

*Evgeny Davydov, Irina Gaponova, Georgy Pariiskii, Tatyana Pokholok  
and Gennady Zaikov*

## REACTIVITY OF POLYMERS ON EXPOSURE TO NITROGEN DIOXIDE

*N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences  
4 Kosygin str., 119334 Moscow, Russia  
pgb@sky.chph.ras.ru*

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**Abstract.** The mechanism of reactions of nitrogen dioxide with polymers of different classes is considered. In reactions with carbon-chain polymers at 298 K, nitrogen dioxide can only add to extrinsic double bonds that are formed in the synthesis of the polymers. These reactions resulted in dinitro compounds and nitro nitrites. At elevated temperatures, carbonyl and hydroxyl groups are formed in these polymers along with nitration products. Active participants of  $\text{NO}_2$  reactions with rubbers are double bonds converting into nitroalkyl and alkyl radicals initiating then free radical conversions of these polymers. Polymers containing amide, urethane and imide groups are rather sensitive to  $\text{NO}_2$ . These materials undergo essential changes in the chemical structure with formation of stable nitrogen-containing radicals. The reactions of nitrogen dioxide provide a simple method of the spin-labeled polymer preparation.

**Keywords:** nitrogen dioxide, carbon-chain polymers, rubbers, polyamides, polymer degradation, stable radicals, spin-labeled macromolecules.

### 1. Introduction

The general review of influence of the pollutants on polymers has been presented by H. Jellinek *et al* [1]. The characterization of reactivity of polymeric materials toward aggressive gases is given therein. The various polymers were used as films of 20  $\mu$  thickness. The thickness is small enough to exclude in most cases the diffusion as the determining factor of the pollutant action. The films were investigated under different conditions: 1) the pollutant action; 2) the oxygen action; 3) ultraviolet (UV) light action; 4) UV light and oxygen; 5) UV light, oxygen and pollutants. For  $\text{NO}_2$ , the exposure of samples was usually realized under the pressure of 2000 Pa for 30 h at 308 K. However, in case of nylon 66 and butyl rubber (BR), the  $\text{NO}_2$  pressure was lowered to 133.3 Pa, and the exposure took place for 30 min. Polyisoprene (PI)

and polybutadiene (PBD) were exposed to  $\text{NO}_2$  during 5 min under the pressure of 133.3 Pa. As a light source ( $\lambda > 290$  nm) a mercury lamp was used. The intrinsic viscosity of polymer solutions was measured before and after exposure of samples in the chosen conditions. The rather high concentration of nitrogen dioxide in these experiences was used to ensure that certain effects can be observed for a reasonable time.

The polymers on the basis of their reactivity with respect to  $\text{NO}_2$  can be divided into two main classes [1]. The saturated polymers, for instance, polyethylene (PE) and polypropylene (PP) belong to the first group, but nylon 66 is not included into this series. The second group covers elastomers. Butyl rubber (BR) undergoes scissions of the main chain, and PBD is restrictedly cross-linked under the action of  $\text{NO}_2$ . These elastomers have approximately the same reactivity with respect to  $\text{NO}_2$  as to ozone. All films exposed to  $\text{NO}_2$  become yellow, and their IR spectra show that nitro groups enter into macromolecules. In polyvinylchloride in the presence of  $\text{NO}_2$ , some decreasing in the amount of chlorine along with the appearance of nitro and nitrite groups are observed from IR spectra.

It is the author's opinion [1] that some estimations concerning influences of so low concentration of nitrogen dioxides in an atmosphere ( $2 \cdot 10^{-9}$ – $2 \cdot 10^{-8}$  mol·l<sup>-1</sup>) on polymeric materials can be obtained from the experiences with using concentrations of the gas of several orders of magnitude higher. The formulated assumption says that there is linear dependence of the concentration effect of aggressive pollutants. This means that the effect of aggressive gases at low concentrations can be determined by the linear extrapolation of results obtained under the influence of high concentrations. The author pointed out that this procedure contains an element of risk because scissions of macromolecules are not always linearly decreasing with the pressure reduction of the aggressive gas, but the rate of breaks can change drastically at very low concentrations.

The procedure of extrapolation was used for an estimation of the scission average number  $\bar{S}$  under the

action of aggressive gases at concentrations of 1 – 5 ppm within 1 hour [1]. This value is given by the equation:

$$\bar{S} = \frac{DP_{n,0}}{DP_{n,t}} - 1 \quad (1)$$

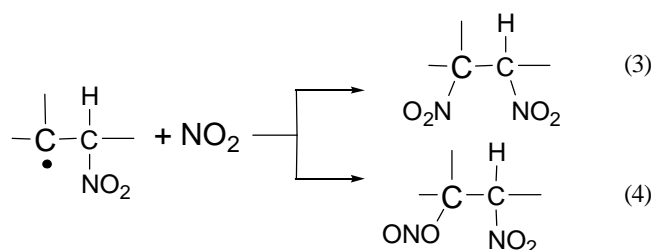
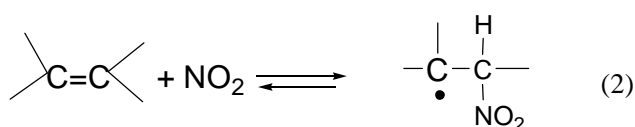
where  $DP_{n,0}$  and  $DP_{n,t}$  are lengths of macrochains at  $t=0$  and  $t$  correspondingly. On the basis of these estimations it was concluded that aggressive gases, for instance  $\text{NO}_2$  and  $\text{SO}_2$ , slightly affect vinyl polymers in concentrations really available in polluted air. Even in a combination with UV light, the deterioration of these polymers is hardly noticeable. However, nylon 66 is quite subjected to the action of small concentrations of  $\text{NO}_2$  with essential degradation.

The investigations performed earlier characterize in general the reactivity of polymers of different classes in their reactions with nitrogen dioxide. However, mechanisms of free radical processes proposed on the basis of the results obtained are formal enough. As a rule they take account of changing molecular weights and the composition of final molecular products of the nitration. In connection with this, the study of structures of free radicals forming in primary and intermediate stages of polymer conversions is of special interest. Such researches allow drawing conclusions on the mechanism of initiation of free radical conversions dependent on nature of functional groups of macromolecules. In the present article, the features of the mechanism of reactions of nitrogen dioxide and also dimers of  $\text{NO}_2$  with extensively used polymers containing different functional groups are considered. Special attention is given to the analysis of structure of stable nitrogen-containing radicals and mechanism of their formation.

