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Reactions of nitrogen oxides with polymers †

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Abstract. The mechanisms of the reactions of nitrogen oxides and different classes of solid polymers are considered. Particular emphasis is given to the analysis of the mechanisms of the formation of stable nitroxyl radicals. Double bonds and amide groups of macromolecules, as well as hydroperoxides and peroxide macroradicals are shown to be involved in the reactions with nitrogen oxides. The application of nitrogen oxides for the preparation of spin-labelled polymers and the use of the ESR imaging technique (ESR tomography) for the investigation of the structure of the reaction front during nitration of solid polymers are considered. The bibliography includes 111 references.

I. Introduction

Investigations aimed at finding relations between the processes of thermal, thermal-oxidative, photolytic, photo-oxidative and mechanochemical ageing of different classes of polymers and destruction effects, as well as studies on stabilisation of polymers to withstand these effects have been carried out for a long time. The main goal of these investigations is to retain the operating characteristics of polymeric materials.

Among numerous publications devoted to generalisation of the results obtained in this area of scientific exploration (see, *e.g.*, Refs 1 – 20), monographs by Emanuel and Buchachenko [2,4] can be highlighted. In these studies, the kinetics of the ageing of polymers under the action of different factors have been analysed taking account of specific features of elementary acts of the corresponding solid-phase chemical transformations.

In the mid-twentieth century, it was recognised that the increasing amount of industrial waste discharged to the atmosphere pollutes it with such aggressive compounds as sulfurous anhydride, different nitrogen oxides and ozone. These give rise to acid rains and smogs,[21] which cause deterioration of structural materials (concrete, marble, bricks, polymeric materials, lacquers and paints).

Reactions of polymers with nitrogen oxides constitute an important factor responsible for deterioration of the functions of polymers. Studies on nitration of organic compounds both in the liquid and gas phases began in the mid-nineteenth century. Both nitric acid and nitrogen oxides were used as nitrating agents. The nitration of aromatic compounds is, as a rule, an ionic process,[22 – 24] whereas that of the paraffin hydrocarbons is a free-radical process initiated by nitrogen dioxide, NO_2.[25 – 27] In this case, nitric acid served as a source of nitrogen oxides. The addition of small amounts of nitrogen dioxide initiates degenerate branched chain oxidation of hydrocarbons in the liquid phase and, on the other hand, results in chain termination of oxidation reactions.[28]

Systematic studies of the effect of nitrogen oxides on the stability of polymeric materials began in the late 1950s.[29 – 32] The major contribution to the solution of this problem was made by Jellinek who studied degradation of different classes of polymers in an atmosphere of nitrogen dioxide and its dimer at ambient temperatures and under the combined action of nitrogen dioxide, oxygen and near-UV light and visible light.[32]

Eight oxides of nitrogen are known; however, only three of them, *viz.*, NO, NO_2 and N_2O_4, are thought to be air pollutants.[33] The atmospheric concentrations of other nitrogen oxides are too low to have a pronounced effect on the ageing of polymers under natural conditions.

The concentrations of nitrogen oxides in the atmosphere are subject to diurnal and seasonal variations over a rather wide range and depend on the position and weather conditions. The maximum permissible concentrations of nitric oxide in urban atmospheres are 2×10^{-8} mol litre^{-1} (the peak concentration) and 2×10^{-9} mol litre^{-1} (the daily average concentration). The maximum permissible concentration of nitrogen dioxide is 1.85×10^{-9} mol litre^{-1} in both cases. In the production areas, the permissible concentration of NO_2 is about 1.1×10^{-7} mol litre^{-1} (Refs 34, 35).

Nitrogen dioxide always exists in equilibrium with its colourless linear dimer, N_2O_4. The heat of formation of N_2O_4 is -61.4 kJ mol^{-1} at 298 K.

$$2NO_2 \rightleftharpoons O_2N-NO_2 .$$

The equilibrium constant decreases with the increase in the total pressure of $NO_2 + N_2O_4$ (P) and is 0.1415 atm at $P = 4.3 \times 10^{-2}$ atm and $T = 298$ K.[36]

Based on experimental and calculated data,[37 – 40] it was assumed that nitrosation of alkenes in non-polar solvents is the result of the reaction of carbon – carbon double bonds with nitroso nitrate, $ON-ONO_2$, a less stable isomer of linear N_2O_4.

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† Dedicated to the memory of Academician N M Emanuel (1915 – 1984).

Some additional remarks are to be made before analysing the results of investigations on the reactions of polymers with nitrogen oxides and establishing the possibility of extrapolating them in order to assess the ageing of polymers in a polluted atmosphere. Since the atmospheric concentrations of nitrogen oxides are low, the rates of their reactions are also low. Therefore, the ageing processes due to other factors (*e.g.*, thermal oxidation, photo-initiated oxidation, ozone ageing, biodegradation of polymers *etc.*) can compete with or be more efficient than the reactions involving nitrogen oxides. Therefore, the results of tests under natural conditions can hardly be used for evaluation of the contribution of the processes initiated by nitrogen oxides. These reactions are usually studied at the concentrations of air pollutant gases which are several orders of magnitude higher than their atmospheric concentrations. The results obtained under these conditions are, as a rule, linearly extrapolated to the atmospheric concentrations. Such *a priori* extrapolation is not obvious, since the contributions of particular stages to the overall ageing process under the conditions of accelerated tests can vary depending on the experimental conditions.

Ageing of polymers exposed to nitrogen oxides is due to the reactions of gases diffusing into the polymer with reactive groups of macromolecules. These processes are characterised by non-uniform propagation of the reaction through the bulk of the sample and require complicated description of their kinetics.

'Kinetic inequivalence' of reactants is typical of the chemical reactions in solid polymers.[2,4] This means that the species with the same chemical structure have different nearest environments and therefore react with different rate constants. As a consequence, the most reactive species are consumed rapidly so that the overall rate constants decrease with time. However, relaxation processes occurring in polymers favour the recovery of the initial distribution of reactivities of the species. Therefore, the reaction kinetics appears to be dependent on the ratio of the rates of chemical reactions and relaxation processes.[41] This also requires a critical view on simple transfer of the results of accelerated tests to the ageing of polymers in atmospheres polluted with nitrogen oxides.

Finally, it should be noted that most of the studies of the effect of nitrogen oxides on polymeric materials involve the determination of changes in the average degree of polymerisation. However, this parameter characterises only one reaction, *viz.*, degradation of macromolecules, though this is of prime importance. A detailed study of degradation in reactions of various polymers with nitrogen dioxide was carried out by Jellinek.[32] He has divided all polymers into three main groups differing in stability toward NO_2. In the present review, the results will also be analysed using this classification. Changes in the mechanical properties can be considered as important operating characteristics of a polymer as a structural material; however, this parameter provides no direct information on the chemical transformations and structure of macromolecules. This information can be obtained using IR spectroscopy, but changes in the absorption spectra can usually be detected only at rather high degrees of conversion. Therefore, the use of other physicochemical methods for the analysis of the transformations occurring in the polymers exposed to nitrogen oxides, as well as the analysis of the distribution of the reaction over the bulk of the sample are of crucial importance for the elucidation of complicated mechanisms of these reactions. Sometimes, ageing products can be more reactive towards nitrogen oxides than the initial polymer.

In the present review, we considered the results obtained in studies on the ageing of different classes of polymers by traditional methods of physicochemical analysis and in the investigations of these processes by ESR spectroscopy, which allow one to draw conclusions on free-radical stages of the ageing of polymers involving nitrogen oxides from the structure of stable nitrogen-containing macroradicals produced in the reactions.

II. Reactions of polymers with nitrogen dioxide

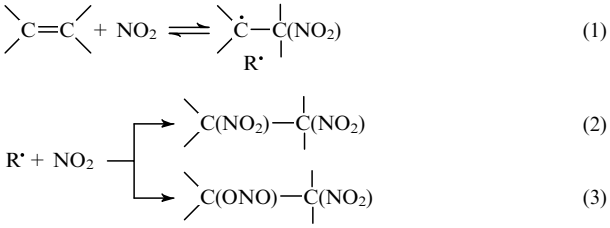
Nitrogen dioxide plays the role of a moderately reactive free radical (the strength of the ONO–H bond is 322 to 326 kJ mol^{-1}),[42] which can initiate several types of reactions, *e.g.*, hydrogen abstraction from molecules of organic compounds and reversible addition to carbon–carbon double bonds. Additionally, NO_2 and its dimer can enter into specific reactions with functional groups of macromolecules.

1. Carbon-chain polymers containing no carbon–carbon double bonds

Carbon-chain polymers containing no carbon–carbon double bonds in both the main chain and side groups [*e.g.*, polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinyl chloride) (PVC) and poly(vinyl fluoride) (PVF)] are characterised by insignificant changes in their properties under the conditions of accelerated tests (Jellinek *et al.*[43,44] carried out their experiments at a NO_2 concentration of 7.8×10^{-3} mol litre^{-1} and $T = 308$ K; the exposure time was ~ 30 h). Linear extrapolation of the results obtained to the NO_2 concentration typical of polluted atmospheres predicts a long-term stability of the polymers.[45]

Let us consider the results of investigations of the effect of NO_2 on particular representatives of these polymers in more detail.

Pioneering studies of the reaction of nitrogen dioxide with PE and PP have been carried out by Ogihara *et al.*[30,31] Using IR spectroscopy, they have found that nitrogen dioxide cannot abstract secondary and tertiary hydrogen atoms from the PE and PP molecules at 298 K. It can only add to the vinyl, vinylene and vinylidene units that are formed in the synthesis of, *e.g.*, PE. These reactions resulted in dinitro compounds and nitro nitrites.



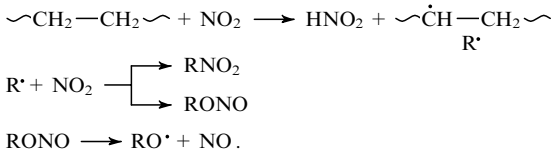
(1)

(2)

(3)

At $T \geqslant 373$ K, nitro, nitrite, nitrate, carbonyl and hydroxy pendent groups are formed in these polymers.

The following reaction mechanism was proposed:



Subsequent reactions involving the RO$^{\bullet}$ radicals result in macromolecular nitrates, alcohols and carbonyl compounds. This scheme allows rationalisation of the accumulation of the nitro groups, which proceeds at a constant rate, and autoaccelerated formation of nitrates, alcohols and carbonyl compounds; however, it provides no explanation for the S-shaped dependence of the accumulation of nitrites.

The activation energy (E_a) for the NO_2 addition to the double bonds of PE obtained by different methods is 8 to 16 kJ mol^{-1}. The activation energy for hydrogen abstraction lies between 56 and 68 kJ mol^{-1} for PE and is 60 kJ mol^{-1} for PP.

