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Ozone and its reactions with diene rubbers

The reactions of ozone with 1,4-cis-polybutadiene (SKD); Diene 35 NFA [having the following linking of the butadiene units in the rubber macromolecules: 1,4-cis (47%), 1,4-trans (42%), 1,2- (11%)]; 1,4-cis-polyisoprene (Carom IR 2200), 1,4-trans-polychloroprene (Denka M 40), and 1,4-trans-polyisoprene have been investigated in CCl_4 solutions. The changes of the viscosity of the polymer solutions during the ozonolysis have been characterized by the number of chain scissions per molecule of reacted ozone (φ). The influence of the conditions of mass-transfer of the reagents in a bubble reactor on the respective φ values has been discussed. The basic functional groups-products from the rubbers ozonolysis have been identified and quantitatively characterized by means of IR-spectroscopy and ^{1}H-NMR spectroscopy. A reaction mechanism, that explains the formation of all identified functional groups, has been proposed. It has been shown that the basic route of the reaction of ozone with elastomer double bonds – the formation of normal ozonides does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature. The most favourable conditions for ozone degradation emerge when the cage interaction between Criegee intermediates and respective carbonyl groups does not proceed.

The amounts of measured different carbonyl groups have been used as an alternative way for evaluation of the intensity and efficiency of the ozone degradation. The thermal decomposition of partially ozonized diene rubbers has been investigated by DSC. The respective values of the enthalpy, the activation energy and the reaction order of the 1,2,4-trioxolanes have been determined.

Key words: ozone, ozonolysis, diene rubber, mechanism, degradation, kinetics, reactivity

Reakcje ozonu z kauczukami dienowymi

Zbadano działanie ozonu na następujące kauczuki (w postaci roztworów w CCl_4): 1,4-cis-polibutadien (SKD); Diene 35 NFA [o konfiguracjach merów butadienowych w makrocząsteczkach: 1,4-cis- (47%), 1,4-trans- (42%), 1,2- (11%)]; 1,4-cis-poliizopren (Carom IR 2200), 1,4-trans-polichloropren (Denka M40) i 1,4-trans-poliizopren. Zmiany lepkości roztworów polimerowych podczas ozonolizy powiązano z liczbą rozszczepień łańcucha przypadającą na cząsteczkę oddziaływującego ozonu (φ). Przeanalizowano wpływ warunków przenoszenia masy w reaktorze barbotażowym na wartość φ. Podstawowe grupy funkcyjne produktów ozonolizy kauczuków identyfikowano i oznaczano ilościowo za pomocą pomiarów spektroskopii IR i spektroskopii ^{1}H-NMR. Zaproponowano mechanizm reakcji wyjaśniający powstawanie wszystkich zidentyfikowanych grup funkcyjnych. Dowiedziono, że podstawowy sposób reagowania ozonu z podwójnymi wiązaniami elastomeru – tworzenie normalnych ozonków – nie prowadzi bezpośrednio do zmniejszenia masy cząsteczkowej makrocząsteczek elastomeru, ponieważ 1,2,4-trioksolany są relatywnie stabilne w temperaturze otoczenia. Najkorzystniejsze warunki do degradacji ozonowej powstają wtedy, gdy nie zachodzą interakcje klatkowe pomiędzy związkami przejściowymi Criegee'a i odpowiednimi grupami karbonylowymi. Pomiar ilości różnych ugrupowań karbonylowych może służyć jako alternatywny sposób oceny intensywności i efektywności degradacji ozonowej. Rozkład termiczny kauczuków dienowych poddanych częściowemu ozonowaniu zbadano metodą DSC. Zostały określone dpowiednie wartości entalpii, energii aktywacji i rząd reakcji 1,2,4-trioksolanów.

Słowa kluczowe: ozon, ozonoliza kauczuk dienowy, mechanizm, degradacja, kinetyka, reaktywność

I. Introduction

The interest in the reaction of ozone with polydienes is due mainly to the problems of ozone degradation of rubber materials [1-4] and the application of this reaction to the elucidation of the structures of elastomers [5-8]. It is also associated with the possibilities of preparing bifunctional oligomers by partial ozonolysis of some unsaturated polymers [9-12]. Usually the interpretation of experimental results are based on a simplified scheme of Criegee's mechanism of C=C-double bond ozonolysis, explaining only the formation of the basic product – ozonides [13, 14].