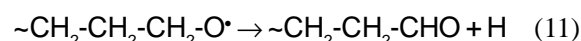
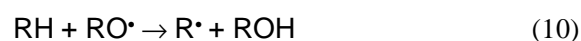
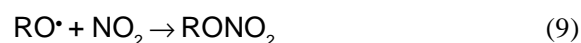
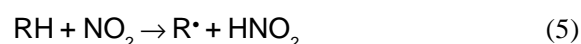
## 2. Results and Discussion

### 2.1. Interaction of Carbon-Chain Polymers with $\text{NO}_2$

Pioneering studies of the reaction of nitrogen dioxide with polyethylene (PE) and polypropylene (PP) have been carried out by Ogihara *et al.* [2, 3]. Using IR spectroscopy, they have found that nitrogen dioxide cannot abstract secondary and tertiary hydrogen atoms from PE and PP at 298 K. It can only add to the vinylene and vinylidene units that are formed in the synthesis of the polymers. These reactions resulted in dinitro compounds and nitro nitrites:



At  $T > 373$  K, nitro, nitrite, nitrate, carbonyl, and hydroxy groups are formed in these polymers. The following reaction mechanism at high temperatures was proposed:



This scheme allows rationalization 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 *S*-shaped dependence of the accumulation of nitrites. The activation energies for the  $\text{NO}_2$  addition to the double bonds of PE are 8–16  $\text{kJ}\cdot\text{mol}^{-1}$ . The activation energy for hydrogen abstraction is within 56–68  $\text{kJ}\cdot\text{mol}^{-1}$  for PE, and of 60  $\text{kJ}\cdot\text{mol}^{-1}$  for PP.

At room temperature and at  $\text{NO}_2$  concentrations of  $5.4\cdot 10^{-4}$ – $5.4\cdot 10^{-3}$   $\text{mol}\cdot\text{l}^{-1}$ , the characteristics of PE, PP, polyacrylonitrile and polymethylmethacrylate are changed only slightly even if they simultaneously undergo a combined action of  $\text{NO}_2$ ,  $\text{O}_2$  and UV radiation [4]. Reactions of  $\text{NO}_2$  with polyvinylchloride and polyvinyl fluoride resulted in a slight decrease in the content of chlorine and fluorine atoms, respectively [1, 4].

In the temperature range of 298–328 K nitrogen dioxide ( $7.8\cdot 10^{-3}$ – $3.4\cdot 10^{-2}$   $\text{mol}\cdot\text{l}^{-1}$ ) can abstract tertiary hydrogen atoms from polystyrene (PS) molecules to introduce nitro and nitrite groups into macromolecules in the result of subsequent reactions [1]. This process proceeds at low rates and is accompanied by chain scissions [1, 5, 6]. The number of chain scissions at time  $\alpha(t)$  was determined from intrinsic viscosity using Eq. (1):  $\bar{S} = a(t)P_{n,0}/100000$ . The experiments have been carried out at the temperature range of 298–328 K. According to H. Jellinek, the dependence of the decrease in

the degree of polymerization of PS on the exposure time in  $\text{NO}_2$  has three linear regions: initial, middle and final. A decrease in the apparent degradation rate was observed in 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. PS films were also simultaneously exposed to  $\text{NO}_2$  ( $1.1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ ) and light ( $\lambda > 280 \text{ nm}$ ) [6]. No polymer degradation was observed in the initial stage during 10 h. Then chain scission occurred at a constant rate.

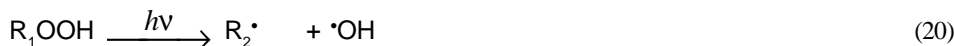
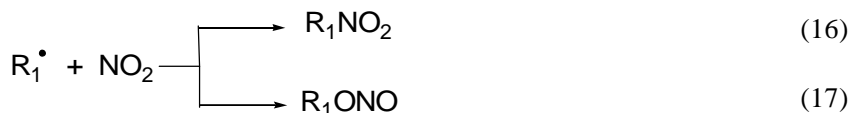
An attempt to determine quantitative characteristics of the ageing of PS and poly-*t*-butylmethacrylate (PTBMA) under the action of  $\text{NO}_2$  has been undertaken by A. Huber [7]. The samples were exposed to a stream of air containing  $\text{NO}_2$  ( $2.5 \cdot 10^{-6}$ – $3.7 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ) at 300 K and simultaneously irradiated with light ( $\lambda > 290 \text{ nm}$ ). The number of chain

scissions per 10000 monomer units  $\alpha(t)$  can be described by the empirical equation:

$$a = \frac{P}{Q}(\exp Qt - 1) \quad (12)$$

where  $P$  and  $Q$  are constants. This equation describes an autocatalytic process. At  $Q \rightarrow 0$ , degradation occurs at a constant rate. 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.

The autocatalytic path of degradation of PTBMA was associated [7] with the photo-induced formation of isobutylene, which reacts with  $\text{NO}_2$ , thus initiating free-radical degradation processes of macromolecules. The IR spectrum of PS exposed to  $\text{NO}_2$  and light exhibits two bands at 1686 and 3400  $\text{cm}^{-1}$  corresponding to the carbonyl and hydroxyl groups, respectively. The formation of nitrogen-containing products has not been observed in both PTBMA and PS. The following reactions have been proposed [7] in PS:



It is believed that the decomposition of hydroperoxides exposed to  $\text{NO}_2$  and light leads to autocatalytic degradation of PS.

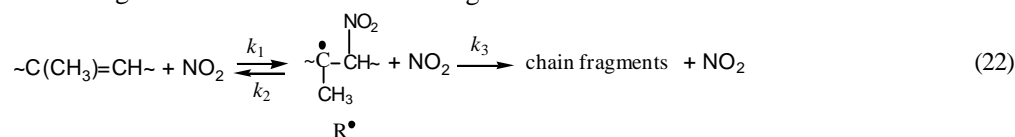
## 2.2. Interaction of Rubbers with $\text{NO}_2$

Rubbers are much more susceptible to  $\text{NO}_2$  than the polymers containing no double bonds. First, this is due to the ability of  $\text{NO}_2$  to add reversibly to carbon-carbon double bonds to give nitroalkyl radicals (reaction (2)), thus initiating free radical conversions of elastomers. Second, nitrogen dioxide is able of abstracting hydrogen atoms in *b*-position to the double bond to give allyl radicals, which then recombine with  $\text{NO}_2$  [8]. Depending on the structure of the alkenes, the reaction resulting in the formation of the allyl radical can be either weakly exothermic or weakly endothermic. For instance, the strength of the weakest

C–H bond in the structure  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{–H}$  is only 314  $\text{kJ} \cdot \text{mol}^{-1}$  [9].