At room temperature and NO_2 concentrations lying between 5.4×10^{-4} and 5.4×10^{-3} mol litre^{-1}, the characteristics of PE, PP, PAN and PMMA change only slightly even if they are simultaneously exposed to a combination of NO_2, O_2 and UV radiation.[43] The reactions of NO_2 with PVC and PVF resulted in a

slight decrease in the content of chlorine and fluorine atoms, respectively.[32,43]

At temperatures between 298 and 328 K, nitrogen dioxide (7.8×10^{-3}–3.4×10^{-2} mol litre^{-1}) can abstract tertiary hydrogen atoms from PS molecules to form pendent nitro and nitrite groups.[32] These reactions proceed at low rates and are accompanied by chain scissions of the macromolecules.[32,45,46] According to Jellinek, the dependence of the decrease in the average degree of polymerisation of PS exposed to NO_2 on the exposure time has three (initial, middle and final) linear regions. A decrease in the apparent degradation rate was observed during the second stage of the reaction (the middle region of the dependence). Presumably, this was related to the association of the macromolecules in solution, which is due to the effect of polar groups and can affect the results of viscosimetric measurements. Subsequent increase in the apparent degradation rate was attributed to the consumption of these nitrogen-containing groups and to a decrease in the degree of association of the macromolecules.

Polystyrene films were also simultaneously exposed to NO_2 (1.1×10^{-4} mol litre^{-1}) and light ($\lambda > 280$ nm).[46] No polymer degradation was observed in the initial stage (at exposure times of no longer than 10 h). Then chain scissions occurred at a constant rate. After 40 h, degradation ceased. The mechanism of degradation under these conditions was not discussed.

An attempt to carry out a quantitative study of the ageing of PS and poly(*tert*-butyl methacrylate) (PTBMA) under the conditions simulating the ageing of these polymers in an atmosphere polluted with NO_2 has been undertaken by Huber.[47] Glass supports coated with the samples were exposed to a stream of air containing NO_2 (2.5×10^{-6} to 3.7×10^{-5} mol litre^{-1}) at 300 K and simultaneously irradiated with light ($\lambda > 290$ nm). The number of chain scissions per 10 000 monomer units (α) was determined from the data of viscosimetric measurements. The dependence of α on the exposure time can be described by an empirical equation

$$\alpha = \frac{P}{Q}(\exp Qt - 1),$$

where P and Q are constants and t is time. This equation describes an autocatalytic process. At $Q \to 0$, degradation occurs at a constant rate. As the thickness of the sample increases, both constants, P and Q, decrease, the former decreasing faster than the latter. Autocatalytic process is more pronounced for thin films. Degradation of thin PS films under the same conditions occurs slower than that of the PTBMA films and its autocatalytic nature is more pronounced. Possible reasons for the dependence of the kinetic parameters of degradation on thickness of the samples have not been considered.

The autocatalytic type of degradation of PTBMA was associated[47] with the photo-induced formation of isobutylene, which reacts with NO_2, thus initiating free-radical degradation processes of macromolecules.

The IR spectrum of PS exposed to NO_2 and light under conditions mentioned above exhibits two bands at 1686 and 3400 cm^{-1} corresponding to the carbonyl and hydroxy groups, respectively. The formation of nitrogen-containing products has not been observed in both PTBMA and PS. The following reactions have been assumed[47] to proceed in PS:

$$\sim CH_2-C(Ph)H\sim + NO_2 \longrightarrow HNO_2 + \sim CH_2-\dot{C}(Ph)\sim \quad (R^1)^{\bullet}$$

$$(R^1)^{\bullet} + O_2 \longrightarrow R^1O_2^{\bullet}$$

$$R^1O_2^{\bullet} + RH \longrightarrow ROOH + (R^1)^{\bullet}$$

$$(R^1)^{\bullet} + NO_2 \longrightarrow \begin{cases} R^1NO_2 \\ R^1ONO \end{cases}$$

$$R^1ONO \xrightarrow{h\nu} R^1O^{\bullet} + NO$$

$$R^1OOH + NO \longrightarrow R^1O^{\bullet} + {}^{\bullet}OH + NO \quad (4)$$

$$R^1OOH \xrightarrow{h\nu} R^1O^{\bullet} + {}^{\bullet}OH \quad (5)$$

$$R^1O^{\bullet} \longrightarrow (R^2)^{\bullet} + \text{degradation products.}$$

It is believed that the decomposition of hydroperoxides exposed to NO and light [reactions (4) and (5)] leads to autocatalytic degradation of PS.

The results of investigations on the mechanisms and kinetics of the reactions of macromolecular hydroperoxides with nitric oxide are considered in more detail in the forthcoming sections.

2. Reactions of nitrogen dioxide with carbon-chain polymers containing carbon–carbon double bonds

Among the reactions of NO_2 with carbon-chain polymers containing carbon–carbon double bonds, its reactions with rubbers have been studied in most detail. Rubbers are much more susceptible to NO_2 than the polymers containing no double bonds in both the main chain and side groups of the macromolecules. First, this is due to the ability of NO_2 to add reversibly to carbon–carbon double bonds to give nitroalkyl radicals [reaction (1)], thus initiating free-radical transformations of elastomers. Second, it was found[48] that the rate of the formation of products (Prod) of the liquid-phase reactions of NO_2 with alkenes is described by the equation

$$\frac{d[Prod]}{dt} = k'[alkene][NO_2] + k''[alkene][NO_2]^2,$$

where k' is the effective rate constant for the formation of products in the reactions of allyl radicals with NO_2 and k'' is the effective rate constant for the formation of products in reactions (1)–(3).

The second term of this equation dominates at high NO_2 concentrations; this corresponds to the formation of products in the recombination reactions of nitroalkyl radicals with nitrogen dioxide [reactions (1)–(3)]. The first term of this equation dominates at low NO_2 concentrations; this is associated with the ability of nitrogen dioxide to abstract hydrogen atoms in β-position to the double bond to give allyl radicals, which then combine with an NO_2 molecule. Depending on the structure of the alkene, the reaction resulting in the formation of the allyl radical can be either weakly exothermic or weakly endothermic. For instance, the strengths of the weakest C–H bonds in the structural fragment $-C(1)H_2-[C(2)H_3]C=CH-C(3)H_2-$ of synthetic isoprene rubber are 334, 351 and 316 kJ mol^{-1} for the C(1)–H, C(2)–H and C(3)–H bonds, respectively.[49]

In preliminary studies it was shown[43] that exposure of polyisoprene and polybutadiene to nitrogen dioxide leads to both degradation and cross-linking of the macromolecules, whereas butyl rubber (a copolymer of isobutylene with 1.75% of isoprene) only undergoes degradation. Jellinek *et al.*[32,50,51] carried out a detailed study of the ageing of butyl rubber exposed to (i) NO_2 (5.2×10^{-7} to 5.2×10^{-5} mol litre^{-1}) alone, (ii) an NO_2–O_2 mixture and (iii) an NO_2–O_2 mixture plus UV light ($\lambda > 280$ nm). It was found that in the first case the polymer degradation is described by the formula

$$\alpha = k_{ef}t,$$

where k_{ef} depends on the NO_2 pressure. This equation is valid except for the initial portion of the curve where the reaction rate decreases with time. A kinetic scheme of the main-chain scission was proposed.

$$\sim C(CH_3)=CH\sim + NO_2 \rightleftharpoons \sim C^{\bullet}(H_3C)-CH(NO_2)\sim \quad R^{\bullet}$$

$$R^{\bullet} + NO_2 \longrightarrow \text{chain fragments} + NO_2$$

Exposure to a mixture of O_2 (6.8×10^{-4} to 7.8×10^{-3} mol litre^{-1}) and NO_2 (5.2×10^{-7} to 5.2×10^{-5} mol litre^{-1}) leads to an increase in the degradation rate of the

rubber with the increase in the concentrations of both gases. According to Jellinek, there are three factors governing the main-chain scissioning in the polymers exposed to O_2-NO_2 mixtures. These are (i) degradation induced by NO_2 alone, (ii) oxidative degradation of macromolecules and (iii) scissions of macromolecules owing to the synergistic effect of NO_2 and O_2, which in turn is due to the NO_2-induced decomposition of hydroperoxides formed in the reaction.

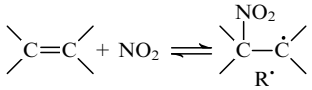
According to Jellinek, the degradation kinetics of butyl rubber exposed to NO_2-O_2 mixture and UV irradiation is described by the following equation:

$$\alpha = k'_{ef}t^2 + k''_{ef}[NO_2][1-\exp(-k'''t)],$$

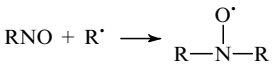
where k' and k'' are the effective rate constants for different groups of reactions and k''' is the rate constant for degradation of the elastomer exposed to NO_2 alone. At low NO_2 pressures, the degradation rate increases with time. At high NO_2 pressures, the reaction slows down.

3. ESR studies of the reactions of nitrogen dioxide with double bonds in solid polymers

As was mentioned above, nitration of aromatic compounds usually follows an ionic mechanism, whereas nitration of aliphatic compounds (in particular, the reaction of NO_2 or its dimer with carbon–carbon double bonds in non-polar media) proceeds by free-radical mechanism.[37,48,52,53] Liquid-phase reactions of low-molecular-mass alkenes with $NO_2-N_2O_4$ mixture produce paramagnetic centres.[54] It was found that the ESR spectra arising are temperature-dependent and that their parameters differed from those of the spectra of nitroalkyl radicals. These spectra were associated with the π-complexes formed in the reactions of nitrogen dioxide with the double bonds of alkenes. Nitroalkyl radicals produced in the styrene–NO_2 (or α-methylstyrene–NO_2) systems were identified by Kommandeur *et al.*[55] in the ESR spectra of the spin adducts of these radicals with nitrosobenzene. Paramagnetic centres observed [54] were assigned to the nitroxyl radicals generated in the reactions



$$R^{\bullet} + NO \longrightarrow RNO \qquad (6)$$



(7)

It is believed that reaction (6) is due to the trace amounts of NO in nitrogen dioxide. Analysis of this scheme shows that the formation of nitroxyl radicals (7) must be autoaccelerated. This was confirmed in further studies.[56]

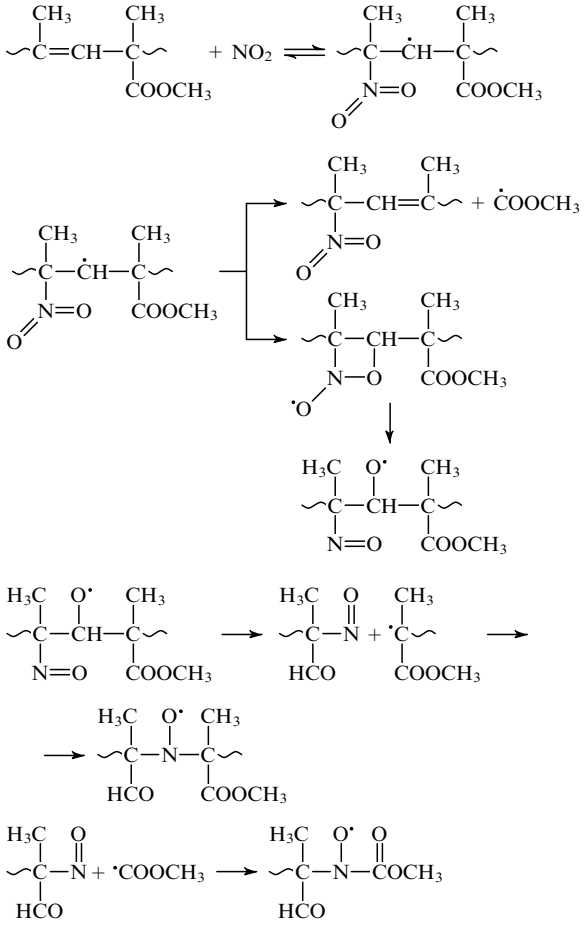
a. Reactions of UV-irradiated poly(methyl methacrylate) with nitrogen dioxide

Nitrogen dioxide virtually does not react with PMMA. On the other hand, it is known that irradiation of this polymer with UV light causes elimination of the ester groups leading mainly to methyl formate, $HCOOCH_3$, and macromolecular structures containing double bonds in the main chain.[57] The reaction of nitrogen dioxide with the double bonds formed must initiate free-radical ageing reactions in the polymer.

