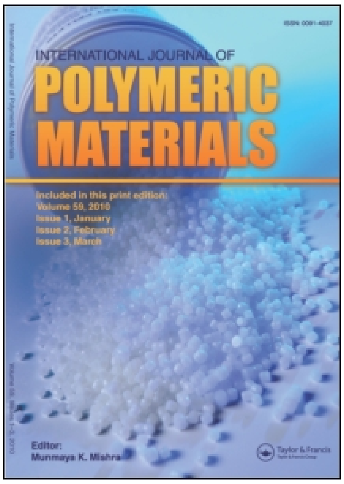


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Interaction Between Polymers and Polluted Atmosphere (Nitrogen Oxides)

G. E. Zaikov[a]; G. B. Pariiskii[a]; I. S. Gaponova[a]; E. Ya. Davydov[a]
[a] Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

To cite this Article Zaikov, G. E. , Pariiskii, G. B. , Gaponova, I. S. and Davydov, E. Ya.(2001) 'Interaction Between Polymers and Polluted Atmosphere (Nitrogen Oxides)', International Journal of Polymeric Materials, 48: 3, 331 — 353
To link to this Article: DOI: 10.1080/00914030108050789
URL: http://dx.doi.org/10.1080/00914030108050789

Intern. J. Polymeric Mater., 2001, Vol. 48, pp. 331 – 353
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Review Article

Interaction Between Polymers and Polluted Atmosphere (Nitrogen Oxides)

G. E. ZAIKOV*, G. B. PARIISKII, I. S. GAPONOVA
and E. YA. DAVYDOV

*Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
Kosygin St., 4, Moscow, 117334, Russia*

(Received 7 October 1999; In final form 8 November 1999)

The mechanism of reactions of nitrogen oxides with various solid polymers has been considered. The active participants of the reactions with nitrogen oxides are double bonds, amide groups of macromolecules and peroxy macroradicals. The reactions of nitrogen oxides provide a simple way for the preparation of spin labeled polymers. The structure of the reaction front during nitration of polyisoprene has been studied using the ESR tomography technique. The structural-physical effect on kinetics and mechanism of reactions of nitrogen oxides has been demonstrated by the example of filled polyvinylpyrrolidone.

Keywords: Nitrogen oxides; Solid polymers; Degradation; Nitroxyl radicals; Spin labels; ESR tomography

The mechanism of the influence of atmospheric deleterious impurities on polymers have generated interest for a long time [1 – 3]. Knowledge of this mechanism is required in order to predict reliably the behavior of polymeric materials in various service conditions. A large body of researches have showed that the most harmful constituents

---

*Corresponding author. Fax: 007-095-137-41-01, e-mail: chembio@glasnet.ru

of the atmosphere are nitrogen oxides, sulfur oxides, ozone, chlorine, and hydrocarbons. Nitrogen oxides are the most important among them. The originally performed investigations of kinetics and mechanism of the interactions of nitrogen oxides with polymers will be considered in this article. In addition, the possibilities of application of the reactions of nitrogen oxides with macromolecules to investigate molecular-dynamical and structural-physical properties of polymers are presented.

NITROGEN OXIDES AS AGENTS OF FREE-RADICAL DEGRADATION OF POLYMERS

Nitrogen dioxide is free radical, and, therefore, its interactions with polymers lead to the initiation of free-radicals. However, NO_2 is

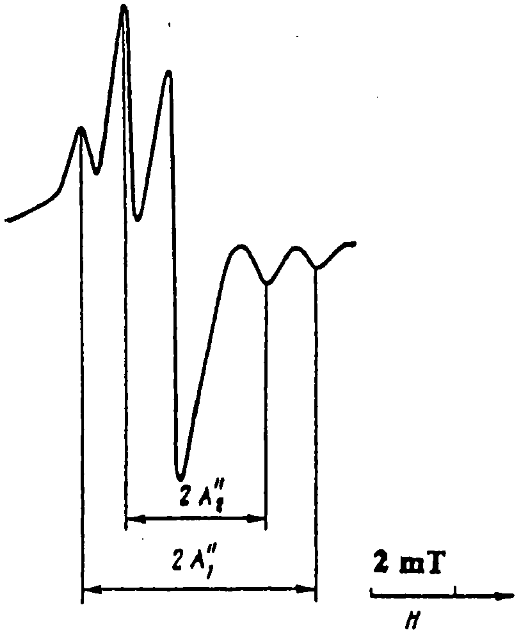
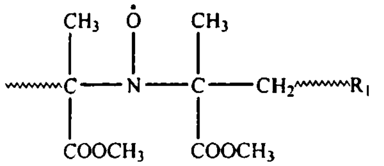


FIGURE 1 ESR of dialkylnitroxyl (R_1) and acylalkylnitroxyl (R_2) radicals in PMMA on exposure to NO_2.

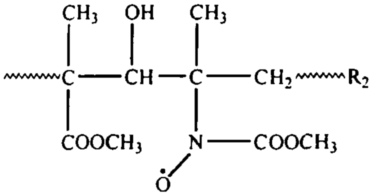
relatively low-active radical. It interacts very slowly with C—H bonds of macromolecules at moderate temperatures. However, NO_2 adds rapidly to compounds containing double bonds with the formation of radicals $O_2N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$ To clear up the nature of radicals formed in solid polymers, the interaction of NO_2 with double bonds of polymethylmethacrylate (PMMA), previously irradiated by light at 293 K, was studied by the ESR method [4]. The observed ESR spectrum is shown in Figure 1.

The spectrum represents a superposition of signals of two nitroxyl radicals at low frequencies of the rotational mobility. Dialkylnitroxyl radicals



$$\sim\!\sim\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-\overset{\displaystyle \dot{O}}{N}-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-CH_2\sim\!\sim R_1$$

give the anisotropic triplet signal with $A_1^{\|} = 3.2 \pm 0.1$ mT, $g_{\|} = 2.0026 \pm 0.0005$, and acylalkylnitroxyl radicals



$$\sim\!\sim\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-\overset{\displaystyle OH}{CH}-\overset{\displaystyle CH_3}{\underset{\displaystyle \dot{O}\!\diagup N-COOCH_3}{C}}-CH_2\sim\!\sim R_2$$

are characterized by the triplet with $A_2^{\|} = 2.1 \pm 0.1$ mT and $g_{\|} = 2.0027 \pm 0.0005$.

The plots of the initial rate of the accumulation of nitroxyl radicals in PMMA *versus* the NO_2 concentration in the gas phase are given in Figure 2. It is obvious from Figure 2 that the initial rate of the radical formation varies in direct proportion to the NO_2 concentration. Kinetics of the radical accumulation in PMMA do not have an induction period. These experimental data permit us to assume that nitroxyl radicals in solid polymers are formed in "cage" reactions with NO_2 rather than as a result of a meeting of macroradicals in the sample volume.