The exposure of PI and polybutadiene (PBD) to nitrogen dioxide leads to both degradation and cross-linking of macromolecules, whereas BR (a copolymer of 99.2 % isobutylene and 0.8 % isoprene units) only undergoes degradation [10]. The detailed study of the ageing BR exposed to  $\text{NO}_2$  ( $5.2 \cdot 10^{-7}$ – $5.2 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ ) alone, an  $\text{NO}_2$ - $\text{O}_2$  mixture and an  $\text{NO}_2$ - $\text{O}_2$  mixture plus UV light ( $\lambda > 280 \text{ nm}$ ) at 298–358 K has been performed by H. Jellinek *et al.* [11, 12]. IR spectra before and after the exposure of the samples show that the band at 1540  $\text{cm}^{-1}$  of  $\sim \text{C}=\text{C} \sim$  bonds disappears, and the new band at 1550  $\text{cm}^{-1}$  arises. The latter belongs to nitro groups appearing as a result of addition to double bonds by the reaction (2).

The chain scission process in BR proceeds by the following scheme:



Then the rate of scissions is:

$$-\frac{d[n']}{dt} = k_3[R^\bullet][NO_2] \quad (23)$$

where  $n'$  is a number of isoprene units in BR. After integration of (23) taking into account stationary concentrations of  $R^\bullet$ , the following equation for the degradation degree is derived:

$$a = \frac{k_1 k_3 [n']_0 [NO_2] t}{[n]_0 (k_2 + k_3 [NO_2])} \quad (24)$$

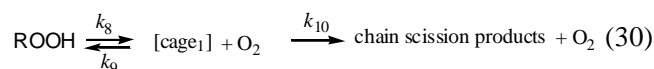
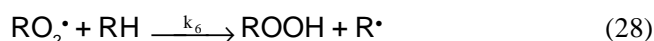
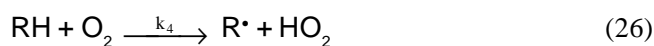
where  $[n']_0$  and  $[n]_0$  are the initial concentrations of isoprene units and all units. The amount of double bonds remains practically constant because only a small number of those are destroyed. Really, only 1/50 of macromolecules of BR are subjected to scissions. Taking into account low concentrations of  $NO_2$ , the linear dependence on time is obtained:

$$a = k_{\text{exp}} t \quad (25)$$

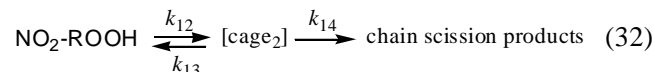
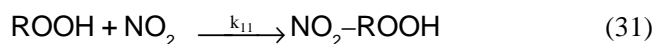
where  $k_{\text{exp}}$  is the experimentally determined constant. This constant is represented by the following Arrhenius equation:

$$k_{\text{exp}} = 3.8 \cdot 10^{-2} e^{-7450/RT}, \text{ h}^{-1}.$$

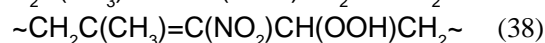
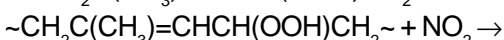
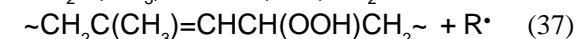
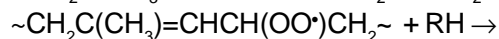
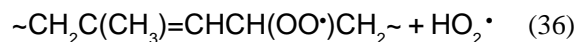
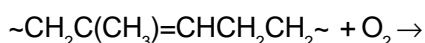
The degradation of BR in a polluted atmosphere runs in three directions: 1) the action of  $NO_2$  alone, 2) the action of  $O_2$ , 3) the combined (synergetic) action of these gases. The general scheme of the process can be represented as follows:



The effect of  $NO_2 + O_2$ :



The synergetic action of  $NO_2$  and  $O_2$  can be seen from the scheme:



BR is not sensitive to UV light ( $> 290$  nm) alone. Probably, UV light in the presence of  $NO_2$  affects nitro groups of macromolecules.

The interaction of PI with  $NO_2$  gives rise to the di-tert-alkylaminoxyl radicals [13]. The ESR spectra of these radicals show a characteristic anisotropic triplet signal (Fig. 1a) with a width of  $2A_{\parallel}^N = 6.2$  mT and  $g_{\parallel} = 2.0028 \pm 0.0005$  in solid polymer and isotropic triplet (Fig. 1b) with  $a^N = (1.53 \pm 0.03)$  mT and  $g = 2.0057 \pm 0.0005$  in dilute solutions. These macroradicals are stable in the absence of  $NO_2$  during storage for many months in both inert atmosphere and air. The proposed scheme to explain the radical formation involves three main stages: generation of N-containing alkyl radicals  $R_{\text{tert}}^\bullet$ , the synthesis of tertiary macromolecular nitrosocompounds and spin-trapping of the tertiary alkyl or radicals:

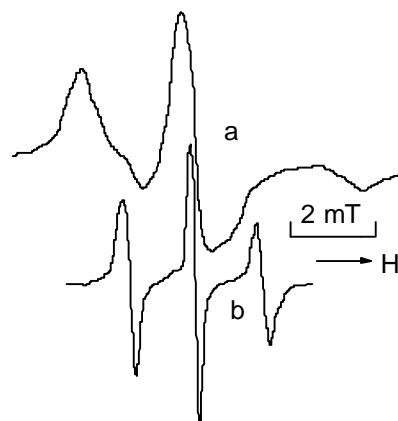
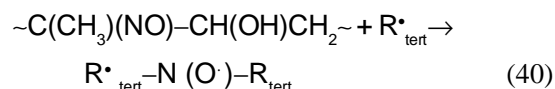
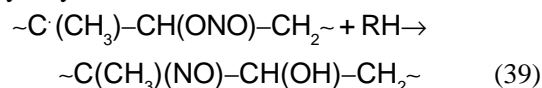
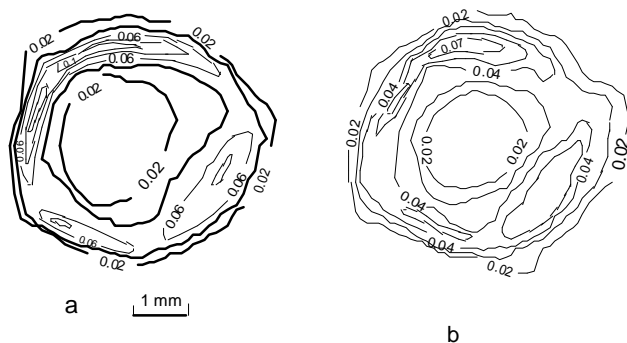