The formation of paramagnetic species in PMMA containing 0.3–0.4 mol kg^{-1} of the $\sim(CH_3)C(COOCH_3)-CH=C(CH_3)-CH_2\sim$ units (produced upon photolysis) under the action of NO_2 has been studied by ESR spectroscopy.[58] The experimental ESR spectrum of the solid polymer is a superposition of two anisotropic triplets typical of dialkylnitroxyl and acylalkylnitroxyl radicals in the solid phase with low frequencies of rotational motions.[59,60] Dialkylnitroxyl macroradicals $R-N(O^{\bullet})-R$ give an anisotropic triplet with $A_{\parallel}^{N} = 3.2\pm0.1$ mT and $g_{\parallel} = 2.0026\pm0.0005$, while the triplet corresponding to acylalkylnitroxyl radicals $RC(=O)-N(O^{\bullet})-R$ is characterised by the parameters $A_{\parallel}^{N} = 2.1\pm0.1$ mT and $g_{\parallel} = 2.0027\pm0.0005$. In a benzene solution of PMMA, these radicals exhibit triplet ESR spectra with the parameters $a^{N} = 1.5\pm0.1$ mT, $g = 2.0064\pm0.0005$ and $a^{N} = 0.8\pm0.1$ mT and $g = 2.0065\pm0.0005$, respectively. The absence of an additional hyperfine splitting in the spectra of these radicals indicates that the carbon atoms neighbouring to the $NO^{\bullet}$ group are tertiary.

The accumulation of dialkylnitroxyl macroradicals occurs without an induction period and its initial rate is proportional to the concentration of nitrogen dioxide in the gas phase.

The kinetics observed shows that the scheme of the formation of dialkylnitroxyl radicals [reactions (1), (6) and (7)] in the liquid phase (see above) is inapplicable to the solid polymer due to the low probability of the encounter of a macroradical with the macromolecular nitroso compound. It was assumed that these radicals are produced as a result of a series of 'pseudocage' reactions such as those shown below:



According to this scheme, the NO_2 group and the free valence are localised on the neighbouring carbon atoms of the primary nitroalkyl radical and can react with each other to produce unstable, four-membered alkoxyalkylnitroxyl radicals, which decompose to give the alkoxyl radical and nitroso group at the adjacent carbon atom. Subsequent decomposition of the alkoxyl macroradical results in an alkyl radical and nitroso compound located in the immediate vicinity of each other. The reaction between them, resulting in the formation of a dialkylnitroxyl macroradical, can be initiated by small-amplitude translational and rotational motions. Acylalkylnitroxyl radicals appear in the reactions of the low-molecular-mass methoxycarbonyl radicals with tertiary nitroso compounds. This reaction scheme ignores concurrent transformations of reactive free radicals, which proceed without formation of nitroxyl radicals. These processes seem to be responsible for the low yield of $R-N(O^{\bullet})-R$ radicals

(about one hundredth of the total number of consumed NO_2 molecules).

The ability of nitro compounds to undergo reduction to nitroso compounds through the stages of formation and decomposition of alkoxyalkylnitroxyl radicals in the liquid phase has been pointed out.[61–63]

It was also concluded that the reaction between the double bonds of PMMA and NO_2 is accompanied by chain scissions in the macromolecules and elimination of the ester side groups.[58] In addition, the structure of the nitroxyl macroradicals produced suggests that NO_2 is added not only to the less sterically shielded carbon atom of the double bond, but also to the neighbouring atom. This was also observed in the liquid-phase reaction of methyl methacrylate with nitrogen dioxide.[64]

b. Nitroxyl radicals produced in reactions of nitrogen dioxide with rubbers

As was mentioned in the preceding Section, macromolecular nitroxyl radicals produced in the reactions of NO_2 with the double bonds of polymers are spin labels which carry information on macromolecular dynamics. Knowledge of the formation rules and structure of nitroxyl radicals allows elucidation of the mechanisms of macromolecular transformations in the polymers.

This approach was used[65] to obtain spin-labelled macromolecules of 1,4-*cis*-polyisoprene (synthetic isoprene rubber, or SKI℠) and a copolymer of ethylene, propylene and dicyclopentadiene (SKEPT-40℠). These spin labels were used to study the macromolecular dynamics in solid SKI℠ and the structure of the reaction front during nitration of the polymer.[66]

Nitroxyl macroradicals formed in these polymers at 293 K exhibit nearly identical ESR spectra. The ESR spectrum of nitroxyl radicals in SKI℠ recorded at 298 K is shown in Fig. 1 *a*. It is an anisotropic triplet with $A_{\parallel}^{N} = 3.10$ mT and $g_{\parallel} = 2.0028 \pm 0.0005$. This indicates that the correlation time, τ_c, of rotational motions at this temperature is longer than 10^{-9} s. As the temperature increases, the spectra become triplets with $a^N = 1.53 \pm 0.03$ mT and $g = 2.0057 \pm 0.0005$ (Fig. 1*b*), which indicates a substantial shortening of the correlation time. The change in τ_c in the temperature interval from 293 to 373 K (Fig. 2) is described by the equation

$$\tau_c = \tau_0 \exp\left(\frac{E}{RT}\right),$$

where $\log\tau_0 = -14.2$ and E is the activation energy for rotational diffusion (34.7 kJ mol^{-1}).

These values are close to the corresponding values determined for SKI℠ using a bulky spin probe.[67]

Studies on the kinetics of the formation of nitroxyl radicals in solid elastomers showed that free-radical transformations of double bonds in the presence of nitrogen dioxide differ fundamentally from analogous liquid-phase reactions.[56]

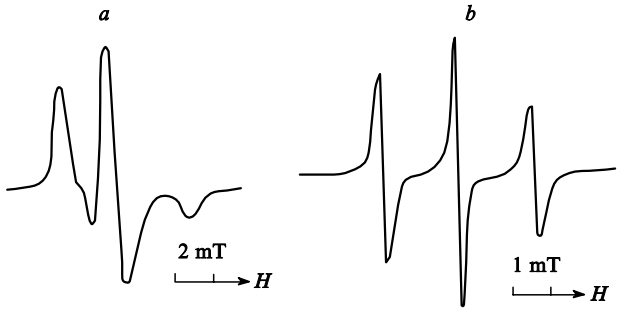


Figure 1. ESR spectra of nitroxyl macroradicals produced in the reaction of nitrogen dioxide with SKI℠-3M at 293 (*a*) and 373 K (*b*).

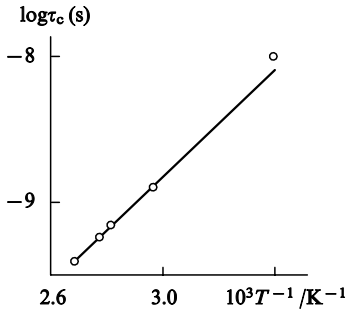


Figure 2. Temperature dependence of the correlation time τ_c of rotational diffusion of SKI℠ macromolecules measured using spin labels obtained in the reaction of polyisoprene with nitrogen dioxide.

The changes in the concentration of nitroxyl radicals as functions of the nitration time of SKI℠ at different concentrations of nitrogen dioxide in the gas phase are shown in Fig. 3 *a*. As in the case of PMMA, these radicals are formed in an $NO_2-N_2O_4$ atmosphere without an induction period and the initial rate of formation is proportional to the concentration of nitrogen dioxide. Initially, the concentration of radicals increases and reaches a maximum value at $[NO_2] = (7-8) \times 10^{-4}$ mol litre^{-1} and then decreases. It was assumed that this shape of the kinetic curves is due to the loss of nitroxyl radicals in the trapping reactions and in the redox reactions involving the nitrogen dioxide dimer.

A long induction period is observed in the presence of O_2 in the gas mixture (Fig. 3 *b*, curve *2*). The apparent accumulation rate of radicals to the end of this period is 50 to 60 times lower than that in the absence of oxygen at the same NO_2 concentration; however, the amount of radicals accumulated is three times as large as that

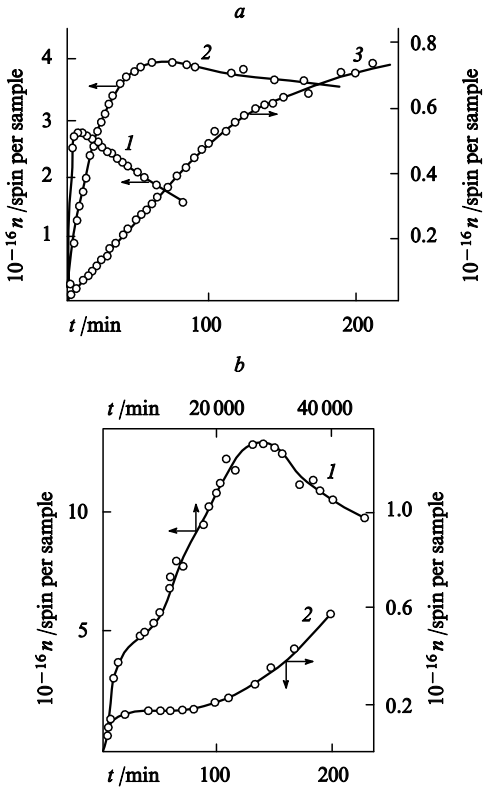


Figure 3. Kinetic curves of accumulation of nitroxyl macroradicals in SKI℠ exposed to NO_2 (*a*) and an NO_2-O_2 mixture (*b*);
(*a*): $[NO_2]$ /mol litre^{-1}: 2.2×10^{-3} (*1*), 7×10^{-4} (*2*) and 10^{-5} (*3*);
(*b*): kinetic curve (*1*) and the initial portion of curve *1* (*2*); $[NO_2] = 7 \times 10^{-4}$ mol litre^{-1} and $[O_2] = 1.2 \times 10^{-2}$ mol litre^{-1}.

accumulated in the former case. It was concluded that in the absence of O_2 nitroxyl macroradicals are formed in two ways. The first mechanism is the same as the liquid-phase one, while the second is a 'pseudocage' mechanism, which predominates if the reaction is carried out in the absence of oxygen. In the presence of O_2, 'pseudocage' reactions are inhibited due to the conversion of initially formed nitroalkyl macroradicals into nitroperoxide radicals. From these data it also follows that the recombination of nitroxyl macroradicals with nitroalkyl and allylic macroradicals in the absence of O_2 must lead to gradual cross-linking of the SKI™ macromolecules.