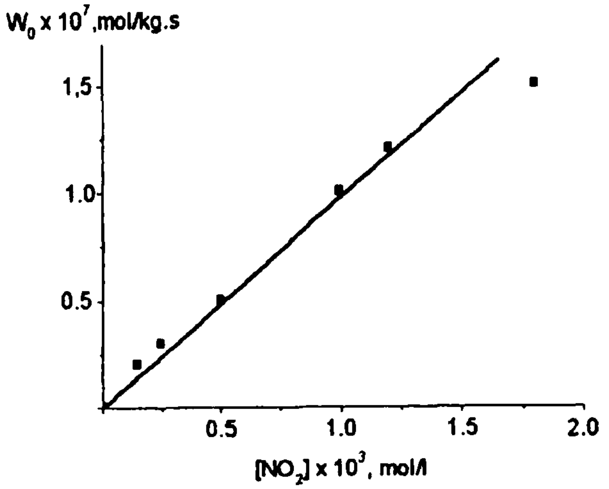
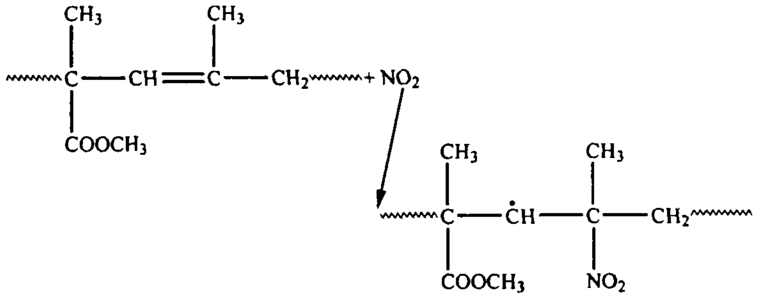
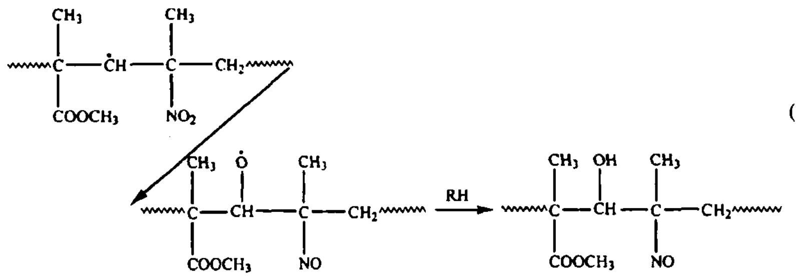


FIGURE 2 Plots of the initial rate of the nitroxyl radical formation in PMMA *versus* the NO_2 concentration.

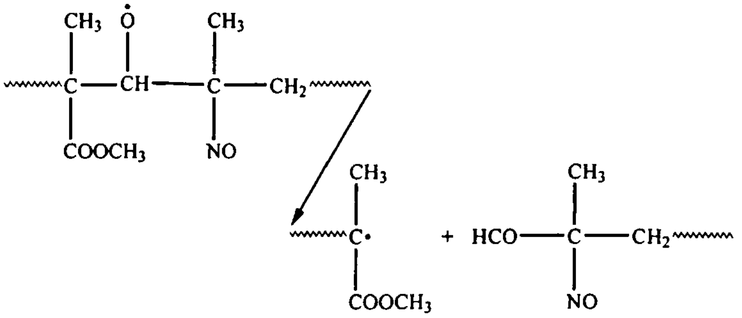
The free-radical process of the NO_2 interaction with PMMA containing double bonds can be represented by the following scheme:

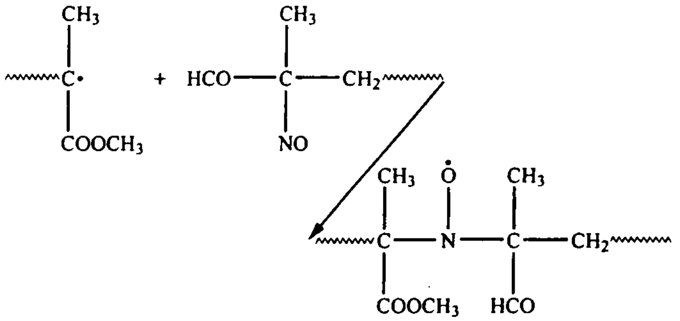


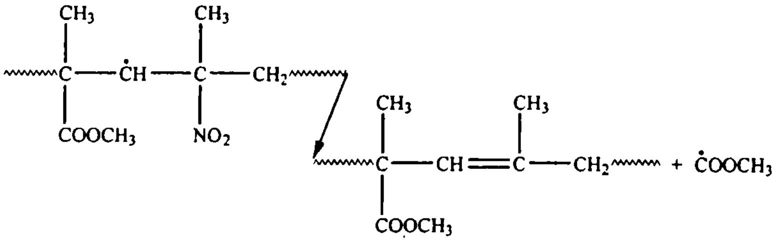
(1)

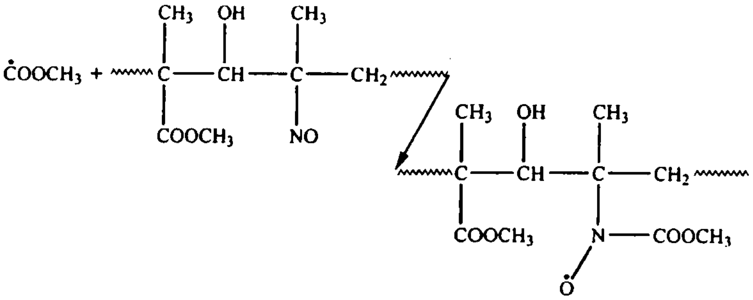


(2)


(3)


(4)


(5)


(6)

The tertiary dialkylnitroxyl macroradicals (R_1) can be obtained as a result of reactions (3) and (4). The small-scale translations and rotational motions are large enough for these reactions to occur. The acylalkylnitroxyl radical (R_2) formation indicates that macrochain decomposition (reactions 5, 6) takes place in the polymer. Thus, the interaction of NO_2 with double bonds initiates free-radical reactions of the polymer degradation even in such conditions when reactions of the hydrogen atom abstraction from C—H bonds are of low efficiency.