Fig. 1. ESR spectra of aminoxyl macroradicals produced in the reactions of PI with  $NO_2$  at 295 K (a) and 373 K (b)

Thus the reactions of  $NO_2$  with double bonds provide a very simple and rapid method for the synthesis of spin labeled macromolecules of rubbers. Using the spin-labeled samples, the temperature variation of the rotational mobility of macromolecules in the block PI has been studied in [13]. The temperature dependence of the rotational correlation time  $t_0$  is described by the equation:  $t_c = t_0 \cdot \exp(E/RT)$ . The  $t_c$  values within the fast motion region ( $t_c < 10^{-9}$  s) are well described with the parameters  $E = 34.7$  kJ·mol<sup>-1</sup> and  $\log t_0 = -14.2$ .

The spatial distribution of these macromolecular aminoxyl radicals allows estimating the spatial distribution of the nitration reaction in bulk of PI. The possibilities of ESR imaging technique to determine the form of the reaction front of PI nitration have been considered in [14]. The ESR imaging spectra were registered in inhomogeneous magnetic field on the cylindrical samples of 0.4 cm diameter and 1 cm height at the  $\text{NO}_2$  and  $\text{O}_2$  concentrations ( $1 \cdot 10^{-4}$ – $2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ ) and ( $2 \cdot 10^{-3}$ – $1.4 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$ ) respectively. The spatial distributions of  $\text{R}_2\text{NO}^\bullet$  radicals at the reaction various times are shown in Fig. 2. The width of the distribution varies over 20–30 % for 740 h. Maximum concentration of aminoxyl radicals is observed in a superficial layer, and it progressively diminishes in the line of the center. The width of this layer is  $\sim 1 \text{ mm}$ , and radicals are unavailable in the sample center. The aminoxyl radical yield with respect to  $\text{NO}_2$  absorbed molecules is 0.01. The shape and variation of the distribution in the  $\text{O}_2$  presence are the same as in the pure  $\text{NO}_2$ , but the reaction front is narrower. The rate of the  $\text{R}_2\text{NO}^\bullet$  formation in the presence of  $\text{O}_2$  is much lower than in the pure  $\text{NO}_2$  at the cost of a decay of alkyl radicals in the reactions with

$\text{O}_2$ :  $W_{\text{NO}_2} / W_{(\text{NO}_2 + \text{O}_2)} = 10^2$ . The distribution view at the fixed distance from a surface is likely determined by macrodefects in the sample volume, namely, the availability of cracks and porosity. The front form is determined by the “membranous” regime of the nitration process rather than by structural changes.

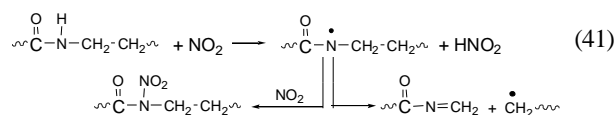


**Fig. 2.** Bulk distribution of aminoxyl macroradicals produced upon nitration of PI by  $\text{NO}_2$  with  $\text{O}_2$  for 2.5 h (a) and 720 h (b)

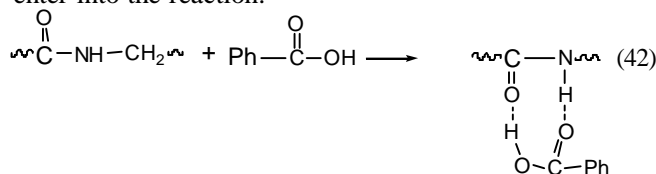
### 2.3. Interaction of Nitrogen Dioxide with Polyamides and Polyurethanes

Polymers containing amide and urethane groups form a particular class of materials sensitive to  $\text{NO}_2$ . H. Jellinek *et al.* [15, 16] showed that exposure of nylon-66 films of different morphology to  $\text{NO}_2$  ( $10^{-5}$ – $2.6 \cdot 10^{-1} \text{ mol} \cdot \text{l}^{-1}$ ) 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 degradation is accelerated in the presence of air and UV light in addition to  $\text{NO}_2$ . The reaction can be inhibited by small amounts of benzaldehyde or benzoic acid. The following mechanism for the polymer degradation under the action of  $\text{NO}_2$  was proposed:

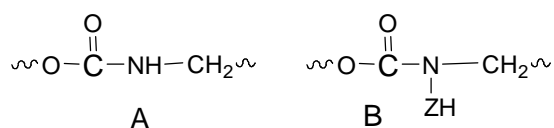


The degradation process can be inhibited by small amounts of benzaldehyde or benzoic acid. It is believed that these compounds block the amide groups and that only a few of them, not involved in hydrogen bonding, enter into the reaction:

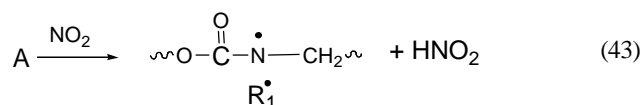


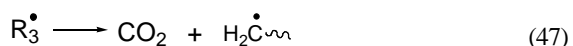
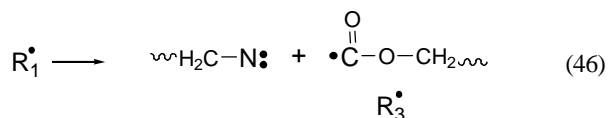
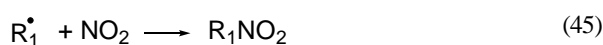
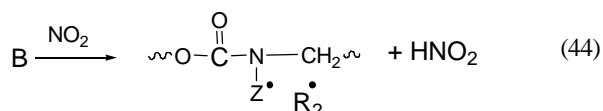
H. Jellinek *et al.* [16, 17] studied the effect of  $\text{NO}_2$  on films of linear polyurethane synthesized from tetramethylene glycol and hexamethylene diisocyanate. It was found that the degradation of polyurethanes is accompanied by cross-linking of macromolecules and that the degree of degradation 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 to nearly zero at 330 K and  $\text{NO}_2$  concentration of  $10^{-3} \text{ mol} \cdot \text{l}^{-1}$ . The number of chain scissions in the sol fraction (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 polyurethane films to  $\text{NO}_2$  is accompanied by liberation of  $\text{CO}_2$ . The IR spectra of the films allow assessment of the consumption of the NH bonds ( $\nu = 3300 \text{ cm}^{-1}$ ).