Similar kinetics of accumulation of nitroxyl macroradicals was also observed for SKEPT-40™, which differs from SKI™ by a substantially lower proportion of double bonds.

The mechanism of formation of nitroxyl radicals in these polymers by the 'pseudocage reactions' is in essence the same as that in the case of PMMA containing double bonds. Alkoxyl macroradicals produced in the 'pseudocage reactions' cause degradation of polymers, while recombination of nitroxyl radicals with nitroalkyl radicals leads to cross-linking of the elastomer.

Reactions of NO_2 with solid polymers can be considered as the interaction between the molecules diffusing from the gas phase and reacting in the bulk of the polymer. In this case, a non-uniform distribution of the reaction front in the bulk of the polymer must be present. The method of ESR tomography (or the ESR imaging technique),[68–70] which has been rapidly developed recently, allows determination of the spatial distribution of paramagnetic species. In the case of reaction of NO_2 with the double bonds of elastomers, the spatial distribution of nitroxyl macroradicals characterises the structure of the reaction front during nitration of the polymers.

The results of investigations of the reactions of SKI™ with NO_2 and NO_2-O_2 mixtures by ESR tomography have been reported.[66] The spatial distributions of nitroxyl macroradicals in the initial and deep stages of the nitration of SKI™ by a $NO_2-N_2O_4$ mixture are shown in Fig. 4 *a* and Fig. 4 *b*, respectively. As can be seen, after the initial 2.5 h the reaction front penetrates the surface of the polymer to a depth of ~ 1 mm. The interior of the sample is inaccessible to nitrogen dioxide. As the reaction time is extended to 740 h, the depth of the reaction zone increases only by 20% to 30%. The extent of the reaction is maximal in the near-surface layer and decreases as the reaction front moves deeper into the sample. The results obtained show that the initial structure of the reaction front is due to the penetration of NO_2 into the bulk of the sample along pores, cracks, sites with low local density and that further propagation of the reaction front is very slow. Studies of the rates of diffusion of the low-molecular-mass radical (2,2,6,6-tetramethyl-4-oxopiperidinoxyl) from the gas phase into the bulk of an SKI™ sample nitrated for different periods of time showed that nitration was accompanied by the efficient formation of a three-dimensional network structure, which precludes the diffusion of low-molecular-mass compounds into the sample.

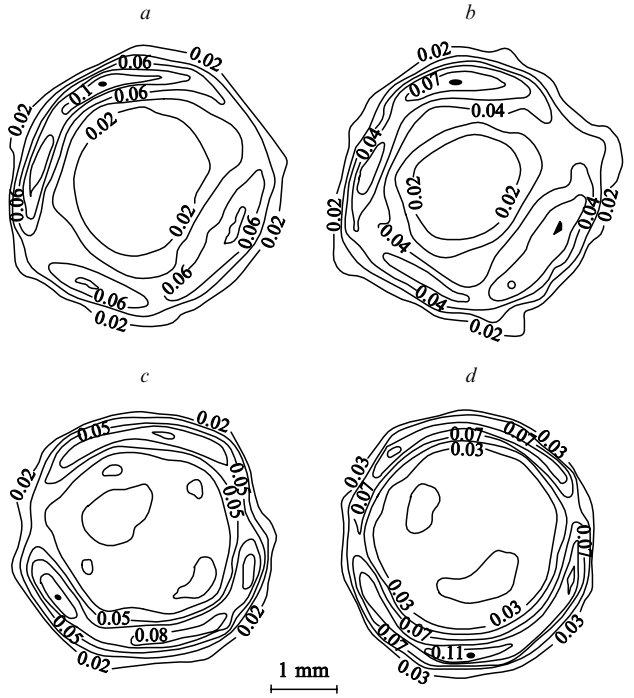


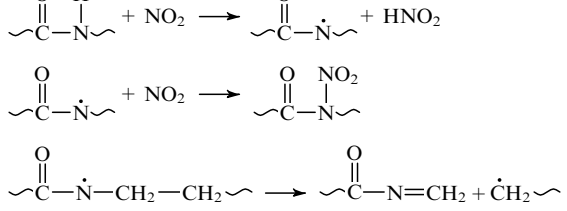
Figure 4. Bulk distribution of nitroxyl macroradicals produced upon nitration of SKI™ by NO_2 with a concentration of 3.8×10^{-4} mol litre^{-1} (*a*, *b*) and a mixture of NO_2 (5.5×10^{-4} mol litre^{-1}) with O_2 (1.5×10^{-3} mol litre^{-1}) (*c*, *d*). Nitration time /h: 2.5 (*a*), 720 (*b*), 168 (*c*) and 505 (*d*). It should be remembered that NO_2 always is in equilibrium with N_2O_4.

When an SKI™ sample is exposed to an $NO_2-N_2O_4-O_2$ mixture, the limitations on diffusion due to the changes in the structure of the polymer must diminish since the concentration of cross-links decreases in the presence of oxygen. Therefore, one could expect a greater depth of the reaction zone and a more uniform distribution of nitroxyl macroradicals in the bulk of the polymer. In fact, the distribution of nitroxyl macroradicals in the bulk of the sample and its change during nitration of the samples with an NO_2-O_2 mixture (Fig. 4 *c*,*d*) are similar to those for the sample exposed to an $NO_2-N_2O_4$ mixture, but the reaction zone penetrates the sample to a smaller depth. This can likely be rationalised by the fact that the structure of the reaction front is due to the membrane-like type of the process.[71] Under these conditions, the propagation velocity of the reaction front is determined by the consumption rate of nitroalkyl macroradicals: the higher the consumption rate, the smaller the depth to which the reaction front penetrates. Introduction of O_2 into the system causes an increase in the consumption rate of nitroalkyl radicals, thus decreasing the depth of the reaction front. Thus, the results obtained by ESR tomography showed that if rubbers are exposed to high NO_2 concentrations, the degradation and cross-linking of macromolecules occur in the narrow (of the order of 1 mm thick) surface layer and that no modification occurs in the bulk of the polymer sample for long.

4. Reactions of nitrogen dioxide with polyamides, polyurethanes and polyamidoimides

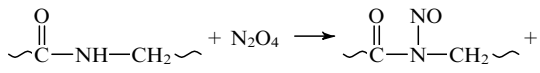
a. Effect of nitrogen dioxide on aliphatic polyamides

Polymers containing amide and urethane groups form a particular class of materials sensitive to NO_2. Jellinek *et al.*[72,73] showed that exposure of nylon-66 films of different morphology to NO_2 (2.6×10^{-5} to 10.4×10^{-5} mol litre^{-1}) causes main-chain scission in the polymers. The degradation of nylon is a diffusion-controlled reaction. Its rate and depth depend essentially on the degree of crystallinity of specimens and on the size of crystallites. The reaction can be inhibited by small amounts of benzaldehyde or benzoic acid. The degradation is accelerated in the presence of air and UV light in addition to NO_2. It is believed that benzoic acid blocks the amide groups and that only a few of them, not involved in hydrogen bonding, enter into the reaction. The following mechanism for the polymer degradation under the action of NO_2 was proposed.



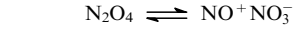
The effect of nitrogen dioxide on nylon fibres has been studied.[74] It was found that long-term storage of samples in an atmosphere with low NO_2 concentration at room temperature did not lead to their darkening or to a decrease in the tensile strength. These characteristics deteriorated at elevated temperatures. Degradation of nylon fibres irradiated with UV light in air was more pronounced in the presence of nitrogen oxides.

The results of the UV, IR and ESR studies on the ageing of polycapramide (PCA) in a nitrogen dioxide atmosphere have been reported.[75] The absorption bands in the region of 390–435 nm typical of *N*-nitroso amides were observed in the UV spectra of PCA films stored in an NO_2 atmosphere.[76] IR studies showed that the intensity of the band at 3293 cm^{-1} assigned to the stretching vibrations of hydrogen-bonded N–H groups decreases on storage of thin PCA films in an NO_2 (4×10^{-5} to 4×10^{-4} mol $litre^{-1}$) atmosphere. The intensities of the bands at 1642 and 1563 cm^{-1} also decrease. A band at 1730 cm^{-1} characteristic of the stretching vibrations of the C=O groups not involved in hydrogen bonding appears instead of these bands, as well as two bands, at 1504 and 1387 cm^{-1}, corresponding to the antisymmetrical and symmetrical stretching vibrations of the –N=O groups of nitroso amides. It was found that under these conditions the initial rate of the nitrosation of PCA is proportional to $[NO_2]^n$, where $n \approx 2$. The formation of the nitroso amide groups can be depicted as follows:

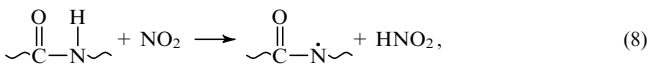


Nitrosation of PCA leads to disappearance of the system of hydrogen bonds, which determines its mechanical properties. After exposure to NO_2, the PCA films degraded at minimum mechanical actions.

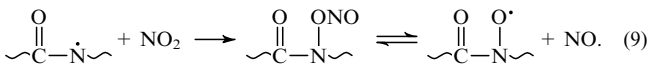
White[77,78] carried out detailed studies of the liquid-phase reactions of low-molecular-mass amides with nitrogen dioxide. He suggested that the action of N_2O_4 used as the nitrosating agent is due to the equilibrium



and that the reaction proceeds by an ionic mechanism. Jellinek *et al.*[72,73] proposed a free-radical mechanism of the interaction of polyamides with NO_2, which implies the formation of an *N*-nitro amide with a characteristic IR absorption band at 1580 cm^{-1} as the main product. However, no formation of this product was detected, probably, due to the low proportion of the free-radical reactions in the overall process. The formation of amidyl radicals was confirmed by the accumulation of acylalkylnitroxyl macroradicals (which occurs without induction period, however).[75] These macroradicals are generated in the reactions



(8)

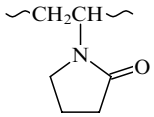


(9)

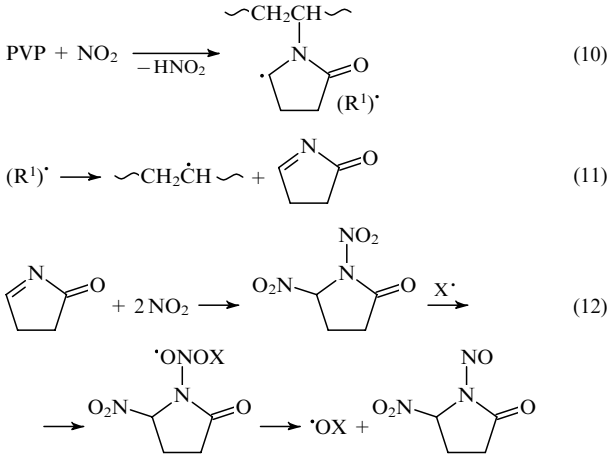
Thus, there are two concurrent mechanisms for the transformation of polyamides in the presence of nitrogen dioxide, namely, the free-radical mechanism with the rate proportional to the concentration of NO_2 and the ionic mechanism, the rate of which is proportional to the square of the NO_2 concentration. The ratio of these processes depends on the concentration of nitrogen dioxide in the gas phase. Therefore, linear extrapolation of the results obtained under the conditions of accelerated tests cannot be used for predicting the stability of polyamides.

b. The effect of nitrogen dioxide on polyvinylpyrrolidone

Polyvinylpyrrolidone (PVP) is a carbon-chain polymer containing a tertiary amide group in the pendent ring.