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2. Aim and background

In most cases, quantitative data on the functional groups formed during the reaction are missing [15-18]. At the same time alternative conversion routes of Criegee's intermediates, which lead to the formation of carbonyl compounds and some other so called „anomalous products" of the ozonolysis, are of great importance for clarifying the overall reaction mechanism [19-21]. The mechanism of ozone degradation of rubbers is also connected with the non-ozonide routes of the reaction, because the formation of the basic product of ozonolysis, normal ozonide, does not cause any chain scission and/or macromolecule cross-linking [22].

In this work the changes in the molecular mass of different types of diene rubbers during their partial ozonolysis in solution have been investigated. By means of IR and ^{1}H-NMR spectroscopy ozonolysis products of the elastomers have been studied. The effects of the nature of the double bond substituents and its configuration on the degradation mechanism have been considered. By using differential scanning calorimetry the thermal decomposition of the functional groups of peroxide type has also been investigated.

3. Experimental

3.1. Materials

Commercial samples of 1,4-*cis*-polybutadiene (SKD); polybutadiene (Diene 35 NFA); 1,4-*cis*-polyisoprene (Carom IR 2200) and polychloroprene (Denka M 40) were used in the experiments (Table 1). The 1,4-*trans*-polyisoprene samples were supplied by Prof. A. A. Popov, Institute of Chemical Physics, Russian Academy of Sciences. All rubbers were purified by threefold

3.2. Ozonation of the elastomer solutions

The ozonolysis of elastomers was performed by passing an ozone-oxygen gas mixture at a rate of $v=1.6 \cdot 10^{-3} \pm 0.1$ $l \cdot s^{-1}$ through a bubbling reactor containing 10-15 ml of polymer solution (0.5-1 g in CCl_4) at 293 K. Ozone concentrations in the gas phase at the reactor inlet ($[O_3]_i$) and outlet ($[O_3]_u$) were measured spectrophotometrically at 254 nm [23]. The amount of consumed ozone (G, mol) was calculated by the equation (1):

$$G = v([O_3]_i - [O_3]_u)t \qquad (Eq. 1)$$

where: t is the ozonation time (s). The degree of conversion of the double C=C bonds was determined on the basis of the amount of reacted ozone and the reaction stoichiometry [23].

4. Results and discussion

Flory [24] has shown that the reactivity of the functional groups in the polymer molecule does not depend on its length. It is also known that some reactions of the polymers proceed much slower as compared with their low molecular analogues (catalytic hydrogenation). The folded or unfolded form of the macromolecules provides various conditions for contact of the reagents with the reacting parts [4, 25]. By using the modified version of this principle [26] it was possible to explain the proceeding of reactions without specific interactions between the adjacent C=C bonds and the absence of diffusion limitations. The study of the mass-molecular distribution (MMD) is in fact a very sensitive method for establishing the correlation between molecular weight (M_w) and reactivity. The theory predicts that the properties of the

Table 1. *Some characteristics of polydiene samples*
Tabela 1. *Wybrane właściwości próbek polidienów*

Elastomer	Monomeric unit	Unsaturation degree, %	1,4-*cis*, %	1,4-*trans*, %	1,2-, %	3,4-, %	$M_v \cdot 10^{-3}$	n
SKD	-CH=CH-	95-98	87-93	3-8	3-5	-	454	2.1
Diene 35 NFA	-CH=CH-	97	47	42	11		298	2.63
Carom IR 2200	-C(CH$_3$)=CH-	94-98	94-97	2-4	-	1-2	380	2.0
1,4-*trans* PI	-C(CH$_3$)=CH-	95-97		95-97			310	2.3
Denka M40	-C(Cl)=C-	94-98	5	94	-	-	180	1.8

Note: M_v is the average molecular weight, determined viscosimetrically after equation $[\eta]=k \cdot M_v^{\alpha'}$, where $[\eta]=(\eta_1/C)(1+0.333\eta_1)$, $\eta_1=\eta_{rel}-1$, η_{rel} - is the intrinsic viscosity; C – solution concentration; $k=1.4 \cdot 10^{-4}$ – Staudinger constant and α' = 0.5-1.5 – constant depending on the rubber type, being one for natural rubber; $M_v \approx M_w$; $n=M_w/M_n$, where M_w and M_n are the average weight and number average molecular mass, respectively [22].

precipitation from CCl_4 solutions with excess methanol. The above mentioned elastomer structures were confirmed by means of ^{1}H-NMR spectroscopy.

