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Aminoxyl radicals as crosslinks for macromolecules of polyvinylpyrrolidone

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Using polyvinylpyrrolidone as an example, it has been shown that photolysis of ceric ammonium nitrate at room temperature can result in crosslinking of macromolecules. This process correlates with the formation of stable aminoxyl radicals, which are registered by EPR. The mechanism involves photodissociation of nitrate radicals produced in the primary reaction into nitric oxide or nitrogen dioxide depending on the wavelength of the light, and simultaneous formation of macroradicals. The accumulation of aminoxyl radicals occurs owing to the acceptance of macroradicals by nitroso or nitro groups according to which mechanism of the nitrate radical photodissociation prevails. Similar radical reactions are observed in *N*-methyl-2-pyrrolidone.

Introduction

Radicals of nitrogen trioxide differ from those of other nitrogen oxides in having high activity in reactions with various organic compounds.[1–6] Characteristic reactions of these radicals are hydrogen atom abstractions from C–H bonds and addition to double bonds. Besides which, nitrogen trioxide can appear as an oxidiser of organic substances. Along with it, the NO_3 radicals are subjected to decomposition in thermal and photochemical processes. The thermal decomposition of nitrogen trioxide generated by pulse radiolysis of concentrated aqueous solutions of a nitric acid, proceeds with a high rate ($k_{298\ K} = 8 \cdot 10^3\ s^{-1}$) by the reaction (1):[7]

$$NO_3 \longrightarrow NO_2 + O \qquad (1)$$

The NO_3 radicals have three bands of absorption in the visible region of an optical spectrum with λ_{max} at 600, 640 and 675 nm, and in the UV region at 340–360 nm.[1,4,7,8–10] The action of light on NO_3 radicals causes their dissociation by two mechanisms: with formation of NO_2 and atomic oxygen similarly to reaction (1) along with the formation of nitric oxide and molecular oxygen (reaction (2)):[8]

$$NO_3 \longrightarrow NO + O_2 \qquad (2)$$

The efficiency of the NO_3 transformations by one or another of the pathways is determined by the spectral composition of light. The approximate border of wavelengths for NO_3 dissociation by these mechanisms has been determined. Above 570 nm, NO_3 is dissociated into NO and O_2 with a large (~ 1) quantum yield; but below 570 nm, the products of photolysis are NO_2 + O.[8]

One of the most widespread ways of generating NO_3 is photolysis of the Ce(IV) nitrates, in particular ceric ammonium nitrate (CAN):

$(NH_4)_2Ce(NO_3)_6$. The absorption spectra of CAN are characterised by a wide and intensive band with a maximum at 305 nm (ε = 5890 l mol^{-1} cm^{-1}), which is caused by a charge transfer from the nitrate anion to Ce^{4+}.[11] During action of light in the given spectral region, a photoreduction of CAN takes place by the reaction (3):[11,12]

$$Ce^{4+}NO_3^- \xrightarrow{h\nu} Ce^{3+} + NO_3 \qquad (3)$$

Thus, in the course of the CAN photolysis, along with nitrogen trioxide, other active radical particles can be generated: NO, NO_2 and atomic oxygen. Use of light with different spectral distributions allows generation of the radical species in varying ratio. Thereby there is an opportunity in principle for research of the mechanism of radical reactions with participation of nitrogen oxides based on purposeful regulation of a yield of those or other products of these reactions. In this connection there is certain interest in the use of the CAN photolysis for generation of the nitrogen-containing stable radicals, which find wide applications as spin probes and labels.[13] It is shown by the EPR technique, that the interaction of nitrogen dioxide with some functional groups of high-molecular and low-molecular substances results in formation of stable radicals.[14–16] For example, the effective formation of such radicals occurs in an atmosphere of NO_2, if macromolecules contain double carbon–carbon bonds or amide groups. Nitric oxide is less reactive than nitrogen dioxide, but NO readily reacts with free radicals to give nitroso compounds, which are effective spin traps. Therefore photolysis and radiolysis of a number of polymers (polytetrafluoroethylene, polymethylmethacrylate, cellulose triacetate) are accompanied by the appearance of stable nitrogen-containing radicals.[14] Stable radical generation in this way takes place in sufficiently drastic conditions of γ-radiolysis and direct action of UV light on macromolecules, resulting in essential damage of the chemical structure and formation of various products owing to collateral thermal and photochemical reactions. From this viewpoint the CAN photolysis has certain advantages, because light used for generation of active radicals is not absorbed by macromolecules. In that case primary macroradicals are formed in reactions of hydrogen atom abstractions by atomic oxygen in the ground triplet state from C–H bonds of monomer units.[17] Since the atomic oxygen should be rather active in reactions with C–H bonds, the stable radical generation during the CAN photolysis does not require an availability of the functional groups reactive to nitrogen oxides. In the present work, by using the example of polyvinylpyrrolidone (PVP), widely used in pharmacology and medicine, the features of the stable aminoxyl radical formation during the CAN photoreduction are considered.