The interaction of PVP with NO_2 has been described.[75] Two absorption bands, at λ_{max} = 413 and 435 nm, were observed in the UV spectra of products of the reaction of NO_2 with PVP. As in the case of PCA, these peaks can be assigned to the absorption of the nitroso amide groups $N(NO)-C(=O)-(CH_2)_3$ formed in PVP due to the elimination of the side cyclic fragments.



(10)

(11)

(12)

X is a free radical.

ESR studies of the reaction of NO_2 (10^{-4} to 10^{-3} mol $litre^{-1}$) with PVP revealed two additional mechanisms for the transformation of the polymer.

The ESR spectrum of paramagnetic species formed in this polymer (Fig. 5) is a superposition of the signals of iminoxyl and acylalkylnitroxyl radicals with the parameters $A_{\parallel}^{N}$ = 4.33 mT, $A_{\perp}^{N}$ = 2.44 mT, $g_{\parallel}$ = 2.0029 and $g_{\perp}$ = 2.0053 and $A_{\parallel}^{N}$ = 1.94 mT and $g_{\parallel}$ = 2.003, respectively.

The iminoxyl radicals are produced as follows. Nitric oxide recombines with $(R^1)^{\bullet}$ to give nitroso compounds which undergo

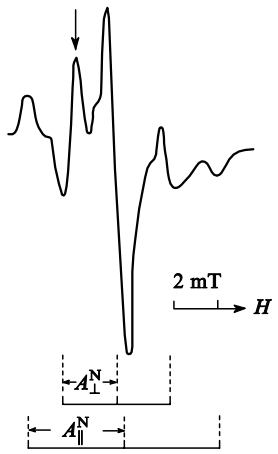
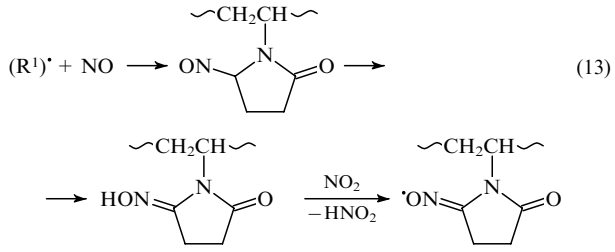


Figure 5. The ESR spectrum of paramagnetic species formed in the reaction of PVP with nitrogen dioxide. The low-field component of the hyperfine structure of acylalkylnitroxyl macroradicals is shown by an arrow.

isomerisation into oximes to produce iminoxyl radicals in the reaction with NO_2

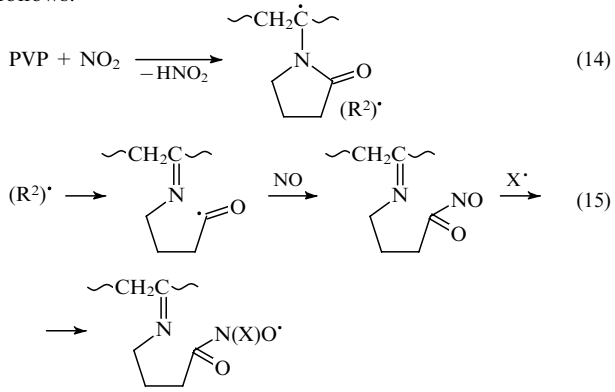


(13)

Nitrous acid is the source of nitric oxide in the system

$$2HNO_2 \longrightarrow H_2O + NO_2 + NO.$$

The formation of acylalkylnitroxyl radicals can be represented as follows.



(14)

(15)

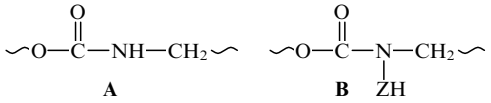
It was found that the kinetics of the accumulation of iminoxyl and acylalkylnitroxyl radicals are different. The concentration of iminoxyl radicals increases initially (the rate of accumulation decreases with time), reaches a maximum value and then decreases. The accumulation of acylalkylnitroxyl radicals occurs initially in an autoaccelerated manner and then the rate of the process decreases and the concentration of the radicals reaches a constant value. This indicates that nitrogen-containing radicals are produced from different precursors following reactions with different rate-limiting stages. It was found that the structure and properties of the matrix affect the relative rates of the formation of nitrogen-containing radicals in PVP samples filled with aerosil.[79]

Thus, one can conclude that the presence of tertiary amide groups in the monomer units of PVP leads to weakening of the C–H bonds in the >CH– and $-CH_2-$ groups neighbouring to the nitrogen atom. Nitrogen dioxide can abstract hydrogen atoms from these groups with ease to produce macroradicals which decompose with the cleavage of the C–C bonds in the β-position to the free valence. Alkyl macroradicals also recombine with nitrogen oxides to give nitrites, nitrates and nitroso compounds and then nitroxyl macroradicals. Trapping of the alkyl macroradicals $(R^1)^\bullet$ and $(R^2)^\bullet$ by the nitroso compounds and nitroxyl radicals must be accompanied by cross-linking of the macromolecules.

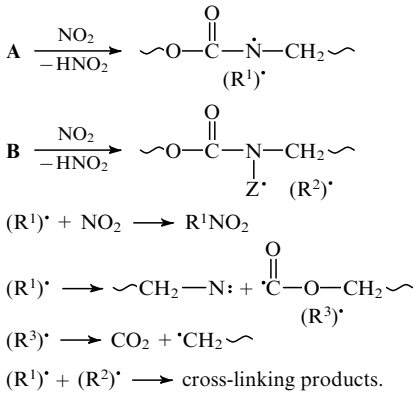
c. Reactions of NO_2 with polyurethanes

Jellinek *et al.*[80,81] studied the effect of NO_2 on films of linear polyurethane (PU) synthesised from tetramethylene glycol and hexamethylene diisocyanate. It was found that the degradation of PU is accompanied by cross-linking of macromolecules and that the degree of degradation and the yield (the weight percentage) of the gel fraction are complex functions of the exposure time. For instance, the yield of the gel fraction initially increases up to 20% and then decreases down to nearly zero at 333 K and a NO_2 concentration of 10^{-3} mol litre^{-1}. The number of chain scissions in the sol fraction (*i.e.*, the degree of degradation) increases initially, then decreases and eventually increases again; however, the final degradation rate is lower than the initial one. Exposure of the PU films to NO_2 is accompanied by evolution of CO_2, which is a monotonic function of the exposure time. The IR spectra of the films allow assessment of the consumption of the NH bonds (ν = 3300 cm^{-1}).

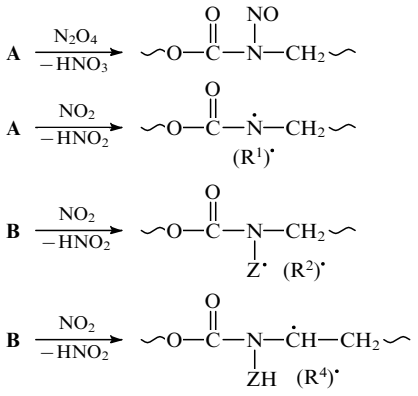
The reaction mechanism proposed by Jellinek *et al.*[80,81] involves the abstraction of hydrogen atoms from two types of structures, namely, a carbamate structure (**A**) and a tertiary amido structure (**B**)



where Z is a side alkyl group, as the initial step. The mechanism involves the following main stages:



According to Jellinek, recombination of the $(R^1)^\bullet$ and $(R^2)^\bullet$ radicals leads to cross-linking of the polymer chains, while decomposition of the $(R^1)^\bullet$ radicals results in the degradation of macromolecules and evolution of CO_2. Energetically, the decomposition of the $(R^1)^\bullet$ radicals seems to be hardly probable since this reaction results in the terminal macroradical $(R^3)^\bullet$ and a nitrene, which is a very reactive species. On the other hand, more probable decomposition reactions of $(R^1)^\bullet$ involving cleavage of the C–C or C–O bonds produce no alkoxycarbonyl macroradicals $(R^3)^\bullet$, which can undergo decarboxylation (see Ref. 82). Taking into account the mechanisms of the reaction of nitrogen dioxide with aliphatic polyamides and PVP, the ageing of PU in an NO_2 atmosphere can be represented as follows:



i = 1–4.

This scheme allows a rationalisation of the degradation accompanied by cross-linking of macromolecules, the consump-

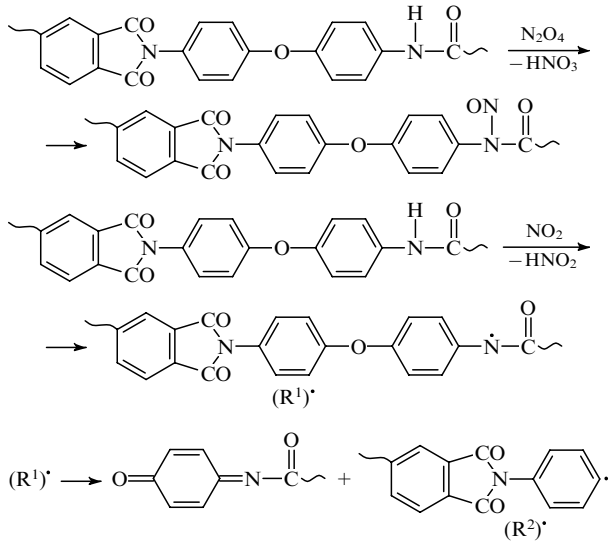
tion of NH groups of the polymer as well as the evolution of carbon dioxide upon degradation.

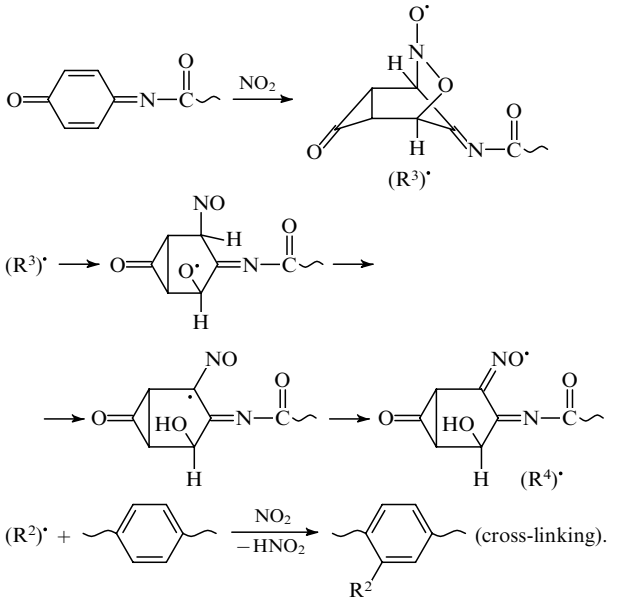
d. The reaction of NO_2 with a polyamidoimide

The effect of NO_2 on the mechanical properties of a polyamidoimide (PAI) obtained by the polycondensation of chloroformylphthalic anhydride with 4,4′-diaminodiphenyl ether has been studied.[83] The experiments were carried out at 323 K and an NO_2 concentration of 5×10^{-3} mol litre^{-1} and involved the measurements of the temperature dependence of the storage modulus E' and the loss modulus E'' for different exposure times of the PAI samples to NO_2. At 473 K, the parameter E' revealed a non-monotonic decrease and the strongest temperature dependence. An increase in E' at the glass transition temperature ($\sim$ 563 K) was observed for the films exposed to NO_2 over a period of eight days. When studying the temperature dependences of the loss moduli E'' of the films exposed to NO_2 for different times, an absorption peak was found to appear at 473 K, which indicates degradation of polymers. All these facts were associated with degradation accompanied by cross-linking of macromolecules.