The presence of nitrogen dioxide is capable of initiating a free-radical degradation of fluorinated polymers, which are often employed in extreme conditions of the action of ionizing radiation, light, mechanical strain. In this case the polymer accumulates peroxide macroradicals which readily react with NO_2 in the air of polluted atmosphere [5]. Using the ESR method, the thermal stability was studied of the products resulting from the reaction of chain peroxide radicals $\sim CF_2—CFO_2—CF_2 \sim (R_cO_2^{\bullet})$ and end peroxide radicals $\sim CF_2—CF_2O_2^{\bullet}(R_cO_2^{\bullet})$ of polytetrafluoroethylene (PTFE) (Fig. 3)

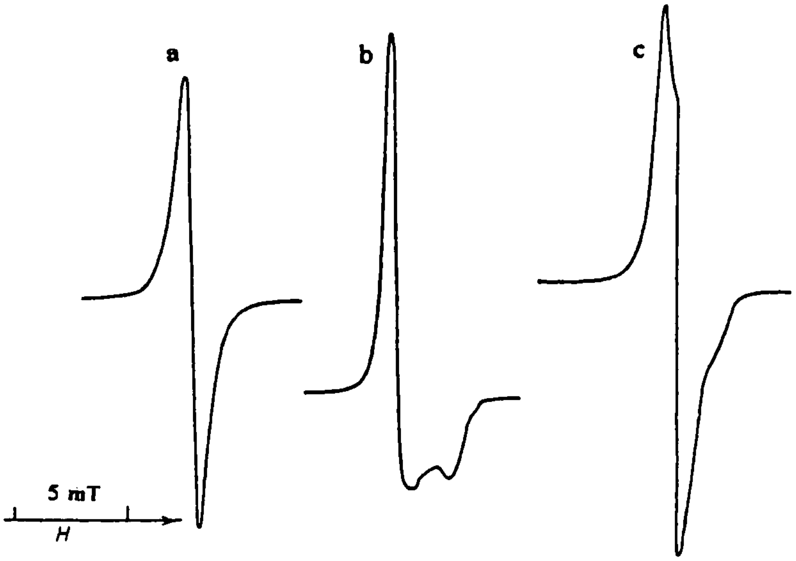


FIGURE 3 ESR spectra of peroxide radicals in PTFE γ-irradiated in the air: (a) – $R_cO_2^{\bullet}$; (b) – $R_cO_2^{\bullet}$; (c) – (a) + (b).

with NO_2. The free-radical process includes the peroxynitrate formation in the primary stage:

$$RO_2^{\bullet} + NO_2 \leftrightarrow RO_2NO_2 \qquad (7)$$

Peroxynitrates were shown to be thermally unstable compounds, which dissociate to yield free radicals. Two routes of their decomposition are possible:

$$RO_2NO_2 \rightarrow RO_2^{\bullet} + NO_2 \qquad (8)$$

$$RO_2NO_2 \rightarrow RO^{\bullet} + NO_3 \qquad (9)$$

In order to predict the stability of poly(tetrafluoroethane) (PTFE) in an atmosphere polluted with NO_2 it is important to consider the possibility of reactions (8) and (9) as well as the ratio of their rates. A reaction route similar to (9) results in the destruction of the polymer macromolecule since the resultant oxy-radicals in the fluorinated polymers cannot enter into the substitution reaction. They quite readily decompose with the main chain of the macromolecule being broken down. For example in PTFE:

$$\sim CF_2{-}CF(O^{\bullet}){-}CF_2 \sim \rightarrow \sim CF_2{-}CFO + {}^{\bullet}CF_2{-}CF_2 \sim \qquad (10)$$

The interaction of NO_2 with PTFE samples containing either chain or end peroxide macroradicals results in gradual decay of these radicals (Fig. 4).

If the sample contains both types of peroxide radicals, the ESR signal shape remains unchanged during their decay, that is, the kinetics of the decay of the radicals of both types are practically identical and are likely to be determined by the rate of NO_2 diffusion into polymer. The sample was exposed to NO_2 atmosphere for various periods of time exceeding the time required for complete decay of the radicals. Then the gas phase was evacuated at the same temperature (313 K). The kinetics of accumulation of paramagnetic centers resulting from the decomposition of the products of the reaction between peroxide radicals and NO_2 was studied in vacuum. It was found that the viability of these products depends on the type of the initial peroxide radicals.

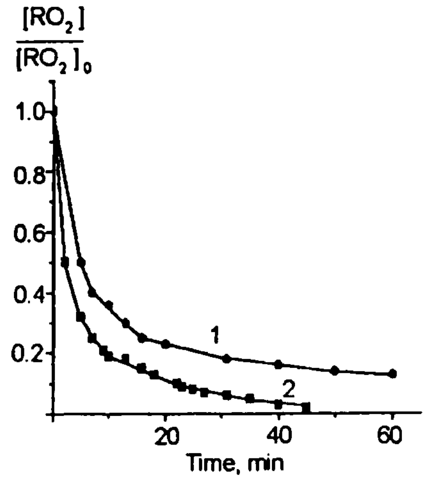


FIGURE 4 Kinetics of decay of peroxide radicals of PTFE in NO_2 at 298 K: 1 – $[NO_2] = 1.6 \cdot 10^{-4}$ mol/l; 2 – $[NO_2] = 9.3 \cdot 10^{-4}$ mol/l.

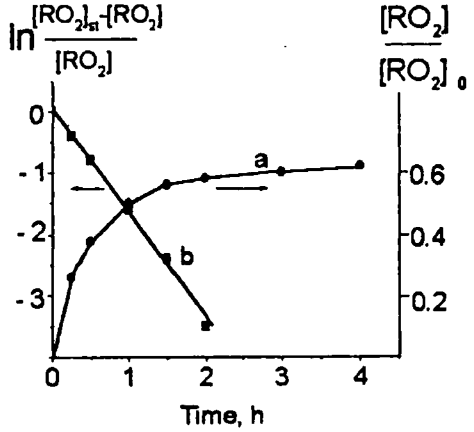


FIGURE 5 The kinetic curve of the $R_cO_2^{\bullet}$ regeneration in PTFE after exposition of the polymer in NO_2 at 313 K (a) and its semilogarithmic anamorphosis (b); $[NO_2] = 2.8 \cdot 10^{-3}$ mol/l.

Evacuation of a sample initially containing chain peroxide radicals results in partial regeneration of $R_cO_2^{\bullet}$ (Fig. 5). However, in the case where the PTFE contained end peroxide radicals, no regeneration was observed of these radicals by the sample after the removal of NO_2.

The reappearance of peroxide radicals in the PTFE samples upon evacuation enabled us to conclude that the product of the $R_cO_2^{\bullet}$ reaction with NO_2 is peroxynitrate. *i.e.*, fluorinated compounds also exhibit the reversible reaction:

$$R_cO_2^{\bullet} + NO_2 \underset{k_1}{\overset{k-1}{\rightleftarrows}} R_c^{\bullet}O_2NO_2 \qquad (11)$$

The kinetics of the peroxide radicals regeneration (Fig. 5) in vacuum at 313 K is described by the equation:

$$[R_cO_2^{\bullet}] = [R_cO_2^{\bullet}]_{\infty}(1 - e^{-k_1 t}) \qquad (12)$$

The value $k_1 = (4.8 \pm 1.5) \cdot 10^{-4}\,s^{-1}$ and depends neither on the initial concentration of $[R_cO_2^{\bullet}]_0$ nor the time of PTFE exposure to NO_2.