Experimental

The commercial CAN "Merck" and PVP with $M_\eta = 3.0 \cdot 10^5$ were used in the experiments. Samples of PVP with additives of

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CAN (0.2–0.05 mol kg^{-1}) were prepared from their combined aqueous solutions as coats of ~ 40 μ thickness on glass plates of size 1 × 4 cm. Before photolysis, samples were carefully dried in a vacuum chamber. Then the plates with a polymeric layer were placed in quartz cells. After pumping to a pressure of ~ 10^{-3} mm Hg, samples were irradiated by filtered light of a mercury lamp with $\lambda > 280$ nm or $280 < \lambda < 400$ nm. The results of photolysis of PVP with CAN are partial crosslinking of macromolecules and appearance of stable radicals. The crosslinking degrees of PVP, depending on CAN concentrations and time of photolysis, were examined by the gel-fraction yield. For measurement of a gel-fraction yield, plates with a polymeric layer previously weighed were treated after photolysis with chloroform for removal from samples of a soluble fraction. Then plates with the rest of the covering were dried and again weighed. This operation was repeated until the weight of a plate became constant. The accuracy of determination of a gel-fraction yield in this way is in the limits of 10%. For comparison, the gel formation was examined in samples during photolysis in the air. For measurement of an amount of stable radicals after irradiation by light, a polymeric layer was removed from the plates and placed in EPR tubes. The EPR spectra were recorded at room temperature on the X-band spectrometer "1306 (USSR)" with 100 kHz modulation. In some experiments, photolysis of samples and registration of EPR spectra were carried out simultaneously at 77 K. The hyperfine coupling constants and *g*-factors of radicals were measured with the help of the standard spectrum of Mn^{2+} ions in MgO. The concentrations of radicals were estimated to an accuracy of 15% by integration of their EPR spectra and by comparison with a standard signal (ultramarine) containing a known quantity of spins. For confirmation of the mechanism of radical reactions in PVP, the photolysis of CAN was examined in *N*-methyl-2-pyrrolidone (MP) "Merck", chosen as a low-molecular analogue of the polymer. Irradiation of MP solutions with CAN ($C_{CAN} = 9.0 \cdot 10^{-3}$ mol l^{-1}) by light with $\lambda > 280$ nm and registration of EPR spectra were carried out at room temperature.

Structures of radicals produced by photolysis of CAN in PVP and MP

The formation of nitrogen dioxide by reactions (3, 1) in the process of the CAN photolysis is confirmed by EPR spectra obtained at 77 K. The spectrum at an initial stage of irradiation by light with $\lambda > 280$ nm is shown in Fig. 1a. It represents basically a triplet signal with obviously expressed anisotropy of the *g*-factor and hyperfine structure. Essentially, it is well in accord with a spectrum of NO_2 radicals trapped in ice at 77 K.[18] The analysis of Fig. 1a has given much the same values of *A* and *g*-tensors: $A_{xx} = 5.31$ mT, $A_{yy} = 4.93$ mT, $A_{zz} = 6.54$ mT, and $g_{xx} = 2.0066$, $g_{yy} = 1.9929$, $g_{zz} = 2.0024$.

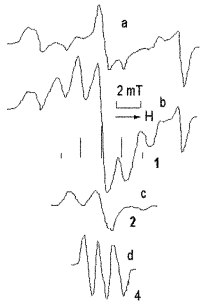


Fig. 1 EPR spectra of PVP (a, b and c) and MP (d) with CAN after irradiation by light with $\lambda > 280$ nm at 77 K (a, b) and 295 K (c, d); time of photolysis 2 min (a), 60 min (b, c and d).