A decrease in the band intensities of the stretching vibrations of the N−H bonds and the appearance of the peaks associated with the addition of NO_2 groups to macromolecules was observed in the IR spectra of the PAI films. No reaction mechanisms were discussed.

To elucidate possible reaction mechanisms, we carried out ESR studies of the effect of NO_2 (10^{-3} mol litre^{-1}, at 293 K) on PAI of the same structure as that of the polymer studied by Kambe and Yokota.[83] Under these conditions, iminoxyl radicals with the ESR spectral parameters $A_{\parallel}^{N}$ = 4.1 mT, $A_{\perp}^{N}$ = 2.1 mT and $g_{\parallel}$ = 2.0028, $g_{\perp}$ = 2.0058 are mainly produced in PAI. The proportion of the acylalkylnitroxyl macroradicals which have nearly the same ESR spectral parameters as those of polyamide and are likely produced by the same mechanism [reactions (8) and (9)] is less than 35%. Formation of iminoxyl radicals in this system is quite unexpected. A conventional mechanism of their formation [reactions of the types (10) and (13) in PVP] involves (i) hydrogen abstraction from the CH_2 group of a molecule, (ii) NO addition to the radical produced and (iii) isomerisation of the newly formed nitroso compound into an oxime. Abstraction of labile hydrogen atoms from the oxime molecules by NO_2 results in iminoxyl radicals. Since the PAI molecules contain no CH_2 groups, this mechanism is impossible. It was assumed that the spin density in the amidyl radicals produced is partially delocalised over the phenyl ring, which facilitates cleavage of the polymer ether bond. The following mechanism of the reaction of NO_2 with PAI was proposed.





Decomposition of the radicals $(R^1)^{\bullet}$ leads to the scission of the main chain of PAI, while their reactions with NO_2, as in the case of PCA, result in acylalkylnitroxyl radicals. The reaction of the radicals $(R^2)^{\bullet}$ with the phenyl rings of neighbouring macromolecules causes cross-linking of the polymer and the reaction with NO_2 results in the appearance of NO_2 groups in the sample.[83]

Kinetic curves of the accumulation of the iminoxyl radicals correspond to the following overall reactions

$$RH + NO_2 \longrightarrow (R^4)^{\bullet},$$

$$(R^4)^{\bullet} + NO_2 \longrightarrow R^4NO_2.$$

Their transformation in the coordinates of the following equation

$$\ln\frac{[R^4]_s^{\bullet}}{[(R^4)^{\bullet}]_s - [(R^4)^{\bullet}]} = \frac{W_0 t}{[(R^4)^{\bullet}]_s},$$

where $[(R^4)^{\bullet}]$ and $[(R^4)^{\bullet}]_s$, are the current and steady-state concentrations of the radicals, respectively, and W_0 is the rate of formation of the iminoxyl radicals, allows the minimum degradation rate of the polymer, W_d, to be determined from the accumulation of the iminoxyl radicals; W_d was found to be 10^{-8} mol kg^{-1} s^{-1}. The mechanism proposed allows a rationalisation of the degradation accompanied by cross-linking of the PAI macromolecules as well as the introduction of the NO_2 groups.[83]

5. On the possibility of polymer degradation resulting from the reaction of nitrogen dioxide with peroxyl macroradicals

As was mentioned above, at room temperature nitrogen dioxide can (i) abstract labile hydrogen atoms from macromolecules to produce alkyl or allyl macroradicals and (ii) add to the double bonds, thus producing the nitroalkyl macroradicals. If the reaction is carried out in air, carbon-centred macroradicals are oxidized to give peroxyl radicals. Presumably, the reactions of the latter with NO_2 must result in relatively unstable peroxy nitrates, $ROONO_2$, similarly to the low-molecular-mass radicals $rO_2^{\bullet}$.[84–86]

Decomposition of peroxyacetyl nitrate, $CH_3C(=O)OONO_2$, was studied in detail and two mechanisms were considered.[87,88]

$$CH_3COONO_2 \underset{}{\overset{k_{16}}{\rightleftharpoons}} CH_3COO^{\bullet} + NO_2 \qquad (16)$$

$$CH_3COONO_2 \xrightarrow{k_{17}} CH_3CO^{\bullet} + NO_3 \qquad (17)$$

Using the spin trap technique, it was shown that peroxyacetyl nitrate decomposes mainly following reaction (16), which is reverse to the formation reaction of $CH_3C(=O)OONO_2$.[89] An analogous conclusion was also drawn based on the results of quantum-chemical calculations.[90] Stabilities and transformation mechanisms of other low-molecular-mass peroxy nitrates have been much less studied.

The thermal stability of products of the reactions of NO_2 with internal $\sim CF_2CF(OO^{\bullet})CF_2\sim$ ($R_{in}O_2^{\bullet}$) and terminal $\sim CF_2-CF_2-OO^{\bullet}$ ($R_tO_2^{\bullet}$) peroxyl macroradicals of poly(tetrafluoroethylene) (PTFE) produced under the action of penetrating radiation or UV light in an O_2 atmosphere was studied by ESR spectroscopy.[91] These macroradicals are stable at $T \leqslant 333$ K but can enter into reactions with nitrogen dioxide.

If the reaction of the type (16) is the only way of the transformation of peroxy nitrates into PTFE, complete regeneration of the initial peroxyl macroradicals must be observed *in vacuo*. The alkoxyl macroradicals produced by the reaction (17) can undergo effective decomposition accompanied by scission of the main chain of the polymer.[92] For instance,

$$\sim CF_2-\underset{\displaystyle O^{\bullet}}{\underset{|}{CF}}-CF_2\sim \xrightarrow{k_{18}} \sim CF_2-\underset{\displaystyle O}{\underset{\|}{CF}} + {}^{\bullet}CF_2-CF_2\sim \quad (18)$$

The reaction of terminal alkyl macroradicals with NO_3 or NO_2 results in the formation of stable products and in a decrease in the degree of regeneration of $RO_2^{\bullet}$.

It was found[91] that $R_{in}OONO_2$ do decompose with partial regeneration of $R_{in}O_2^{\bullet}$ at room and elevated temperatures. At 298 K, the peroxy nitrate molecules which undergo dissociation are kinetically inequivalent. At 313 K, they undergo a unimolecular decomposition with a rate constant of the reaction of the type (16), $4.0\times10^{-4} \leqslant k_{16} \leqslant 4.8\times10^{-4}$ s^{-1} (Fig. 6 *a*), which is independent of either $[R_{in}O_2^{\bullet}]_0$ or the exposure time (t^*) of the samples to nitrogen dioxide. The effective constant k_{16} obtained is about three orders of magnitude smaller than the rate constant for decomposition of $CClF_2O_2NO_2$.[93] This seems to be due to the low probability of the escape of NO_2 molecules from the 'cage' in the solid phase. However, the t^* value determines the limiting concentration of regenerated peroxyl macroradicals, $[R_{in}O_2^{\bullet}]_\infty$ (Fig. 6 *b*)

$$[R_mO_2^{\bullet}]_\infty = \frac{k_{16}}{k_{16}+k_{17}}[R_mO_2^{\bullet}]_0 \exp(-k_{ef}t^*),$$

where k_{ef} is the effective rate constant for various conversions of peroxy nitrate exposed to NO_2 including those involving alkoxyl macroradicals. It was found that $k_{17} < k_{ef} < 7.6\times10^{-5}$ s^{-1}, *i.e.*, the rate constant of a reaction of the type (17), which can result in degradation of the PTFE macromolecules, does not exceed $\sim 20\%$ of k_{16}.

Unexpected results were obtained in studies of the thermal stability of the reactions products of $R_tO_2^{\bullet}$ with nitrogen dioxide. Heating of samples *in vacuo* at temperatures up to 413 K did not lead to production of free radicals. This can be due to either the fact that no peroxy nitrates are formed in this case or to the fact that the reaction proceeds through a six-membered cyclic transition state and results in the fast formation of stable products.

Thus, if a polymer containing rather stable peroxy radicals (*e.g.*, PTFE) is exposed to high concentrations of nitrogen dioxide for long, the second decomposition route of peroxy nitrate [reaction of the type (17)] can lead to a high degree of degradation of the polymer due to the irreversibility of reaction (18) despite the fact that the corresponding rate constant is five or more times smaller than that typical of the first decomposition route [reaction of the type (16)].

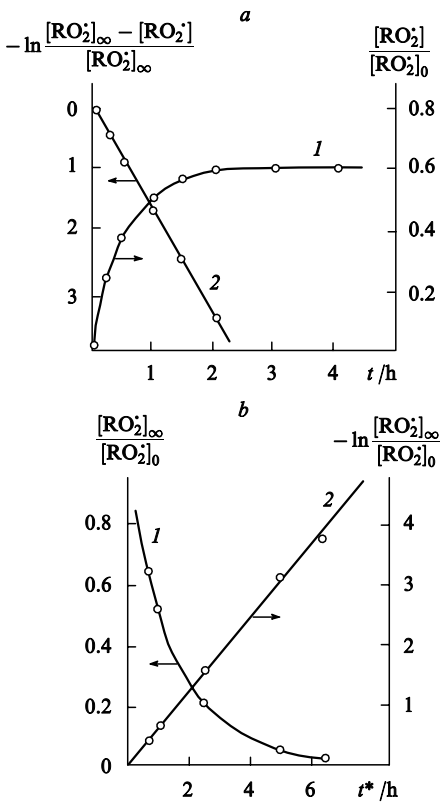


Figure 6. Kinetic curve of regeneration of $R_{in}O_2^{\bullet}$ radicals after exposure of PTFE to NO_2 (2.8×10^{-3} mol litre^{-1}) for 1.5 h (*a*) and the limiting degree of regeneration of $(R_{in}O_2^{\bullet})_\infty$ radicals as a function of the time of preliminary exposure of sample t^* to NO_2 (7×10^{-3} mol litre^{-1}) (*b*). Kinetic curve (*1*) and semilogarithmic transformation of curve *1* (*2*).