The reaction mechanism proposed [15, 16] involves the abstraction of hydrogen atoms from two types of structures, namely, a carbamate structure (A) and a tertiary amide structure (B):



where Z is a side alkyl group. The next stages are represented as follows:

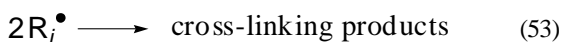
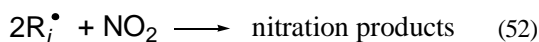
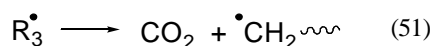
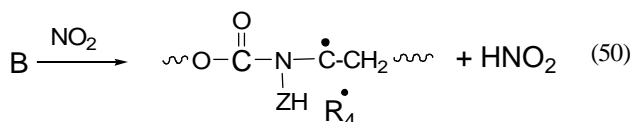
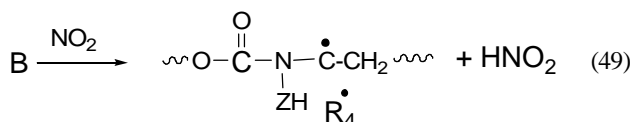




According to H. Jellinek, recombination of  $\text{R}_1^\bullet$  and  $\text{R}_2^\bullet$  radicals leads to cross-linking of the polymer chains. While decomposition of the  $\text{R}_1^\bullet$  radicals results in the degradation of macromolecules and liberation of  $\text{CO}_2$ . Energetically, the decomposition of the  $\text{R}_1^\bullet$  radicals seems to be hardly probable since this reaction results in the terminal macroradical  $\text{R}_3^\bullet$  and a nitrene, which is a very reactive species. On the other hand, more probable decomposition reaction of  $\text{R}_1^\bullet$  involving cleavage of the C–C or C–O bonds produce no alkoxy carbonyl macroradicals  $\text{R}_3^\bullet$ , which can undergo decarboxylation [16]. Therefore, the ageing of polyurethanes in an  $\text{NO}_2$  atmosphere can be represented as follows [17]:

Reaction (43)

Reaction (44)

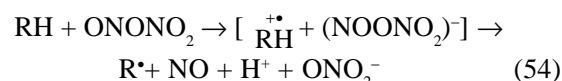


where  $j = 1-4$ . This scheme expresses the degradation accompanied by cross-linking of macromolecules, the consumption of NH groups of the polymer as well as the release of carbon dioxide upon degradation.

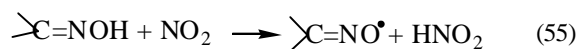
However, it should be kept in mind that  $\text{NO}_2$  is a free radical of moderate reactivity: the ONO–H bond strength [18] is  $320 \text{ kJ}\cdot\text{mol}^{-1}$ . Due to this,  $\text{NO}_2$  can initiate free radical reaction at ordinary temperatures by abstracting hydrogen atoms only from the least strong, for example,

allyl C–H bonds or by attaching to double C=C bonds [8]. Nevertheless, effective formation of stable nitrogen-containing radicals is observed by ESR method also in polymers not containing labile hydrogen atoms or double bonds: polycapraamide (PCA) [19, 20], aromatic polyamides (AP) [21], polyvinylpyrrolidone (PVP) [19, 20]. These facts allow considering other probable mechanisms of radical initiation. The fact is that major radical products of the nitrogen dioxide interaction with PCA, AP and PVP are iminoxyl and acylalkylaminoxyl radicals that are produced from oximes and acyl nitroso compounds [19–21]. The occurrence of these precursors of stable radicals in turn associates with the presence of nitric oxide. In this connection, it is necessary to suppose a participation of  $\text{NO}_2$  dimeric forms in radical initiation. The main dimers of  $\text{NO}_2$  are planar nitrogen tetroxide  $\text{O}_2\text{N}-\text{NO}_2$  (PD) and nitrosyl nitrate  $\text{ONONO}_2$  (NN).

As NN has strong oxidative properties [22], the generation of radicals can take place by an electron transfer from donor functional groups with the formation of transient radical cations



The recombination of radicals with nitric oxide gives nitroso compounds that undergo isomerization into oximes [23] to produce iminoxyl radicals in the reaction with  $\text{NO}_2$ :

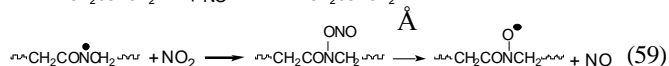
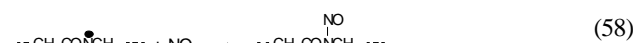
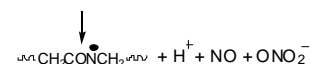
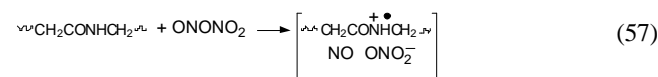


The nitroso compounds are effective spin traps and a source of stable aminoxyl radicals:



Thus the mechanism involving reactions (54–56) formally could explain an appearance of stable radicals in the polymers not containing specific chemical bonds reacting with  $\text{NO}_2$  monoradicals.

Amide groups can appear as electron donors, and the conversion of PCA [24] with formation of nitrosoamides and stable acylalkylaminoxyl radicals is described by the following scheme:

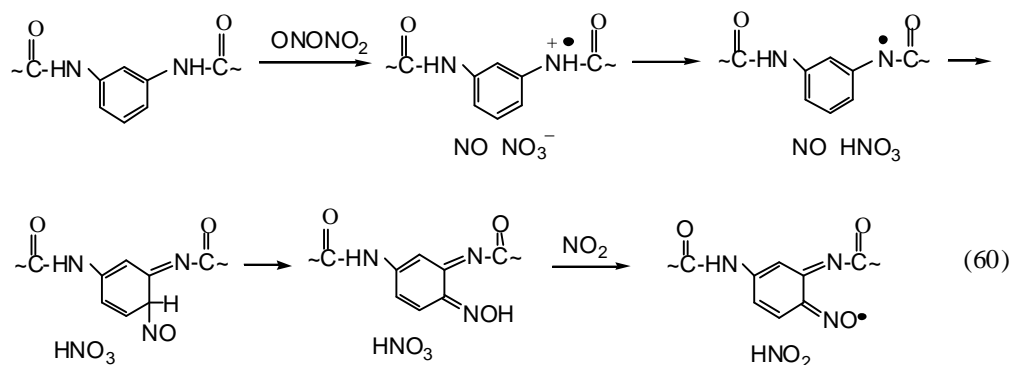


The conversion of N–H groups of PCA into nitrosoamides in reactions (57) and (58) follows from IR spectra. The intensity of the Amide I ( $\nu = 1642 \text{ cm}^{-1}$ ) and