During the further irradiation of samples, additional lines appeared on a background of the NO_2 signal, which belong most likely to radicals of PVP (Fig. 1b). As nitrogen dioxide can not react with the hydrogen atom abstraction at 77 K, a growth of new signals in the EPR spectrum should be attributed to radicals formed by interaction of atomic oxygen with macromolecules, for example, in reaction with least strong tertiary C–H bonds (reaction (4)):

$$\sim CH_2CHXCH_2\sim \overset{+O}{\rightarrow} \underset{\mathbf{1}}{\sim CH_2C^{\bullet}XCH_2\sim} + OH \qquad (4)$$

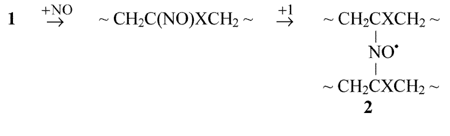
where X is $N{-}[CH_2]_3{-}CO$. The spectrum of macroradicals **1** in PVP represents a five-component signal with a distance between components of ~ 1.8 mT,[19] $g = 2.0036$. These macroradicals can also arise from the subsequent reaction of sufficiently active hydroxy radicals (reaction (5)):

$$\sim CH_2CHXCH_2 \xrightarrow{+OH} \mathbf{1} + H_2O \qquad (5)$$

In addition, the radical **1** formation can take place due to reactions of very active nitrogen trioxide[4] as well as NO_2. Nitrogen dioxide also is capable of initiating the hydrogen atom abstraction from PVP at room temperature (reaction (6)):[14]

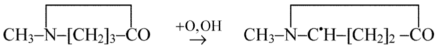
$$\sim CH_2CHXCH_2\sim \xrightarrow{+NO_3,NO_2} \mathbf{1} + HNO_3\,(HNO_2) \qquad (6)$$

The radicals **1** and NO_2 are stabilised only at low temperatures. Photolysis of samples at room temperature results in formation of stable radicals, the EPR spectrum of which is shown in Fig. 1c. It represents a triplet with typical parameters for dialkylaminoxyl radicals with a hindered rotation: $A_{II}^{N} = 3.18$ mT and $g_{II} = 2.0024 \pm 0.0005$ (radical **2**). Spectra of this kind are characteristic for aminoxyl radicals in a polymeric matrix.[14] It is quite reasonable to explain their formation by conversions of macroradicals **1**. One can assume that two radicals **1** in reactions (4, 5) are produced at very close distances in a polymeric matrix. This is because the intermediate radical pairs of macro- and hydroxy radicals are formed in the initial stage of reaction (4). The species of this kind registered by EPR in some glassy, crystal and polymeric media at low temperatures have characteristic distances between radicals of 0.5–0.6 nm.[20] If radicals are stabilised at a little more distance, they can be registered as isolated particles. This case is presumably realised for radicals **1** at 77 K (Fig. 1b). The intermediate radical pairs of **1** and hydroxy radicals can efficiently recombine at room temperature, and apparently this is the main process in PVP. Nevertheless, hydroxy radicals are also capable of reacting with neighbouring macromolecules. Then as a result of the following reaction (5), two closely located macroradicals **1** are generated. The lifetime of the macroradicals until their contact in such a mutual arrangement can be essentially more than that for previous radical pairs because of strong hindrance to molecular motions in solid polymers. Under conditions of photolysis by light with $\lambda > 280$ nm nitric oxide is generated, in parallel with radicals **1**. Small in size NO can diffuse relatively easily to radicals **1** giving nitroso compounds, which after accepting the close spaced second radical turn to radicals **2** (reaction (7)):



$$\mathbf{1} \overset{+NO}{\rightarrow} \sim CH_2C(NO)XCH_2\sim \overset{+1}{\rightarrow} \begin{array}{c} \sim CH_2CXCH_2\sim \\ | \\ NO^{\bullet} \\ | \\ \sim CH_2CXCH_2\sim \\ \mathbf{2} \end{array} \qquad (7)$$

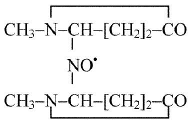
Seemingly in a like manner, stable aminoxyl radicals are formed in MP with additives of CAN in the same conditions. Their spectrum is shown in Fig. 1d. It is an isotropic triplet with peak ratio 1 : 1 : 1 and parameters $a^N = 1.42$ mT and $g = 2.0058$, which indicates a fast rotation of the radicals in the liquid phase. It seems that the least strong C–H bonds in MP belong to α-methylene groups of the ring. Therefore, it is necessary to expect the formation of radicals **3** in primary reaction (8):



$$CH_3\text{–}N\text{–}[CH_2]_3\text{–}CO \xrightarrow{+O,OH} CH_3\text{–}N\text{–}C^{\bullet}H\text{–}[CH_2]_2\text{–}CO \quad (8)$$

