONH_2}{C^{\bullet}}}$$

2

However, it has been noted[12–14] that during the interaction of NO_2 with compounds containing >C=C< double bonds structures of this type could not be registered directly, though nitroxyl radicals of the type  $R^1-\overset{O^{\bullet}}{N}-R^2$ (**3**) are present in the system. These radicals can be formed in the course of the consecutive transformations of type **2** radical forms and the products of their reactions with NO_2 according to the schemes described before.[12,13] The characteristic features of the ESR spectra of radical **3** are the anisotropic hyperfine structure and the anisotropic *g*-factor.

The spectrum which we registered (Fig. 2, *b*) is an anisotropic triplet ($A_{\|} = 3.2$ mT, $g_{\|} = 2.0021$), *i.e.*, it is characteristic of type **3** nitroxyl radicals. The mechanism of the formation of such radicals during the interaction of NO_2 with acrylamide is apparently analogous to that suggested earlier,[12,13] taking into account the initiation and prolongation of the chain during the polymerization. Apparently, our discovery of the nitroxyl radical is indirect evidence of the existence of its short-lived precursor of type **2**, which is actually the initiator of the acrylamide polymerization.

The role of the NO_2 source in the system under investigation could be played by metal nitrates partially hydrolyzed in an aqueous medium:[15]

$$M(NO_3)_n + H_2O \rightleftharpoons M(OH)(NO_3)_{n-1} + HNO_3 .$$

The nitric acid forming is in equilibrium with NO_2:[15]

$$4HNO_3 \rightleftharpoons 4NO_2 + O_2 + 2H_2O.$$

The N_2O_4 present in the system in equilibrium with NO_2 (see Ref. 10) can not affect our conclusions.

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