Ozone was prepared by passing oxygen through a 4-9 kV discharge.

system: polymer-solvent can be described by the parameter of globe swelling (γ) which defines the free energy (F) of the system and thus the rate constant of the reaction. For reversible reaction, i.e. polymerization – depolymerization, the dependence of the rate constant of the

chain length grow on the molecular weight is expressed by the following equation:

$$\ln k_{pj}/k_{p\infty} = - \text{const.}(5\gamma - 3/\gamma) \cdot (d\gamma/dM) \cdot M_0 \quad (Eq.2)$$

where: M is the molecular weight of the studied sample and k_p is the rate constant for infinitely long macromolecules. A good correlation between the theoretical and experimental data for polystyrene solutions in benzene has been found in Ref. 27.

The study of the polymer degradation is complicated by their structural peculiarities on molecular and supramolecular level and diffusion reasons. It is difficult to find simple model reactions for clarification of particular properties and for the express examination of the proposed assumptions. An exception in this respect is the ozone reaction with C=C bonds whose mechanism has been intensively studied and could be successfully applied upon ozonolysis of polymeric materials [28].

In Table 2 are summarized the rate constants of the ozone reaction with some conventional elastomers and polymers and their low molecular analogues, synthesized by us. It is seen that the reactivity of elastomers and polymers and their corresponding low molecular analogues, as demonstrated by their rate constants, are quite similar, thus suggesting similar mechanisms of their reaction with ozone. This statement is also confirmed by: 1) the dependence of k on the inductive properties of substituents like as k of polychloroprene is higher than that of vinylchloride due to the presence of two donor substituents and 2) the dependence of k on the configuration of the C=C bond in *trans*-isomer (gutta-percha) and *cis*-isomer (natural rubber).

Table 2. *Rate constants of ozone with polymers and low molecular analogues in CCl₄, 20°C*
Tabela 2. *Stałe szybkości reakcji ozonu z polimerami i małocząsteczkowymi analogami, w CCl₄ w 20°C*

Compound	M_w	$k \cdot 10^{-4}$, $M^{-1} \cdot s^{-1}$
Polychloroprene	$8 \cdot 10^5$	0.42±0.1
Vinylchloride	62.45	0.18
2-Bromopropene	121	0.28±0.05
Polybutadiene	$3.3 \cdot 10^5$	6.0±1
Cyclododecatriene-1,5,9	162	35±10
Polybutadienestyrene	$8 \cdot 10^4$	6±1
Gutta-percha	$3 \cdot 10^4$	27±5
Natural rubber	$1 \cdot 10^6$	44±10
2-Me-pentene-2	85	35±10
Squalene	410	74±15
Polystyrene	$5 \cdot 10^5$	$0.3 \cdot 10^{-4}$
Cumene	120	$0.6 \cdot 10^{-4}$
Polyisobutylene	$1.7 \cdot 10^5$	$0.02 \cdot 10^{-4}$
Cyclohexane	84	$0.01 \cdot 10^{-4}$

It has been found that the effects related to the change of the macromolecule length or the folding degree do not affect the ozonolysis in solution. Probably this is due to the fact that the reaction is carried out with thermodynamic elastomers solutions in which the macromolecules can do free intramolecular movements and do not react with adjacent macromolecules. Moreover, the rate of macromolecules reorganization is probably higher than the rate of their reaction with ozone since the experiment does not provide evidence for the effects of the change of the parameters pointed above [29].