3

The radicals **3** are converted to aminoxyls **4** by analogy with scheme (7):



4

In principle, it is possible to assume the hydrogen atom abstraction by active atoms and radicals from methyl groups of MP with the formation of radicals **5**:

$$XCH_2\text{–}N(O^{\bullet})\text{–}CH_2X$$

5

However it is known that di(alkyl)aminoxyl radicals containing methylene groups at the radical centre are capable of disproportionating giving nitrone and hydroxylamine (reaction (9)):[21]

$$\mathbf{5} + \mathbf{5} \longrightarrow XCH{=}N^{+}(O^{-})\text{–}CH_2X + XCH_2\text{–}N(OH)\text{–}CH_2X \quad (9)$$

Along with these reasons, the form of their EPR spectrum verifies an accordance of the structure **4** to aminoxyl radicals in MP. It is expected that the additional splitting for each component of a spectrum to quintet must be in the structure **5**. Here α-alkylmethylene protons give the sufficiently large characteristic splitting ~ 1 mT.[22] Possible additional splittings to triplet on methine protons for **4** can be much less (~ 0.15–0.30 mT)[23] seemingly because of the different mutual space orientation of α-C–H bonds and the unpaired electron in comparison with **5**. It may be that these splittings are concealed in the width of main spectral components, which amounts to ~ 0.6 mT (Fig. 1d). It is necessary also to take into account that the disproportionation rate for the aminoxyl radicals having α-alkylmethine protons is strongly slowed down. So, for example, the rate of this process for $(i\text{-}Pr)_2NO$ is approximately 340 times lower than for Et_2NO at 298 K.[21] All these arguments permit us to believe that aminoxyl radicals in MP have structure **4**.

Influence of spectral composition of light on kinetics and mechanism of the aminoxyl radical generation in PVP

On the basis of the EPR spectrum, shown in Fig. 1c, it is possible to conclude that stable radicals of an aminoxyl type are formed during the initial NO_3 generation in PVP. However, strong anisotropy of the hyperfine structure, caused by hindered molecular mobility, does not allow us to draw a conclusion about the nature of the substituents at the radical centre. This spectrum gives only the prerequisites to postulate the mechanism of the stable radical formation by the reactions (4–7). According to this mechanism, aminoxyl radicals are crosslinks for macromolecules, and hence the radical concentration should be connected with yield of a gel-fraction (m_g/m_0) in the course of a sample photolysis.

Kinetic curves of the gel accumulation under action of light with $\lambda > 280$ nm and $280 < \lambda < 400$ nm are given in Fig. 2a, b. As is evident from the figures, if light includes both UV and visible spectral regions, the process is characterised from the outset by monotonous retardation with time. On the contrary, during photolysis only by UV light some induction period is observed, moreover it is especially noticeable at comparatively small initial concentrations of CAN. The availability of the induction period suggests that some intermediate product is formed and initiates crosslinking of macromolecules.

The kinetics of the radical **2** accumulation also demonstrates a qualitatively similar character (Fig. 3a, b). This process under exposure to light with $280 < \lambda < 400$ nm occurs with an acceleration after formation of small radical concentrations at initial stages (Fig. 3b); in this case the initial stages approximately correspond to the induction period of the gel-fraction formation (Fig. 2b). Both processes of gel and aminoxyl radical formation are in direct correlation during photolysis by light with $\lambda > 280$ nm. The linear dependencies shown in Fig. 4a, b indicate that. Formally, the kinetics of any product N formation with monotonously decreasing rate can be represented by the equation (10):

$$N = at^{n} \quad (10)$$

where a and n are empirical parameters, and $0 < n < 1$. As follows from Fig. 4a, b, kinetic curves are linearised in the same co-ordinates of equation (10). The value of parameter $n = 0.88$ is obtained from analysis of kinetic dependencies by a least squares method. Such regularity confirms the mechanism (7), according to which the radicals **2** are formed with participation of nitric oxide and can be considered as crosslinks for macromolecules. The yield of crosslinks is most likely controlled by

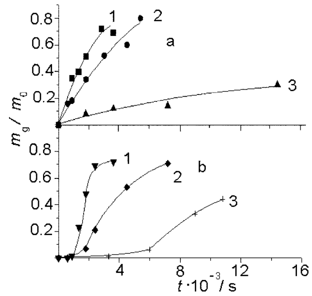


Fig. 2 Kinetics of accumulation of gel-fractions in PVP during photolysis by light with $\lambda > 280$ nm (a) and $280 < \lambda < 400$ nm (b) at C^{0}_{CAN} : 0.19 (1); 0.13 (2); 0.055 mol kg^{-1} (3).