Amide II ( $\nu = 1563 \text{ cm}^{-1}$ ) also drops markedly. Instead of those, the band  $1730 \text{ cm}^{-1}$ , which corresponds to C=O group of nitrosoamides, and the bands  $1504 \text{ cm}^{-1}$ ,  $1387 \text{ cm}^{-1}$  corresponding to the asymmetric and symmetric stretching vibrations of N=O groups of nitrosoamides appear in the spectrum of PCA exposed to  $\text{NO}_2$  [24]. It was found that the initial rate of nitrosoamide group

accumulation is proportional to  $[\text{NO}_2]^2$ . This fact confirms the mechanism nitrosation of PCA based on reactions with the NN participation.

Taking into account the reactions (54, 55), the iminoxyl radical formation in AP synthesised by polycondensation of *m*-phenylenediamine and isophthalic acid can be presented as follows [21]:



The IR spectra of nitrated AP confirm the considered mechanism (60). The appreciable decrease of intensity of stretch band at  $3340 \text{ cm}^{-1}$  of N-H bonds is observed. Also the appearance of new intensive bands at  $1370$  and  $810 \text{ cm}^{-1}$  belonging to nitrate-anions indicates ion-radical conversions of the polymer.

## 2.4. Interaction of Aromatic Polyimides with $\text{NO}_2$

The materials based on polyimides have valuable mechanical and chemical properties [25]. Currently these thermostable polymers are used extensively in aerospace engineering. Investigations of thermal and thermo-oxidative stability of polyimides are carried out in detail [26]. However, the mechanism of action of such aggressive gases as nitrogen oxides on these materials remains practically unexplored. The efficiency of initiation by the ion-radical mechanism (54) is caused by donor properties of functional groups of macromolecules as well as by possible conversions of intermediate radical cations into free radicals. Apparently, these conditions are realized both in aliphatic and aromatic polyimides [21, 24]. However, the chemical structure of some polyimides, for example, polypyromellitimide (PPI), does not involve disintegration of radical cations with detachment of protons through the mechanism similar to that shown by reaction (54). Thus, the study of interaction of PPI with nitrogen dioxide enables other probable ways of ion-radical transformations of macromolecules to be established. The mechanism of stable radical generation in PPI under the action of nitrogen dioxide has been considered using the results of ESR measurements [27].

The exposure of PPI to  $\text{NO}_2$  at room temperature up to 7 days does not give significant ESR signals. After

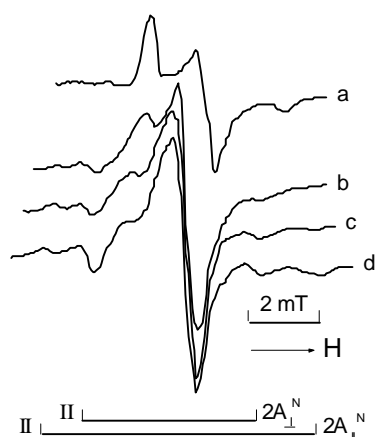
pumping out of  $\text{NO}_2$  from exposed samples, the anisotropic ESR spectrum shown in Fig. 3a was observed. The parameters of this spectrum ( $A_{\text{II}}^{\text{N}} = (2.0 \pm 0.1) \text{ mT}$ ;  $g_{\text{II}} = 2.0018 \pm 0.0005$ ) entirely correspond to

acylarylaminoxyl radicals  $\text{Ph}-\overset{\cdot}{\text{O}}-\overset{\text{O}}{\parallel}{\text{N}}-\overset{\text{O}}{\parallel}{\text{C}}-$  (I) detected in

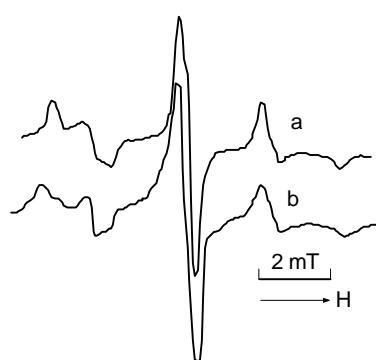
solid polymers [19]. If the same samples are heated at  $373 \text{ K}$  in vacuum, additional signals appear in the spectrum (Figs. 3b and c). In this case the total concentration of radicals considerably increases. The new signals increase if the exposure of PPI to nitrogen dioxide is longer. Such conclusion is reached comparing ESR spectra obtained after the same time of warming PPI in vacuum (8 h), but durations of exposure of the samples to  $\text{NO}_2$  are 5 h and 7 days, correspondingly (Figs. 3c and d). On the basis of spectral splittings and  $g$ -factor values, the side components can be unequivocally attributed to a signal of iminoxyl

radicals  $\text{>C}=\text{N}-\overset{\cdot}{\text{O}}$  (II) with the parameters:  $A_{\text{II}}^{\text{N}} = (4.4 \pm 0.1) \text{ mT}$ ;  $g_{\text{II}} = 2.0022 \pm 0.0003$ ;  $A_{\perp}^{\text{N}} = (2.4 \pm 0.1) \text{ mT}$ ;  $g_{\perp} = 2.0056 \pm 0.0003$ .

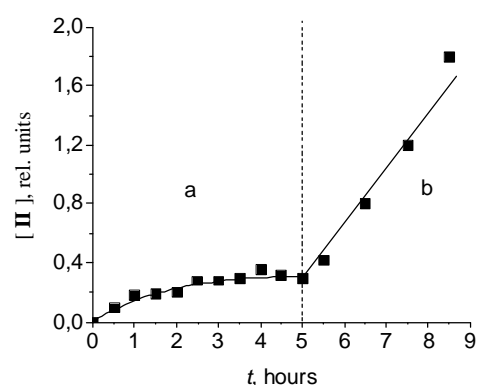
In contrast to the exposure at room temperature, practically only iminoxyl radicals II are accumulated in  $\text{NO}_2$  atmosphere at  $373 \text{ K}$  (Fig. 4a). However, the concentration of radicals II in these conditions becomes steady in 2–3 h (Fig. 5a). A significant increase of radical II concentrations is observed at subsequent heating these samples at  $373 \text{ K}$  in vacuum as shown by Fig. 5b. Their signal in ESR spectrum remains prevailing (Fig. 4b).