However, it should be noted that k of the elastomers are about 2-6 times lower that those of the low molecular analogues. The accuracy of activation energy (E_a) determination does not allow to estimate on account of which of the two parameters pre-exponential factor (A) or E_a one should relate the decrease in k. If we assume that the mechanism of ozone reaction with monomers and elastomers is similar, i.e. the reactions are isokinetic, then $A_{mon} = A_{pol}$. At $k_{mon}/k_{pol} = 2 \div 6$ the difference in E_a at 20°C will be 0.5-1.0 kcal/mol. At the low experimental values of E_a, these differences will become commensurable with them and thus the determination of E_a is not enough accurate. In this case two assumptions could be made which can give a reasonable explanation for the lower values of k_{pol}: 1) reorientation of the macromolecules is a slower process that that of olefins which would results in A_{pol} lower than A_{mon} and 2) the addition of ozone to C=C bonds is accompanied by the rehybridization of the C-atoms from $sp^2 - sp^3$ and the movement of the polymer susbstituents during activated complex (AC) formation will be more restricted than those in olefins mainly because of their greater molecular mass and sizes. This will ultimately result in decrease of the rate constant.

In Table 2 are shown some examples of ozonolysis of saturated polymers – polystyrene and polyisobutylene. These reactions take place not via the mechanism of ozone reaction with the double bonds but through a hidden radical mechanism with rate constants of 4-5 orders lower.

4.1. Polybutadienes

Because of the high viscosity and large rate constants the reaction takes place in the diffusion and mixed region. In order to obtain correct kinetic data we have used the theory of boundary surface [30]:

$$[O_3] = \alpha[O_3]_0 \cdot \exp[-\delta(k \cdot c \cdot D)^{1/2}] \quad (Eq.3)$$

where: $[O_3]$ is ozone concentration at the boundary surface; α – Henry's coefficient; $[O_3]_0$ – ozone concentration in the gas phase at reactor inlet; δ – boundary surface depth; k – rate constant of the ozone reaction with diene; c – concentration of the monomeric units; D – diffusion coefficient of ozone in the liquid phase.

It was found that the relative viscosity decreases exponentially upon ozonation of SKD solutions (Fig.1). As the viscosity is proportional to the molecular weight it follows that the polydiene consumption is described by first or pseudo first order kinetics.
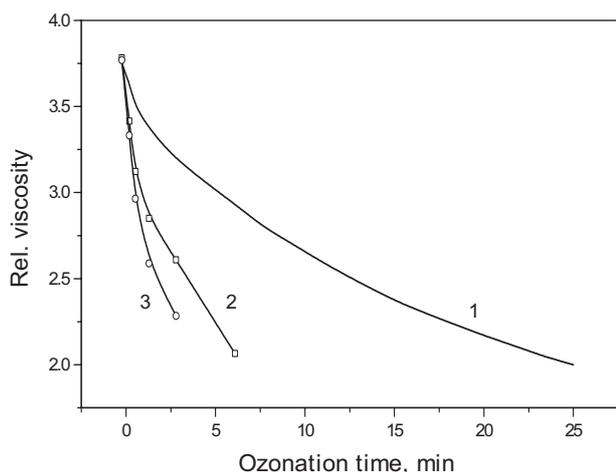
Fig. 1. *Dependence of the relative viscosity (η_{rel}) of SKD solutions (0.6 g in 100 ml CCl$_4$) on reaction time at ozone concentrations of: 1 – 1·10^{-5} M; 2 – 4.5·10^{-5} M; 3 – 8.25·10^{-5} M*

Rys. 1. *Zależność lepkości względnej (η_{rel}) roztworów SKD (0.6 g w 100 ml CCl$_4$) od czasu reakcji przy stężeniach ozonu: 1 – 1·10^{-5} M; 2 – 4.5·10^{-5} M; 3 – 8.25·10^{-5} M*