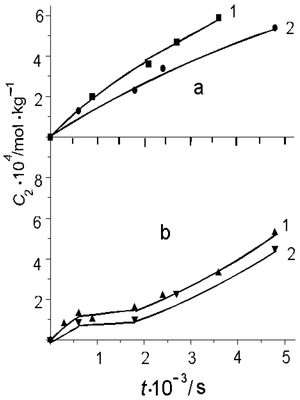


Fig. 3 Kinetics of formation of radicals **2** in PVP during photolysis by light with $\lambda > 280$ nm (a) and $280 < \lambda < 400$ nm (b) in vacuum at C^{0}_{CAN}: 0.19 (1); 0.13 mol kg^{-1} (2).

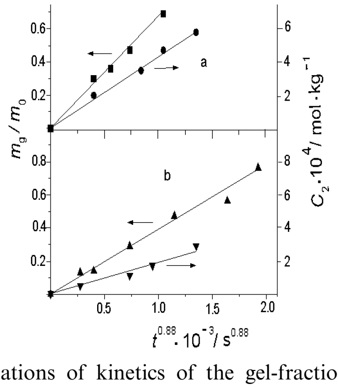
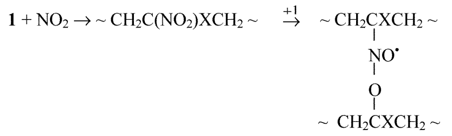


Fig. 4 Linearisations of kinetics of the gel-fraction and radical **2** formation in PVP in coordinates of eqn. (10) during photolysis by light with $\lambda > 280$ nm at: C^{0}_{CAN} 0.19 (a); 0.13 mol kg^{-1} (b).

effectiveness of the hydroxy radical exit from intermediate radical pairs in reaction (4) and the NO diffusion to radicals **1**. If crosslinking were to occur mainly in some other way, for example, by direct recombinations of radicals **1**, then the radical **2** and gel accumulations would not be correlated as follows from Fig. 4a, b. It should be also noted that the limiting concentration of aminoxyl radicals accumulated in samples does not exceed 10^{-3} mol kg^{-1}, which is much less than initial concentrations of CAN in PVP. The reason is that the main part of macroradicals **1** is consumed in side processes without aminoxyl formation. That is why there are grounds also to assume that they can recombine most likely with hydroxy radicals at the primary stage of radical generation. The kinetics observed (Fig. 3a) shows that the formation of aminoxyl radicals as a result of consecutive encounters of macroradicals **1** with the macromolecular nitroso compound is hardly possible in solid PVP. In this case the process must be autoaccelerated. Therefore, radicals **2** during photolysis by light with $\lambda > 280$ nm are produced as a result of "pseudocage" reactions of closely located macroradicals **1** with NO.

Another situation is observed during UV photolysis of samples (Fig. 2b). The induction period in the kinetics of the gel formation assumes a peculiar mechanism of the aminoxyl radical generation in these conditions. It must be remembered that the NO_3 dissociation by reaction (2) is strongly depressed, and the main path of photo-transformation of nitrate radicals is their decomposition into NO_2 and atomic oxygen. Thus primary closely located macroradicals **1** formed in reactions (4, 5) can recombine with nitrogen dioxide. Similarly to nitroso compounds, nitro compounds are capable of adding alkyl radicals with the formation of a stable spin adduct. Such an eventuality was shown by EPR on an example of aromatic nitro compounds.[24] For PVP the process resulting in radicals **2** can be presented as follows (reaction (11)):



$$\mathbf{1} + NO_2 \rightarrow \sim CH_2C(NO_2)XCH_2 \sim \overset{+1}{\rightarrow} \sim CH_2C(-NO^{\bullet}-O-CXCH_2\sim)XCH_2 \sim \qquad (11)$$

6

The alkoxyaminoxyl radicals **6** are unstable at ordinary temperatures[15] and break down into alkoxy radicals and nitroso compounds (reaction (12)):

$$\mathbf{6} \rightarrow \underset{\mathbf{7}}{\sim CH_2C(O^{\bullet})XCH_2 \sim} + \sim CH_2C(NO)XCH_2 \sim \qquad (12)$$

Alkoxy radicals **7** are very active in reactions of hydrogen atom abstraction[25] and are converted to radicals **1** by interaction with tertiary C–H bonds of neighbouring macromolecules (reaction (13)):

$$\mathbf{7} + \sim CH_2CHXCH_2 \sim \longrightarrow \mathbf{1} + \sim CH_2C(OH)XCH_2 \sim \qquad (13)$$