Peroxide radicals, which are in equilibrium with $R_cO_2NO_2$, can react with nitrogen oxide either present in the initial mixture or formed in the system:

$$R_cO_2^{\bullet} + NO \rightarrow R_cO^{\bullet} + NO_2 \rightarrow \text{product} \qquad (13)$$

The existence of this reaction is confirmed by the decrease of the constant in the presence of air. The thermal decomposition of oxy-radicals, obtained by the reaction (13), leads to fluoroalkyl radical formation as indicated by reaction (10) for chain oxyradicals, or by the following reaction for end oxyradicals (Fig. 6):

$$\sim CF_2{-}CF_2O^{\bullet} \rightarrow CF_2O + {}^{\bullet}CF_2{-}CF_2 \sim \qquad (14)$$

The free radical degradation induced by NO_2 was observed by ESR and UV techniques in polyvinylpyrrolodone (PVP) [6]. Absorption bands at 413 nm and 435 nm were observed in the UV spectrum of the reaction products of the interaction of PVP with NO_2 (Fig. 7). The peculiar spectral region makes possible the assignment of these bands to nitrosoamide groups [7]. Based upon the nature of monomer links, the following cyclic structure may be attributed to nitrosoamides: $N(NO)COCH_2CH_2CH_2$. The formation of these compounds in PVP must be associated with the splitting off of the side cyclic fragments from the main chain. In addition, the UV absorption in the region of

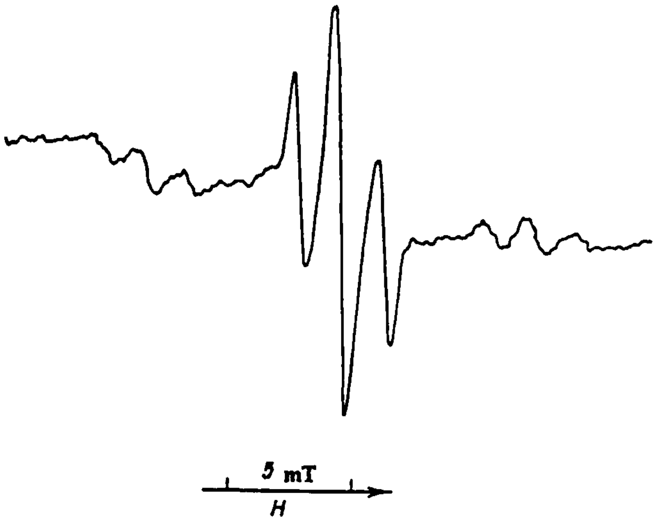


FIGURE 6 ESR spectrum of fluoroalkyl radicals resulting in the oxyradical thermal decomposition (373 K).

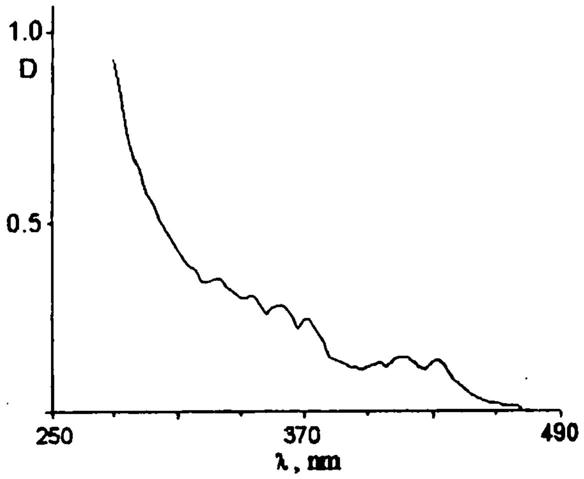
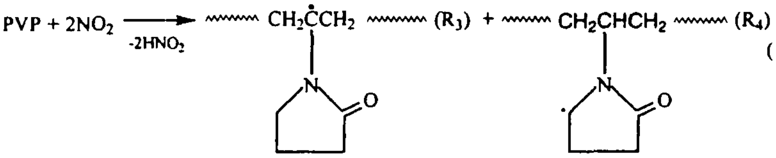


FIGURE 7 UV spectrum of PVP after exposure to NO_2.

320–380 nm was observed with a set of bands spaced at 10 nm apart. This fact indicates that alkylnitrites [8] are formed in the course of the reaction.

The ESR spectra observed when NO_2 is admitted into PVP, are shown in Figures 8(a), (b). These spectra represent a superposition of signals of two radical types: acylalkylnitroxyl radicals (R_1) and iminoxyl radicals (R_2). The anisotropic triplet signal with the constant of HFI of $A_{\parallel}^{N} \approx 1.94\,\mathrm{mT}$ and $g_{\parallel}$ corresponds to R_1. The anisotropic signal with parameters $A_{\parallel}^{N} = 4.33\,\mathrm{mT}$, $A_{\perp}^{N} = 2.44\,\mathrm{mT}$, $g_{\parallel} = 2.0029$ and $g_{\perp} = 20053$ corresponds to R_2.

The results of analysis of the UV and ESR spectra permit to propose the following mechanism of PVP conversion initiated by NO_2. Most likely C—H bonds, which are in the α-position with respect to the amide groups, show activity in the reaction of hydrogen atom abstraction. There are two kinds of such C—H bonds closely related to the scission energy, and, consequently, one can expect the formation in the primary reaction of two macroradicals with free radicals localized in the main chain and side group:



(15)

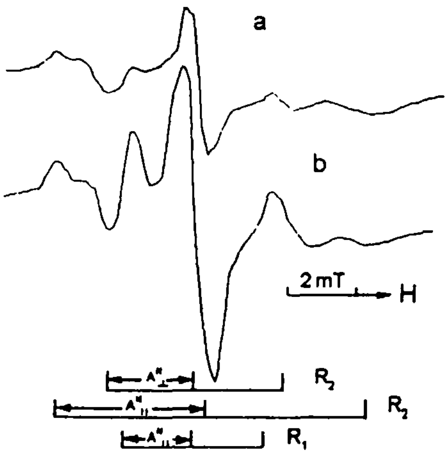
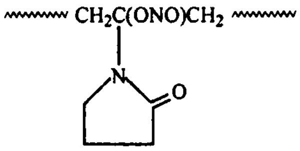
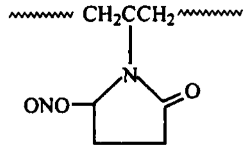


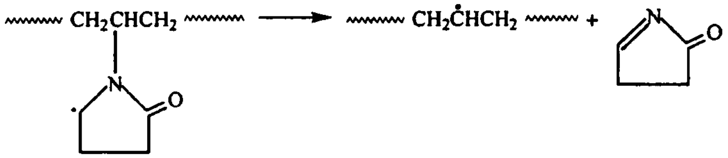
FIGURE 8 ESR spectrum of PVP after exposure to NO_2 without (a) and with 50% aerosil (b) at 323 K.