III. The effect of nitric oxide on polymers

Nitric oxide is less reactive than nitrogen dioxide. Currently, it is known with certainty that at room temperature nitric oxide cannot abstract tertiary or allylic hydrogen atoms from organic molecules, since the H–NO bond with a strength of 208.6±2.1 kJ mol^{-1} is weaker than the C–H bonds in organic compounds. Nitric oxide cannot also add to isolated double bonds.[94–96] Opinions differ widely as to the ability of NO to react with low-molecular-mass dienes and polyenes. It is known that NO can add to substituted *o*-quinodimethane, phorone and β-carotene to produce free radicals.[97–99] It is also believed that the reactions of NO with dienes are actually initiated by admixtures of NO_2.[96] In any case, it is of interest to study the regularities of the reaction of nitric oxide with the ageing products of polymers, *e.g.*, hydroperoxides.[100, 101] In addition, NO readily reacts with free radicals to give nitroso compounds, which are efficient spin traps for the free radicals. Analysis of the kinetic curves of the formation and the structures of nitrogen-containing radicals which are stabilised in this case makes it possible to draw conclusions on the mechanisms of free-radical processes in the polymers.

1. Photolysis and radiolysis of poly(methyl methacrylate) and cellulose triacetate in the presence of nitric oxide

Photolysis of PMMA exposed to NO leads to the formation of stable nitrogen-containing radicals. The structures of the radicals formed depend on the temperature and the wavelength of the photolysing light.[102] For instance, acylalkylnitroxyl radicals, $R^1N(O^{\bullet})C(=O)OR^2$, are produced upon photolysis of PMMA by unfiltered light of a mercury lamp at 298 K. In solid PMMA, they exhibit an anisotropic triplet ESR spectrum with $A_{\|}^N = 2.1\pm0.1$ mT and $g_{\|} = 2.0027$ (Fig. 7 *a*). In a solution of the polymer, the parameters of the ESR spectrum of these radicals are $a^N = 0.8\pm0.1$ mT and $g_{\|} = 2.0065$. Not only acylalkyl, but also dialkylnitroxyl radicals, $RN(O^{\bullet})R$, are produced in the samples photolysed at 383 K. The latter exhibit the ESR spectra

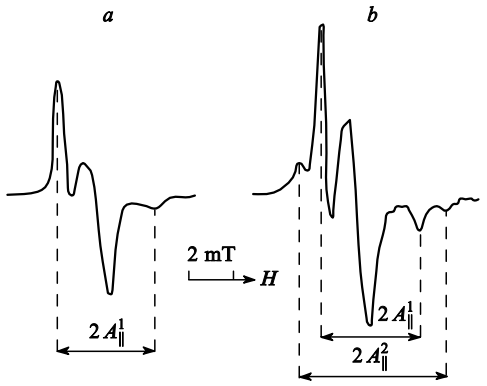


Figure 7. ESR spectra of solid PMMA photolysed in an NO atmosphere at 298 (*a*) and 383 K (*b*). The parameters $2A_{\parallel}^{1}$ and $2A_{\parallel}^{2}$ correspond to the components of hyperfine structure (HFS) of the acylalkyl and dialkylnitroxyl radicals, respectively.

with the parameters $A_{\parallel}^{N} = 3.2\pm0.1$ mT and $g_{\parallel} = 2.0026$ for the solid phase (Fig. 7 *b*) and $a^{N} = 1.5\pm0.1$ mT and $g = 2.0064$ for a solution. Under the action of UV light ($260 < \lambda < 400$ nm) alone, iminoxyl macroradicals are also formed, which exhibit triplet ESR spectra with $a^{N} = 2.8$ to 3.1 mT and $g = 2.0050$ (in solution).

The formation of acylalkylnitroxyl radicals indicates that methoxycarbonyl radicals, $CH_3OC^{\bullet}(=O)$, are split off during photolysis. Dialkylnitroxyl radicals are produced as a result of both decomposition of tertiary $\sim CH_2(CH_3)C^{\bullet}CH_2\sim$ macroradicals at 383 K and depolymerisation of the chain carrier radicals. The formation of iminoxyl radicals implies generation of $(CH_3)C(COOCH_3)C^{\bullet}H(CH_3)C(COOCH_3)\sim$ radicals during photolysis. In an atmosphere of nitric oxide, the latter are converted into nitroso compounds, which isomerise into oximes [the reactions are similar to the process (13)].

Radiolysis of PMMA at room temperature results in the formation of acylalkylnitroxyl and iminoxyl macroradicals,[102] the proportion of the latter being much higher than in the case of photolysis. The results obtained show that radiolysis causes an increase in the contribution of the reaction of hydrogen abstraction from the alkyl groups of the polymer to the overall reaction.

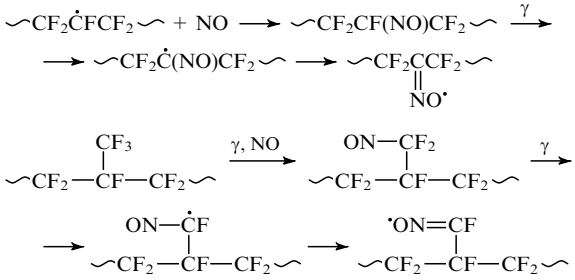
Photolysis of cellulose triacetate (CTA) in an atmosphere of NO at 298 K leads to the production of dialkylnitroxyl and acylalkylnitroxyl radicals, which exhibit the ESR spectra with the parameters $A_{\parallel}^{N} = 3.1\pm0.1$ mT, $g_{\parallel} = 2.0026$ and $A_{\parallel}^{N} = 2.0\pm0.1$ mT and $g_{\parallel} = 2.0032$, respectively. Removal of NO causes a substantial increase in the intensities of the spectral components assigned to acylalkylnitroxyl radicals, which seems to be due to decomposition of the diamagnetic complexes of these radicals with NO. Dialkylnitroxyl radicals are known to form no such complexes.[103] The appearance of acylalkylnitroxyl radicals indicates that the acetate groups decompose with the elimination of $CH_3C^{\bullet}(=O)$ radicals. Methyl radicals possibly participate in the formation of dialkylnitroxyl radicals.

The very weak signal observed during radiolysis of CTA exposed to NO precludes elucidation of the nature of the radicals formed. After long-term evacuation of the samples, an ESR spectrum appears. The main signal in this spectrum is assigned to iminoxyl radicals ($A_{\parallel}^{N} = 4.5\pm0.1$ mT, $A_{\perp}^{N} = 2.4\pm0.1$ mT, $g_{\parallel} = 2.0025$ and $g_{\perp} = 2.0054$). In addition, a weak signal of acylalkylnitroxyl radicals is observed, which has the same parameters as in the case of photolysis. This composition of radicals indicates that hydrogen abstraction from the CH_3 groups of macromolecules plays a significant role during radiolysis.

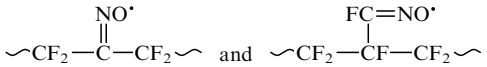
Carrying out free-radical processes in the polymers exposed to nitric oxide is in essence a specific modification of the spin trap technique. This method is, as a rule, used in the studies of the composition of free radicals in the liquid phase where the ratio of the spin adducts is determined by the composition of the radicals that are trapped, the rate constants for their reactions with nitroso compounds and by the stabilities of the nitroxyl radicals formed. In the liquid phase, the encounter of reagents is due to diffusion, which is not the limiting stage of a process. In solid polymers, nitric oxide, low-molecular-mass free radicals and nitroso compounds formed from them can diffuse with relative ease. The encounter of macromolecular species can occur only if efficient mechanisms of free valence migration exist. Under the conditions discussed here, such encounters can be the limiting steps of the reactions. In particular, this is responsible for the formation of only acylalkylnitroxyl radicals during photolysis of PMMA exposed to NO at room temperature despite the decomposition of the ester group to give methoxycarbonyl and tertiary alkyl macroradicals, which are converted in the presence of nitric oxide into macromolecular nitroso compounds. Dialkylnitroxyl radicals are produced only at elevated temperatures, where the free valence migration occurs due to the depolymerisation reaction.

2. Free-radical processes in poly(perfluoroalkenes) exposed to nitric oxide

γ-Radiolysis of PTFE and a copolymer of tetrafluoroethylene with hexafluoropropylene exposed to NO revealed the crucial role of the motion of radical centres. In this case, reactions



produce only iminoxyl macroradicals [104]



No nitroxyl radicals are formed in perfluoroalkenes under these conditions. However, they can be generated in the post-radiation reactions proceeding in an NO atmosphere.[105, 106] For instance, terminal and internal peroxyl macroradicals are stabilised in the γ-radiolysis of PTFE in air at room temperature. If the samples evacuated after γ-radiolysis are exposed to nitric oxide for a rather long time, the ESR spectrum of nitroxyl radicals $\sim CF_2N(O^{\bullet})CF_2\sim$ is observed after removal of NO. The ESR spectra of oriented films (Fig. 8) are quintets of triplets with the parameters $A_{\parallel}^{N} = 0.46$ mT, $A_{\parallel}^{F} = 1.11$ mT, $g_{\parallel} = 2.0060$; $A_{\perp}^{N} = 1.12$ mT, $A_{\perp}^{F} = 1.61$ mT and $g_{\perp} = 2.0071$. The following mechanism for production of these radicals was proposed.[105] In

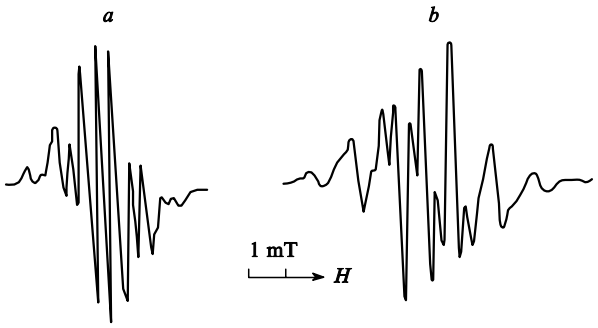


Figure 8. ESR spectra of oriented PTFE films γ-irradiated in air and exposed to NO for 96 h at 298 K. The angle between the direction of film orientation and the permanent magnetic field is 0 ° (*a*) and 90 ° (*b*).

the case of γ-radiolysis of PTFE in oxygen-containing atmosphere, a certain fraction of internal alkyl macroradicals has no time to be oxidised and undergoes decomposition accompanied by scission of the main chain of the polymer.

$$\sim CF_2-CF_2-C^{\bullet}F-CF_2\sim \longrightarrow \sim C^{\bullet}F_2 + CF_2=CF-CF_2\sim$$

The terminal alkyl groups are oxidised into terminal peroxide groups so that the neighbouring terminal peroxyl macroradicals and terminal double bonds are stabilised in the polymer. After exposure of such samples to NO, the peroxyl radicals can be converted as follows:

$$\sim CF_2-CF_2OO^{\bullet} + NO \longrightarrow \sim CF_2CF_2O^{\bullet} + NO_2,$$

$$\sim CF_2CF_2O^{\bullet} + NO \longrightarrow \sim CF_2CF_2ONO,$$

$$\sim CF_2CF_2ONO \longrightarrow \sim CF_2CF_2O^{\bullet} + NO,$$

$$\sim CF_2CF_2O^{\bullet} \longrightarrow \sim C^{\bullet}F_2 + COF_2.$$

Terminal alkyl macroradicals recombine with NO to produce terminal nitroso groups neighbouring to the terminal double bonds, which interact with terminal nitrosyl fragments to generate nitroxyl macroradicals

$$\sim C^{\bullet}F_2 + NO \longrightarrow \sim CF_2NO,$$

$$\sim CF_2NO + CF_2=CFCF_2\sim \longrightarrow \sim CF_2N(O^{\bullet})CF_2C^{\bullet}FCF_2\sim,$$

$$\sim CF_2N(O^{\bullet})CF_2C^{\bullet}FCF_2\sim + NO \longrightarrow$$

$$\longrightarrow \sim CF_2N(O^{\bullet})CF_2CF(NO)CF_2\sim.$$

It was found [107] that low-molecular-mass perfluoroalkenes of different structures as well as hydrogen- or fluorine-containing nitroso compounds can enter in these reactions. Similar radicals were also produced in the copolymer of tetrafluoroethylene with hexafluoropropylene.[106] This copolymer was used to generate yet another type of radicals, namely, $\sim CF_2N(O^{\bullet})CF_3$, with an ESR spectrum consisting of eight HFS components split by 0.88 ± 0.02 mT and $g = 2.0067$. These parameters nearly coincide with the corresponding values for low-molecular-mass perfluoronitroxyl radicals of a similar structure in the liquid phase.[107] The pattern of the ESR spectrum of the internal nitroxyl macroradical is due to partial averaging of the anisotropy of HFS and *g*-factor owing to fast rotation of the nitroxyl fragment about the long axis of the macromolecule. The mobility of the radical fragment in terminal nitroxyl radical is much higher, which in fact is responsible for a complete averaging of the anisotropy of the hyperfine interaction and *g*-tensors in its ESR spectrum.