If radicals **1** are allocated in the range of accepting with nitroso groups they turn to radicals **2** by reaction (7). However, additional intermediate reactions including decomposition of alkoxyaminoxyl radicals and changing of alkoxy to alkyl radicals make the spin trapping process in this case seemingly less preferable from the kinetic point of view. In the course of the reaction (13), a spatial separation implying an exit of radicals **1** and nitroso groups from the reacting "cage" can happen. As a consequence, a difficulty for their approach appears in conditions of hindered molecular mobility. This effect can be especially appreciable at the beginning of photolysis, when concentrations of nitro groups in macromolecules are rather small, and the radical decay in recombination with NO_2 prevails over spin trapping. Owing to this the induction period of a gel accumulation is observed in the absence of a competitive way of aminoxyl formation connected with the nitric oxide photogeneration (Fig. 2b). The auto-accelerated character of the radical **2** formation in samples on exposure to UV light (Fig. 3b) is also in agreement with the scheme (11–13).

Table 1 Concentrations of radicals **2** in gel-fractions of PVP with CAN during photolysis; $C_{CAN}^{0} = 0.19$ mol kg^{-1}

	$C_2 \cdot 10^4$/mol kg^{-1}	
$t \cdot 10^{-3}$/s	$\lambda > 280$ nm	$280 < \lambda < 400$ nm
1.2	6.2	—
1.5	7.3	—
2.1	9.8	—
2.4	—	5.6
2.7	9.8	—
3.6	9.6	4.9
4.8	—	5.5

One can observe in Fig. 2 a,b that the gelation rate can be higher under the UV light action after an induction period than during photolysis by light with $\lambda > 280$ nm. This effect is most pronounced at low concentrations of CAN. Such behaviour is explicable if it is remembered that light with $\lambda > 280$ nm generates oxygen in reaction (2). As oxygen is accumulated in samples, the oxidation of nitric oxide begins. Besides, the conversion of radicals **1** to peroxy radicals takes place. Both the processes must decrease the yield of crosslinks; peroxy radicals do not give stable adducts in reactions with nitroso compounds. In support of this interpretation, photocrosslinking of samples in air has been studied. One can see from Fig. 5 that an induction period is apparent in the gel formation during irradiation by light with $\lambda > 280$ nm. Furthermore, the crosslink yield is noticeably decreased in comparison with photolysis in vacuum at the same concentration of CAN. Apparently, the presence of oxygen in samples inhibits the reactions of the radical **2** formation through nitric oxide and makes possible to a certain extent only the mechanism connected with reactions (11–13).

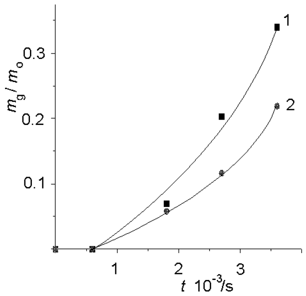


Fig. 5 Kinetics of accumulation of gel-fraction in PVP during photolysis in air by light with $\lambda > 280$ nm (1) and $280 < \lambda < 400$ nm (2) at C_{CAN}^{0} of 0.19 mol kg^{-1}.

Measurements of the radical **2** concentrations separately in gel-fractions show that, as expected, they are higher than those averaged over the sample (Table 1). In essence, their values at late stages of photolysis are invariable. By an approximate estimation on the basis of EPR measurements of the radical **2** concentrations, it is believed that one crosslink accounts for two original macromolecules of PVP.

Conclusions

The results obtained illustrate an application of the nitrogen trioxide photoreactions for generation of stable aminoxyl radicals both in liquid low-molecular compounds and in solid polymers. This method of obtaining the spin-labelled molecules is comparatively simple and can be used in those systems in which CAN is sufficiently dissolved. Carrying out of the CAN photolysis in diluted solutions of polymers in specified solvents can prevent crosslinking to a great extent and give spin labelled macromolecules as aminoxyl radicals containing low-molecular fragments of the solvent. The CAN photolysis in solid polymers provides a way of preparing the polymeric gels, in particular hydrogels, which find use as specific sorbents.[26] The simple technique of crosslinking of macromolecules may be of interest in photolithography. In the considered procedure, the estimation of the crosslink number does not require an application of special techniques, and can be achieved by the direct EPR measurements of concentrations of stable aminoxyl radicals.

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