**Fig. 3.** ESR spectra of PPI exposed to  $\text{NO}_2$  at 295 K for 5 h (a, b, c) and 7 days (d) after pumping out at 295 K (a) and subsequent heating at 373 K in vacuum 1 h (b) and 8 h (c, d).

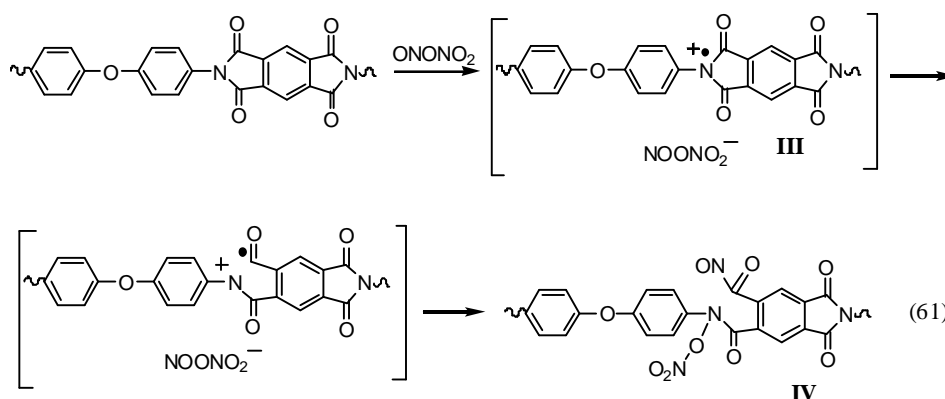


**Fig. 4.** ESR spectra of PPI exposed to  $\text{NO}_2$  for 5 h at 373 K (a) and after subsequent heating at 373 K in vacuum (b)

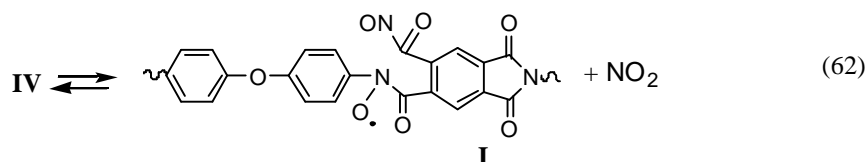


**Fig. 5.** Kinetics of the radical **II** accumulation on exposure of PPI to  $\text{NO}_2$  ( $3.7 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ ) at 373 K (a) and after subsequent heating at 373 K in vacuum (b)

It is expected [27] that the primary act is the oxidative interaction of imide groups with  $\text{NO}_2$  dimers  $\text{NN}$ :



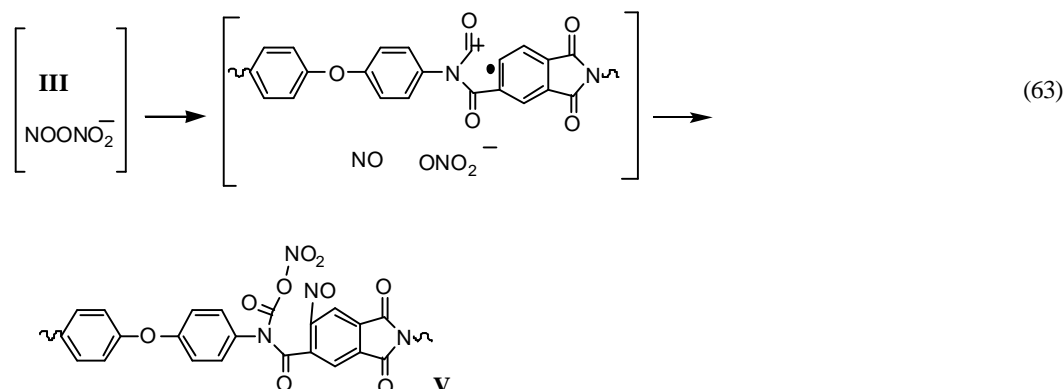
As a result of this primary stage, radical cations **III**, nitric oxide and nitrate-anion are formed. The dissociating decomposition of radical cations and following cage recombination of the primary stage products give compounds **IV**. These compounds being apparently intermediates are converted into stable acylarylaminoxyl radicals **I** due to reversible dissociation with detachment of  $\text{NO}_2$ :



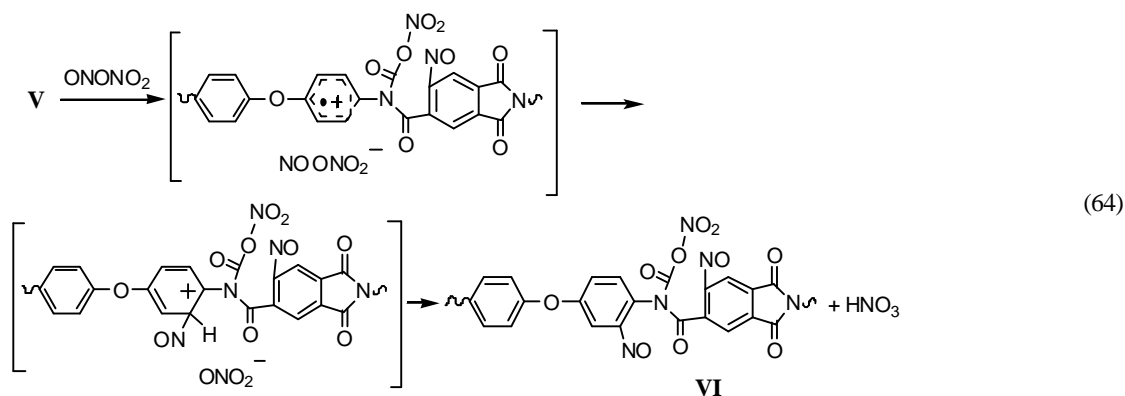
In  $\text{NO}_2$  atmosphere at room temperature, the equilibrium (62) is shifted to the left, and any paramagnetic products are not detected in PPI in these conditions. However, this equilibrium is shifted to radicals **I** by pumping out nitrogen dioxide from samples (Fig. 3a).