The recombination of R_3 and R_4 with NO_2 results in the formation of nitrites:



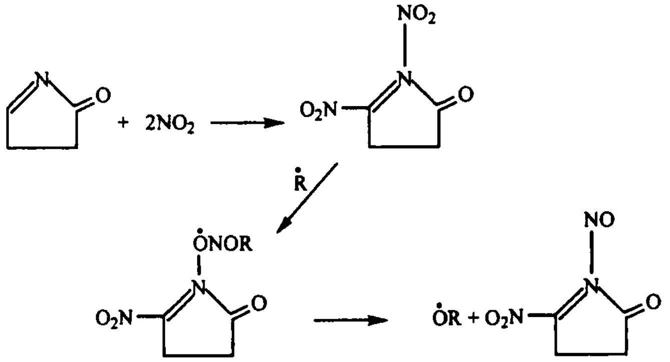


The formation of nitrosoamides is possible as a result of *β*-decomposition of R_4. As this takes place, the splitting off of the ring occurs



(16)

Thereafter the NO_2 reaction with the double bonds of this fragment gives rise to the end product:

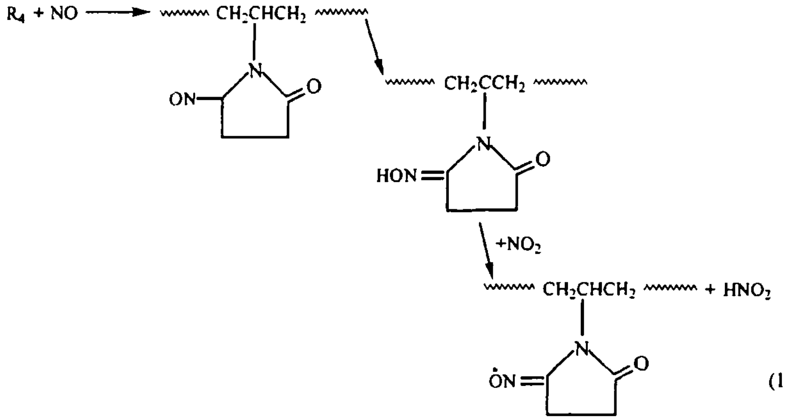


(17)

Nitrous acid is thought to be the contributor of nitrogen oxide in the given system.

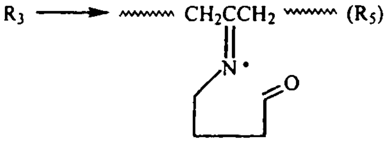
$$2HNO_2 \rightarrow H_2O + NO_2 + NO \tag{18}$$

The recombination of NO and R_2 initiates the formation of iminoxyl radicals R_2. This process includes the following consecutive reactions: the formation of nitroso compounds, their isomerization into oxime, the abstraction of hydrogen atom by NO_2 from oxime.



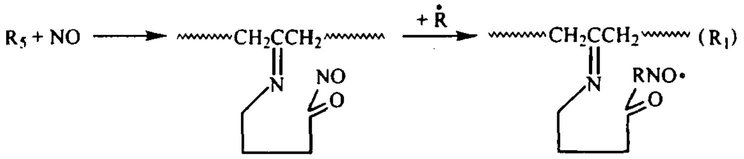
(19)

The formation of NO by reaction (18) can explain the appearance of acylalkylnitroxyl radicals R_1. To do this would require an assumption of the R_3 decomposition with opening of the pyrrolidone cycle:



(20)

Furthermore, acylnitroso compounds and then R_1 are formed in the reaction of the twofold radical acceptance:



(21)

Note that any unstable at ordinary temperature free radicals, for example, R_3, R_4, R_5 may be regarded as $R^{\bullet}$.

Thus, the dominant molecular products of the PVP nitration by NO_2 are nitrosoamides and nitrites. Along with them, stable nitroxyl radicals are formed. Their structure and the formation mechanism indicate that the primary reaction of the hydrogen atom abstraction from macromolecules is selective. The C—H bonds in the α-position with respect to the amide groups take part in this reaction.

APPLICATION OF NITROGEN OXIDES IN ORDER TO OBTAIN SPIN-LABELED MACROMOLECULES

ESR investigations in physical chemistry of polymers frequently employ the method of spin labels, generated by nitroxyl radicals covalently bound to macromolecules. This technique is used to determine the frequencies of molecular motions and detect changes in them caused by various external factors acting upon the solid polymers.

Spin-labeled elastomer molecules are usually obtained by various methods, which require complex chemical reaction. We propose here, a very simple and rapid method for the synthesis of spin-labeled macromolecules of rubbers *via* a reaction of block polymer samples with gaseous NO_2 [9]. Interaction of gaseous NO_2 with polyisoprene (PI) sample gives rise to an ESR signal, depicted in Figure 9.

The spectrum shows a characteristic anisotropic triplet signal from nitroxyl radicals in the region of their slow motions ($10^{-9}\,s < \tau_c < 10^{-7}\,s$) with a width of $2A_{zz} = 6.20\,mT$ and $g_z = 2.0028 \pm 0.0005$. Upon dissolving the polymer in toluene, the spectrum exhibits a triplet signal with $A^N = 1.53 \pm 0.03$, $g = 2.0057 \pm 0.0005$, and the component intensity ratio is slightly different from 1 : 1 : 1. This spectrum is characteristic of di-tert-alkylnitroxyl radicals in the region of their fast motions ($10^{-9} > \tau_c > 5 \cdot 10^{-11}\,s$) (Fig. 8(b)). In the absence of NO_2, the nitroxyl macroradicals in the sample were stable during storage for many months in both inert atmosphere and in air.