Thus, thermally stable spin-labelled macromolecules are generated in the bulk of the samples as a result of post-radiation, free-radical transformations in fluorinated polymers exposed to NO. Their concentration is sufficiently high to allow the ESR studies on molecular dynamics in polymers. The advantage of this method for the introduction of a spin label is that the free-radical (nitroxyl) group can be introduced into various chain fragments, which allows one to obtain optimum information on the macromolecular dynamics.

3. Interaction of polypropylene hydroperoxides with nitric oxide

Polymeric hydroperoxides are reactive intermediates in the oxidative degradation of polymers. Investigations of the reactions of nitrogen oxides with these species furnishes insights into the mechanisms of the effect of air pollutant gases on the stabilities of polymeric materials. For instance, autoaccelerated degradation of PS macromolecules subject to the combined action of NO_2, air and UV radiation was associated with the NO-induced decomposition of hydroperoxides.[47] It is believed (see, *e.g.*, Refs 100 and 108) that the process begins with the reaction

$$ROOH + NO \longrightarrow RO^{\bullet} + HNO_2. \qquad (19)$$

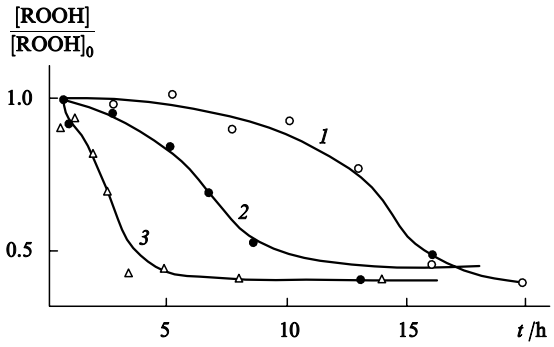


Figure 9. Kinetic curves of consumption of PP hydroperoxides at NO concentrations (in the gas phase) of 1.6×10^{-3} (*1*), 3.2×10^{-3} (*2*) and 4.1×10^{-2} mol litre^{-1} (*3*).

It was also assumed (see Ref. 101) that the reaction proceeds to give the peroxyl radicals.

$$ROOH + NO \longrightarrow ROO^{\bullet} + HNO. \qquad (20)$$

At high concentrations of hydroperoxides, NO-induced decomposition of their dimers was postulated for the liquid phase.[108]

$$(ROOH)_2 + NO \longrightarrow ROO^{\bullet} + HNO_2 + ROH. \qquad (21)$$

The decomposition kinetics of PP-derived hydroperoxides at 298 K and different NO pressures has been studied in detail.[109] The kinetic curves for decomposition of hydroperoxides are shown in Fig. 9. As can be seen, the rate of hydroperoxide consumption is initially low and then increases substantially. Reactions (19)–(21) cannot provide an explanation for this type of reaction kinetics. Using ESR spectroscopy, it was found that the decomposition of hydroperoxides is accompanied by accumulation of dialkylnitroxyl macroradicals and that the induction period is long. The duration of the induction periods for the decomposition of hydroperoxides and the formation of nitroxyl macroradicals increases as the concentration of nitric oxide in the gas phase decreases and is dependent on the presence of trace amounts of impurities (in particular, NO_2) at a given NO concentration. It was concluded that the primary step in the decomposition of hydroperoxide is initiated by N_2O_3 rather than NO.

$$ROOH + N_2O_3 \longrightarrow [ROONO] + HNO_2.$$

This reaction results in a thermally unstable peroxy nitrite, which can either undergo a fast 'intracage' conversion into nitrate

$$[ROONO] \longrightarrow [RO^{\bullet} + NO_2] \begin{cases} \longrightarrow RONO_2 \\ \longrightarrow RO^{\bullet} + NO_2 \end{cases}$$

or decompose into alkoxyl macroradical and nitrogen dioxide, which then pass in the bulk of the sample. In turn, the alkoxyl radicals can either decompose or enter into substitution reaction, thus producing internal ($R^{\bullet}_{in}$) and terminal ($R^{\bullet}_{t}$) alkyl macroradicals and low-molecular-mass alkyl radicals $r^{\bullet}$ (see Ref. 100). These radicals react with NO to give nitroso compounds.

$$RO^{\bullet} \longrightarrow R^{\bullet}_{in}(R^{\bullet}_{t}, r^{\bullet}),$$

$$R^{\bullet}_{in}(R^{\bullet}_{t}, r^{\bullet}) + NO \longrightarrow R_{in}NO(R_tNO, rNO).$$

Acceleration of peroxide decomposition can be associated with the reactions which involve nitroso compounds [110]

$$ROOH + rNO \longrightarrow RO^{\bullet} + rN(O^{\bullet})OH,$$

$$rN(O^{\bullet})OH \longrightarrow r^{\bullet} + HNO_2.$$

Alkyl radicals formed in the system can initiate decomposition of hydroperoxides.

$$r^{\bullet}(R^{\bullet}_{in}, R^{\bullet}_{t}) + ROOH \longrightarrow rH(R_{in}H, R_tH) + RO^{\bullet}_2$$

$$RO^{\bullet}_2 + NO \longrightarrow [ROONO] \begin{cases} \longrightarrow RO^{\bullet} + NO_2 \\ \longrightarrow RONO_2 \end{cases}$$

Yet another process which can be responsible for the increase in the hydroperoxide decomposition rate is disproportionation of NO into N_2 and NO_3 in the reactions with the nitroso compounds.[94]

$$RNO + 2NO \longrightarrow [R{-}N{=}N{-}ONO_2] \longrightarrow$$

$$\longrightarrow [R^{\bullet} + N_2 + {}^{\bullet}ONO_2] \begin{cases} \longrightarrow RONO_2 + N_2 \\ \longrightarrow R^{\bullet} + N_2 + NO_3 \end{cases}$$

The ONO_2 radical is a highly reactive species (the O_2NO-H binding energy is 423 kJ mol^{-1}, see Ref. 111), which can abstract hydrogen atoms from the PP macromolecules, thus increasing the concentration of free radicals in the polymer

$$RH + {}^{\bullet}ONO_2 \longrightarrow R^{\bullet} + HNO_3,$$

and also reacts with NO

$$NO + NO_3 \longrightarrow 2NO_2,$$

which results in an increase in the concentration of nitrogen dioxide.

Thus, taking PP as an example, it was found that decomposition of hydroperoxides in an atmosphere of NO is initiated by higher nitrogen oxides and proceeds by an autocatalytic mechanism.

In an atmosphere polluted with nitrogen oxides, the primary step of the decomposition of hydroperoxides can be their nitrosation by the dimeric form of nitrogen dioxide, the concentration of which is much higher than that of nitrous anhydride N_2O_3. On account of the great excess of oxygen compared to nitrogen oxides, the probability of the formation of nitroso compounds, which play the key role in the development of autoaccelerated reaction under the conditions used by Gaponova and Pariiskii,[109] must be rather low in a polluted atmosphere due to the oxidation of alkyl radicals into peroxyl radicals. Investigation of the ROOH – NO system showed [109] that the results obtained under conditions of accelerated tests must be used with great caution when assessing the stability of polymers in atmosphere polluted with nitrogen oxides.

IV. Conclusion

The results summarised in this review show that nitrogen dioxide, which is an inorganic free radical of moderate reactivity, can perform some functions in the ageing of polymers in polluted atmosphere. On the one hand, at ambient temperatures it can abstract labile hydrogen atoms (tertiary hydrogen atoms in PS and polyvinylpyrrolidone and allylic hydrogen atoms in the polymers containing carbon – carbon double bonds in the main chain) and add to the double bonds of macromolecules, thus generating free radicals and, hence, initiating free-radical ageing processes in the system. At elevated temperatures ($T \geqslant 373$ K), NO_2 also reacts with stronger C – H bonds, *e.g.*, in the CH_2 groups of polymers. On the other hand, it can react with alkyl, alkoxyl and peroxyl macroradicals generated in the reactions, thus inhibiting free-radical transformations of polymers and resulting in valence-saturated products of different thermal stabilities.

The dimer of nitrogen dioxide, N_2O_4, is an efficient nitrosating agent and its reactions are responsible for the ageing of the polymers containing amide groups (polyamides, polyurethanes and polyamidoimides). Free-radical reactions initiated by NO_2 are accompanied by production of stable nitrogen-containing radicals. Analysis of their structures and kinetics of formation provides additional information on the free-radical stages of complex processes of nitration of polymers under various conditions.

Nitric oxide, NO, is also a paramagnetic molecule, which is much less reactive than nitrogen dioxide. At ambient temperatures, it cannot abstract even the most mobile (labile) hydrogen atoms from the molecules of organic compounds or add to isolated double bonds to produce free radicals. In addition, it is an efficient acceptor of free radicals which can inhibit free-radical chain reactions. Nitroso compounds formed in the reactions with alkyl radicals are efficient spin traps and can in turn inhibit free-radical processes in polymers. However, at high NO pressures their reactions with nitroso compounds lead to disproportionation of NO into N_2 and ONO_2, which is a reactive radical capable of initiating free-radical processes in polymers. This reaction seems to be the stage responsible for autoaccelerated decomposition of hydroperoxides in an atmosphere of nitric oxide.

Free radicals in solid polymers can be generated by photolysis, γ-radiolysis, thermal decomposition of initiators *etc*. Free-radical processes in solid polymers carried out in an atmosphere of NO are accompanied by production of nitrogen-containing macroradicals of different structures. Analysis of their structures and kinetics of formation allows one to obtain additional information on the mechanisms of the above-mentioned processes. Performing free-radical reactions in chemically inert, insoluble polymers [*e.g.*, poly(perfluoroalkenes)] in an atmosphere of nitric oxide makes it possible to prepare spin-labelled macromolecules with either internal or terminal $NO^{\bullet}$ groups. These spin labels perturb the polymer chain dynamics to the smallest extent and are therefore the most appropriate for using in the ESR studies.

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