The generation of iminoxyl radicals **II** after exposure of PPI to  $\text{NO}_2$  at room temperature followed by warming samples in vacuum at 373 K (Fig. 3b, c and d) or in the course of exposure to  $\text{NO}_2$  at the same temperature (Fig. 4a) is seemingly conditioned by specific products. The disintegration of radical cations **III** arises probably as a result of dissociation of other bonds of imide cycles:

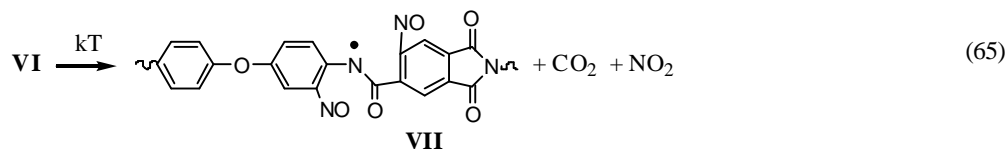




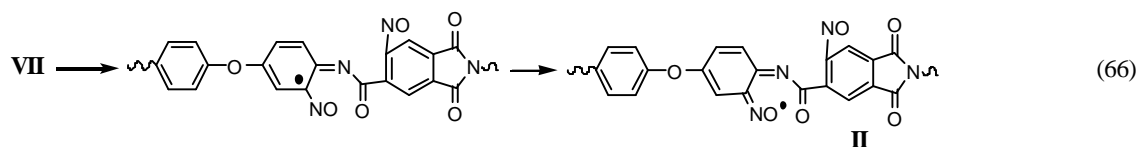
In the primary oxidative reaction, the formation of radical cations of PPI can take place also owing to an electron transfer from phenyl rings to nitrosyl nitrate. Such possibility follows from the available data of UV spectroscopy according to which nitrosyl nitrate is capable of forming charge transfer complexes with aromatic compounds [28]. As a result of the oxidative reaction, aryl radical cations appear. These species give intermediate aryl nitroso compounds after detachment of protons. If the nitrosation process takes place in monomer units modified by nitrogen-containing groups as in **V**, these consecutive reactions can be represented as follows:



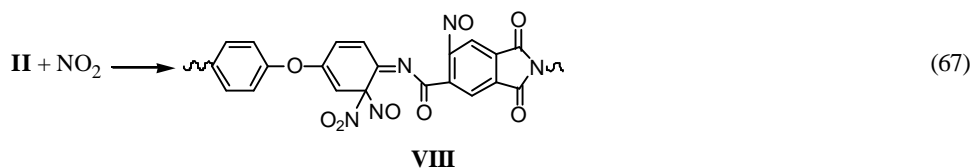
Due to the thermal decomposition of compounds **VI** during heating, amidyl radicals **VII** are formed:



The radicals **VII** may also be present in other isomeric forms, for instance, as nitrosoalkyl radicals which in turn have isomerized into iminoxyl radicals **II** [29, 30]:



The steady-state level of the radical **II** concentration on exposure of PPI to nitrogen dioxide at 373 K (Fig. 5a) is caused by the recombination of formed iminoxyl radicals with  $\text{NO}_2$ :



The products **VIII** are thermally less stable compared with **VI** and decompose into initial components. In this case, the replacing of **VI** by **VIII** takes place during exposure of PPI to  $\text{NO}_2$  at 373 K. Therefore, the rate of accumulation of **II** at subsequent heating PPI in vacuum (Fig. 5b) is four times higher than that for samples exposed at room temperature when products **VIII** are not generated and **VI** is the sole precursor of iminoxyl radicals.

### 3. Conclusions

Nitrogen dioxide radicals are capable of abstracting hydrogen atoms only from the least strong, for example allyl C–H bonds or attaching to C=C bonds of macromolecules initiating free-radical degradation of polymers at room temperature. At the same time,  $\text{NO}_2$  can inhibit the free-radical reactions giving nitrogen-containing molecules by the reactions with alkyl-, alkoxy- and peroxy radicals. The thermal and photochemical conversions of these products also affect the ageing process of polymeric materials. Nitrogen dioxide is the initiator of the free-radical degradation of polyolefines at elevated temperatures. The low stability of polyamides to the  $\text{NO}_2$  action is sufficiently surprising, because the N–H bond of amide groups is rather strong. Therefore, the mechanism of the polyamide conversion due to the hydrogen atom abstraction by  $\text{NO}_2$  from N–H bonds is not quite evident. The significant reactivity of aliphatic and aromatic polyimides and aromatic polyimides can be explained by the concept of transient radical cations formed as a result of the primary oxidizing reaction with participation of  $\text{NO}_2$  dimers in the form of nitrosyl nitrate. Amide and imide groups as well as phenyl rings of the polymers can act as electron donors. In the subsequent reactions of radical cations, nitroso compounds, nitrites, and oximes are formed. Generation of stable radicals occurs by reactions of these products at room or elevated temperatures. Thus, the specific ion-radical initiation can provoke essential reactivity of such thermally stable and chemically inert polymers as aromatic polyamides and polyimides in the presence of nitrogen dioxide. In this connection the reactions considered permits rather simple synthesis of spin-labeled macromolecules.

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### РЕАКЦІЙНА ЗДАТНІСТЬ ПОЛІМЕРІВ ПІД ДІЄЮ ДІОКСИДУ АЗОТУ

*Анотація.* Розглянуто механізм реакції діоксиду азоту з полімерами різних класів. Встановлено, що у реакціях з карболанціюговими полімерами при 298 К діоксид азоту здатний тільки приєднуватись до набутих подвійних зв'язків, які утворюються при синтезі полімерів. Ці реакції призводять до утворення динітросполук та нітронітритів. За підвищених температур в цих полімерах разом з продуктами нітрування утворюються карбонільні та гідроксильні групи. Активними учасниками реакцій  $\text{NO}_2$  з каучуками є подвійні зв'язки, що переходять в нітроалкільні та алільні радикали, які потім ініціюють вільнорадикальні перетворення цих полімерів. Полімери, які містять амідні, уретанові та імідні групи, досить чутливі до  $\text{NO}_2$ . Ці матеріали суттєво змінюють свою хімічну структуру з утворенням стабільних азотовмісних радикалів. Реакції діоксиду азоту можуть також бути використані як простий метод одержання спин-мічених полімерів.

*Ключові слова:* діоксид азоту, карболанціюгові полімери, каучуки, поліаміди, деструкція полімерів, стабільні радикали, спин-мічені макромолекули.