The set of possible reactions necessary to explain the formation and conversion of the nitroxyl macroradicals in PI can be represented as follows. The proposed scheme involved four main stages:

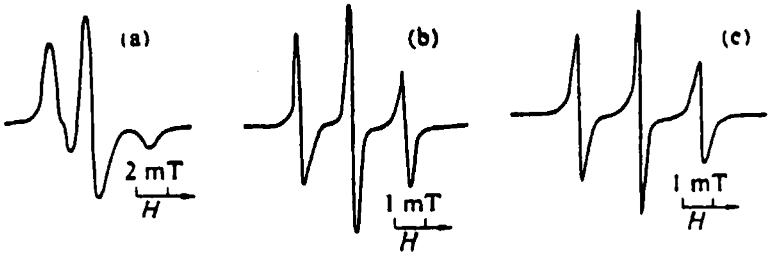
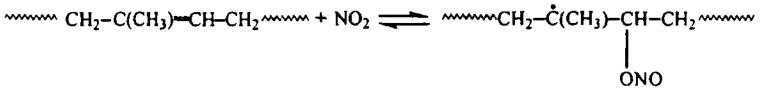
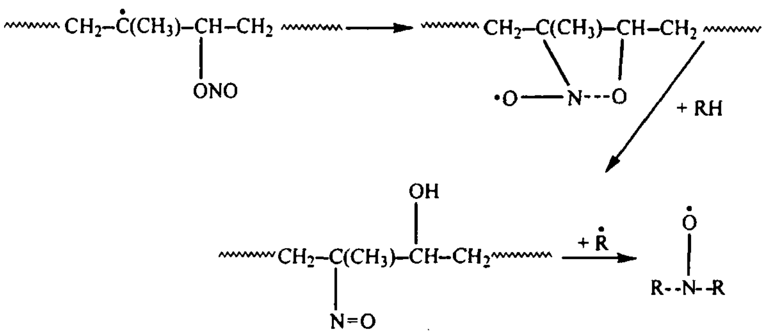


FIGURE 9 ESR spectra of nitroxyl macroradicals synthesized in reaction of PI with NO_2: (a, c) – block sample; (b) – 1% toluene solution; $T = 293$ (a, b); 373 K(c).

(i) generation of alkyl macroradicals by the reaction of NO_2 with elastomers; (ii) synthesis of tertiary macromolecular nitroso compounds; (iii) accepting of the tertiary alkyl or allyl macroradicals; and (iv) loss of nitroxyl macroradicals.



$$\sim\sim CH_2{-}C(CH_3){=}CH{-}CH_2\sim\sim + NO_2 \rightleftharpoons \sim\sim CH_2{-}\dot{C}(CH_3){-}\underset{ONO}{\underset{|}{C}H}{-}CH_2\sim\sim \quad (22)$$



(23)

Using the spin-labeled samples obtained, the temperature variation of the rotational mobility of macromolecules in the block PI has been studied (Fig. 10), and analysis performed over the entire temperature range studied within the framework of the isotropic rotation model. The temperature dependence of the rotational correlation time is described by the equation $\tau_c = \tau_0 \exp(E/RT)$. The τ_c values in the region of fast rotations are well described with the parameters $E = 34.7$ kJ/mol and $\log \tau_0 = -14.2$. It was established that the nitroxyl macroradicals formed in reaction of PI with NO_2 are stable at temperatures up to 373 K both in solution and in the bulk polymer.

When the reactivity of the macromolecule is low, spin labels can be synthesized by reactions in which macroradicals produced using one method or another are accepted by low-molecular nitrosocompounds, nitrons, or nitroxyl radicals dissolved in the polymer. However, it is a difficult problem to introduce such spin traps into the bulk of PTFE, which is chemically inert, rigid, and insoluble. Exposure to nitrogen oxide of PTFE containing a mixture of middle and terminal peroxy radicals and γ-irradiation at room temperature in air leads to the formation of nitrogen-containing radicals whose ESR spectrum at 298 K are displayed in Figure 11 [10].

Formation of these radicals requires an extended exposure time of the sample to NO (48 h or longer), and when the NO was removed from the samples in 30 or 60 min after the decay of the initial radicals,

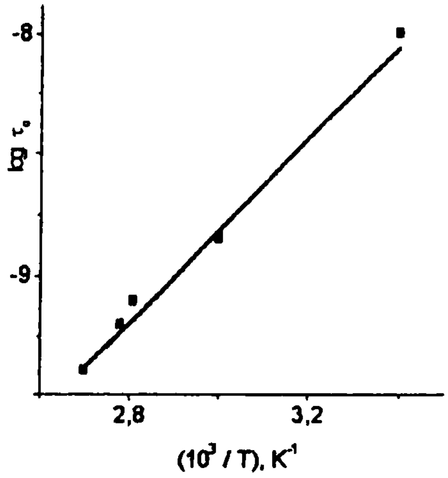


FIGURE 10 The temperature dependence of the correlation time of rotational diffusion of PI macromolecules.

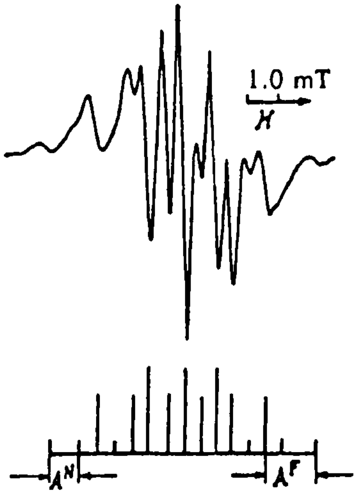


FIGURE 11 ESR spectrum of ~ CF_2—N(O$^\bullet$)—CF_2 ~ macroradicals.

no nitrogen-containing radicals were detected even after longtime storing the samples in vacuum. The mechanism must be such that nitroxyl radicals formed as a result of a sequence of several reactions. In an oxygen-containing atmosphere part of the middle alkyl radicals formed in the course of γ-irradiation under the effect of high-energy factors is capable of decomposing with a rupture of the main macromolecule chain:

$$\sim CF_2{-}CF_2{-}C^{\bullet}F{-}CF_2\sim \rightarrow \sim C^{\bullet}F_2 + CF_2{=}CF{-}CF_2\sim \qquad (24)$$

In the presence of oxygen, the terminal alkyl macroradicals can be oxidized to form the terminal peroxy radicals

$$\sim C^{\bullet}F_2 + O_2 \rightarrow \sim CF_2{-}CF_2OO^{\bullet} \qquad (25)$$

Samples containing neighboring terminal double bonds and peroxy radicals the latter are converted under the action of NO into macromolecular. nitrates and nitrites:

$$\sim CF_2{-}CFOO^{\bullet} + NO \rightarrow \sim CF_2O^{\bullet} + NO_2 \qquad (26)$$

$$\sim CF_2O^{\bullet} + NO \rightarrow \sim CF_2ONO \qquad (27)$$

$$\sim CF_2ONO \leftrightarrow \sim CF_2O^{\bullet} + NO \qquad (28)$$

$$\sim CF_2{-}CF_2O^{\bullet} \rightarrow \sim CF_2^{\bullet} + COF_2 \qquad (29)$$

The adjacent terminal double bands and formed terminal nitroso compounds can enter in a reaction to synthesize nitroxyl radicals:

$$\sim CF_2^{\bullet} + NO \rightarrow \sim CF_2{-}N{=}O \qquad (30)$$

$$\begin{aligned} &\sim CF_2{-}N{=}O + CF_2{=}CF{-}CF_2\sim + NO \\ &\quad \rightarrow \sim CF_2{-}N(O^{\bullet})CF_2{-}CF(NO){-}CF_2\sim \qquad (31) \end{aligned}$$

Thus, conducting free radical PTFE conversions in an NO atmosphere enables the synthesis in the bulk polymer of terminally stable spin-labeled macromolecules whose concentration is quite ample to investigate the molecular dynamics of this polymer by ESR spectroscopy. The advantage of the suggested method is that the nitroxyl free-radical fragment is incorporated in the basic macromolecule chain and is not disturbing its orientation.

ESR TOMOGRAPHIC STUDY ON NITRATION OF POLYISOPRENE BY NO_2

As discussed above, the nitration of rubbers is accompanied by the formation of nitroxyl radicals $(R)_2NO^{\bullet}$, which are spin labels. The spatial distribution of nitroxyl radicals permits us to judge the efficiency of the nitration process throughout the whole sample volume. The possibilities of the ESR tomographic technique application to determine the form of the reaction front of the PI nitration are considered in the work [11]. The tomographic ESR spectra were registered in non-homogeneous magnetic field on cylindrical samples of 0.4 cm diameter and 1.5 cm height. The reaction was conducted at NO_2 and O_2 concentrations of $10^{-4} - 2 \cdot 10^{-3}$ mol/l and $2 \cdot 10^{-3} - 1.4 \cdot 10^{-2}$ mol/l, respectively.

The spatial distribution of $(R)_2NO^{\bullet}$ radicals at various reaction times is shown in Figure 12. It is seen, that the spatial distribution in the samples remains constant after 2.5 h. The width of this distribution varies over only 20–30% for 740 h reaction. The maximum concentration of radicals is observed in an exterior layer, and is progressively decreased towards the center of the sample. The width of the external is ~1 mm, and radicals are unavailable in the sample center. The distribution seen at fixed distances from the surface is likely determined by macro-defects in the sample bulk, namely, the availability of pores and cracks. The nitroxyl radical yield with respect to the NO_2 absorbed molecules is 0.01. This accumulation of radicals indicates that in these areas the polymer behaves as if it is a crosslinked polymer network.

One would expect that the diffusion limitations for the PI nitration reaction caused by structural changes could be relieved in the presence of oxygen, because the network formation probability is decreased in this case. As this takes place, more uniform distribution of radicals and thicker layer of the reaction should be observed. However the results of tomographic measurements do not support these concepts. The spatial distributions of nitroxyl radicals in the presence of O_2 are

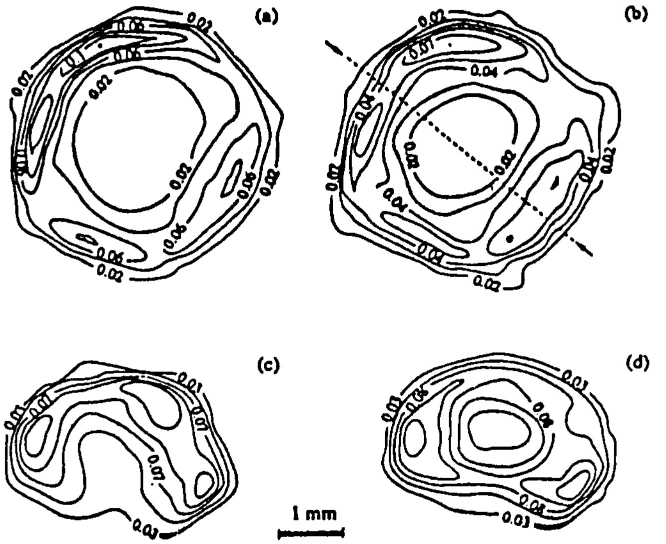


FIGURE 12 Pseudo-three-dimensional distributions of $(R)_2NO^{\bullet}$ radicals produced during nitration of PI samples by NO_2: (a) $t = 2.5$ h; (b) $t = 740$ h; (c) sample (b) cut across the line pointed in (b); (d) sample (c) exposed for 17 h at the same NO_2 pressure.

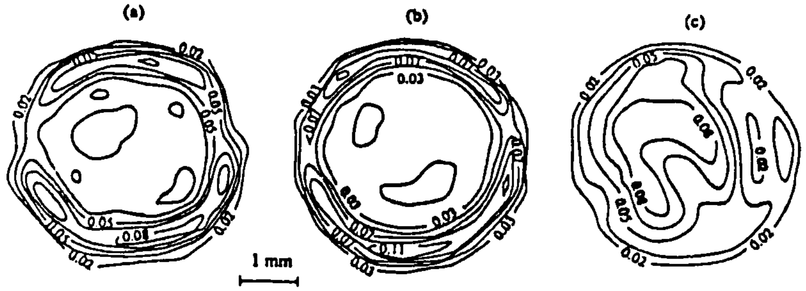


FIGURE 13 Pseudo-three-dimensional distribution of $(R)_2NO^{\bullet}$ during PI nitration in the presence of $O_2(P_{NO_2} = 10$ torr, $P_{O_2} = 280$ torr): (a) $t = 168$ h; (b) $t = 505$ h; (c) $t = 865$ h.

shown in Figure 13. One can see from this figure that the shape and variation of the distribution in the presence of O_2 are the same as in the pure NO_2, but the reaction front is narrower. The results observed suggest that the front form is determined by the "membranous" regime of this process rather than by structural changes. The rate of the reaction front movement at this regime is considerably lower than the rate of the neutral gas diffusion. The rate of the $(R)_2NO^{\bullet}$ formation in the presence of O_2 must be much lower than in the pure NO_2 at the cost of a decay of alkyl radicals in the reactions with O_2 : $W_{NO_2}/W_{NO_2+O_2} = 10^2$.

The results obtained imply the possible use of ESR tomography to elucidate structural modifications in solid polymers in the course of their interactions with aggressive gases.

EFFECT OF THE STRUCTURAL-PHYSICAL MODIFICATION OF POLYMERS ON THE KINETICS OF RADICAL FORMATION IN REACTIONS WITH NO_2

To solve the stabilization problem it is essential to clarify the role of the structural-physical organization of polymers in the kinetics and the mechanism of these reactions. It is interesting to consider, therefore, the interconnection between the reactivity of macroradicals and changes of the physical structure of polymer medium, for instance, as a result of the interface layer formation in filled composites. The investigations of the influence of the filler (aerosil) content on the kinetics of radical reactions in PVP induced by NO_2 have been studied in the work [12].

The quantitative dependence of the yield of acylalkylnitroxyl (R_1) (reaction (21)) and iminoxyl (R_2) radicals (reaction (19)) on the aerosil content in PVP in the reaction with NO_2 has been studied by ESR method. Fractions of R_1 as a function of the exposure time in NO_2 at different temperature are shown in Figures 14(a), (b), (c), for non-filled PVP, and with 25 and 50% of aerosil. The fraction of R_1 for non-filled PVP is only 6–7% at room temperature and does not change with time during three hours. Its growth up to 20% was observed during longer time. The R_1 fraction at elevated temperatures increases at the beginning of PVP exposure, but then it reaches a plateau, where the limiting values of the R_1 fraction are higher as the temperature increases.

Behavioral irregularities were observed in filled samples. The fraction of R_1 at room temperature is somewhat increased up to 8–10% at the beginning and subsequently remains constant. Whereas the monotonic growth of the R_1 fraction with time was observed at

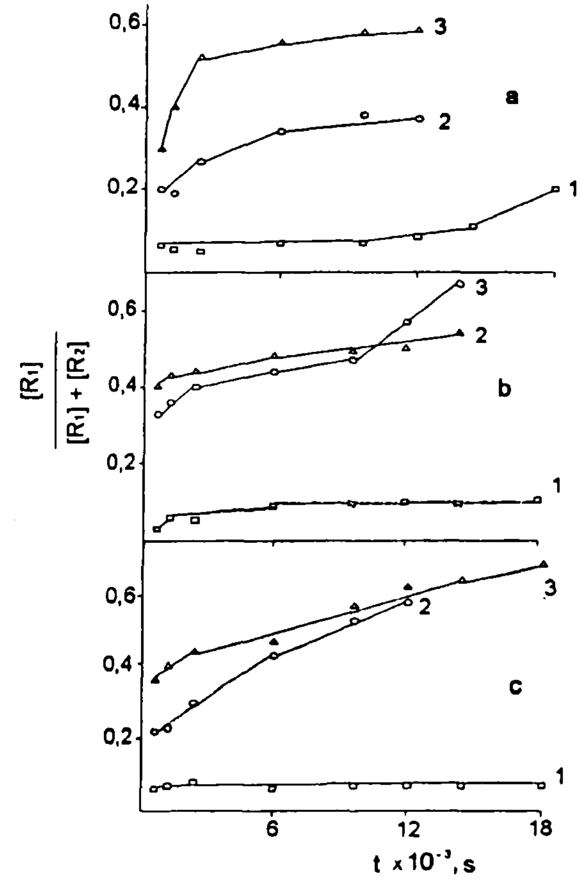


FIGURE 14 Fractions of R_1 as a function of the exposure time in NO_2 for non-filled PVP (a), with 25 (b) and 50% of aerosil (c) at 295 K (1), 323 K (2) and 363 K (3).

323 K and 363 K. In this case the R_1 fraction in the initial stages of the process increase with elevated temperature, as in the non-filled PVP. However, the rate of its increase at 323 K is higher than at 363 K. As a consequence, after a time the R_1 fraction begins to exceed at 323 K the corresponding value at 363 K in sample with 25% of aerosil. These results show that the structural reorganization of the polymer phase in interfaces aids in the R_2 decay. The approach based on analysis of the dependence of the nitroxyl radicals composition on the content of aerosil was put forward in [12]. It is known that the structural-physical modification of filled polymers at interfaces is

exhibited by a density change of the molecular packing and the molecular mobility intensity. A structural effect of this kind can influence differently the rate of R_1 and R_2 formation. More friable molecular packing in interfaces, as compared with that in a polymer bulk results from the hinderence of relaxation processes in the course of shaping of filled polymers. Thus, the structural-physical reorganization of PVP upon filling affects the ratio of the conversion rates of nitroxyl macroradicals. The appreciable changes in the radical composition permit to consider the exposure in NO_2 as a sensitive method of detection of the structural-physical modification in filled polymer composites at the molecular level and to use this process for investigations of features of the mechanism of free-radical reactions in these systems.

CONCLUSION

Nitrogen oxides are toxic and aggressive constituents of the atmosphere. The interaction with polymeric materials can initiate degradation processes involving the chemical modification of macromolecules and disruption of the main chain. The type of active bonds of monomer links and the nature of free radicals must be identified in order to recognize the features of the degradation mechanism of polymers in the presence of nitrogen oxides. Available data show that the active participants of the reactions with nitrogen oxides are double bonds and amide groups of the macromolecules. High activity is exhibited in the presence of peroxides. Even stable PTFE is capable of breaking the main chain through reactions of NO and NO_2 with peroxy macroradicals.

Reactions of nitrogen oxides provide a simple way of preparation of spin labeled polymers in which spin labels are nitroxyl radicals. This method does not require reacting special substances with the functional groups of macromolecules. In parallel with studying the molecular mobility in spin labeled polymers, there also is a possibility of using ESR tomography to follow the reaction front structure during nitration of polymeric materials.

Reactions of nitrogen oxides with polymers demonstrate clearly the effects of physical structure on kinetics and mechanism. The exposure in NO_2 may be considered as a sensitive method of detection of structural modifications, for instance, in filled polymer composites.

References

[1] Ranby, B. and Rabek, J. F., *Photodegradation, photo-oxidation and photostabilization of polymers*, Wiley-Interscience, London, 1975.

[2] Razumovskii, S. D. and Zaikov, G. E., *Ozone and its reactions with organic compounds*, Nauka, Moscow, 1974.

[3] Zaikov, G. E., Maslov, S. A. and Rubailo, V. L., *Acid rains and environment*, Khimiya, Moscow, 1991.

[4] Pokholok, T. V., Pariyskii, G. B. and Bragina, G. O. (1989). *Vysokomolek. Soed.*, **A31**(10), 2049.

[5] Gaponova, I. S. and Pariyskii, G. B. (1991). *J. Chem. Biochem. Kinetics*, **1**(4), 349.

[6] Gaponova, I. S., Davydov, E. Ya., Makarov, G. G., Pariyskii, G. B. and Pustoshnyi, V. P. (1998). *Vysokomolek. Soed.*, **A40**(4), 551.

[7] Djerassi, C., Lund, L., Bunnenberg, E. and Sjoberg, B. (1961). *J. Amer. Chem. Soc.*, **83**(10), 2307.

[8] Ungrande, H. E. and Smiley, R. A. (1956). *J. Org. Chem.*, **21**(9), 393.

[9] Pokholok, T. V. and Pariyskii, G. B. (1997). *Vysokomolek. Soed.*, **A39**(7), 1152.

[10] Gaponova, I. S. and Pariyskii, G. B. (1997). *Chem. Phys. Reports*, **16**(10), 1795.

[11] Degtyarev, E. N., Pokholok, T. V. and Pariyskii, G. B. (1994). *J. Phys. Chem.* (in Russian), **68**(3), 461.

[12] Davydov, E. Ya., Pustoshnyi, V. P., Pariyskii, G. B. and Zaikov, G. E. (1999). *Intern. J. Polymeric Mater*, **44**(3-4), 241-258.