The value of ϕ, standing for the number of degraded polymeric molecules per one absorbed ozone molecule can be used to calculate the degradation efficiency. The value of this parameter (ϕ) may be estimated using the following equation:

$$\phi = 0.5\ [(M_{vt})^{-1} - (M_{vo})^{-1}] \cdot P/G \qquad \text{(Eq.4)}$$

where: M_{vt} is the molecular weight at time T; M_{vo} – the initial molecular weight; P – the polymer amount; G – amount of consumed ozone.
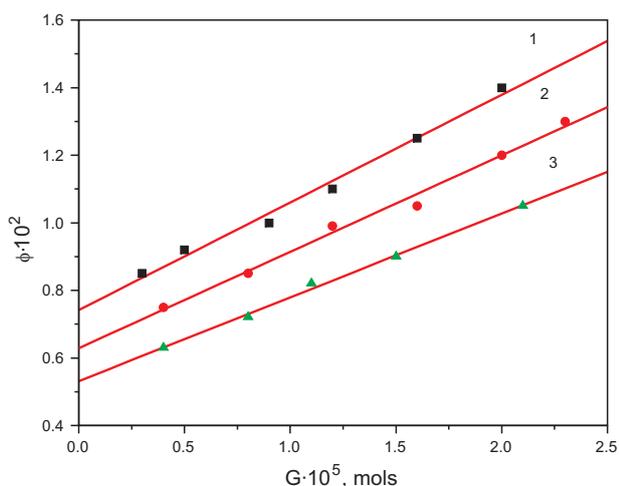

Fig. 2. *Dependence of ϕ on G for SKD (0.6/100) at various ozone concentrations: 1 – 1·10^{-5} M; 2 – 4.5·10^{-5} M; 3 – 8.25·10^{-5} M*

Rys. 2. *Zależność ϕ od G dla SKD przy różnych stężeniach ozonu: 1 – 1·10^{-5} M; 2 – 4.5·10^{-5} M; 3 – 8.25·10^{-5} M*
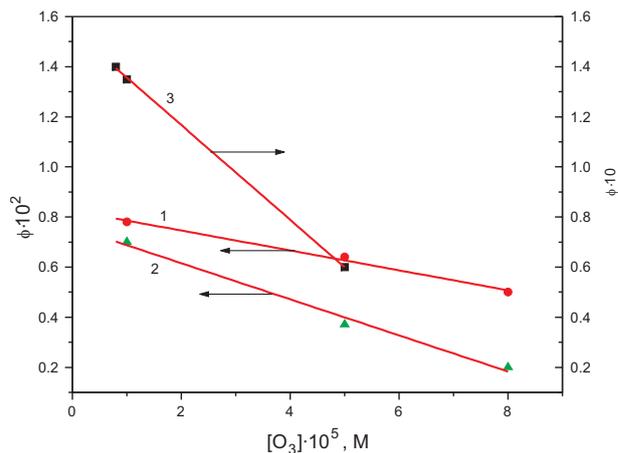

Fig. 3. *Dependence of ϕ on ozone concentration for elastomer solutions: 1 – SKD (0.6/100); 2 – Carom IR 2200 (0.6/100); 3 – Denka M40 (1/100)*

Rys. 3. *Zależność ϕ od stężenia ozonu dla roztworów elastomerów: 1 – SKD (0.6/100); 2 – Carom IR 2200 (0.6/100); 3 – Denka M40 (1/100)*

The dependence between ϕ and G is a straight line for a given reactor and depends on the hydrodynamic conditions in the reactor. It is seen from Fig. 2 that the ϕ values increase linearly with the reaction time and decrease with increase in ozone concentration. The corresponding dependences for Carom IR 2200 and Denka M40 ozonolysis are similar. The ϕ values for G→0 were used to avoid the effect of hydrodynamic factors on them.

The values of ϕ found for SKD, Carom IR 2200 and Denka M40 at [O$_3$] = 1·10^{-5} M amount to 0.7·10^{-2}, 0.78·10^{-2} and 0.14, respectively, and the slopes are: -40, -70 and 200 M^{-1}, respectively. Substituting with the known values for the parameters in equation 3 we have obtained δ within the range of 1·10^{-3} – 2·10^{-4} cm, which indicates that the reaction takes place in the volume around the bubbles, and hence in the diffusion region.

The ozonolysis of polydienes in solutions is described by the Criegee mechanism. The C=C bonds in the macromolecules are isolated since they are separated by three simple C-C bonds. According to the classical concepts, the C=C bonds configuration and the electronic properties of the groups bound to them affect also the polymer reactivity; similarly they do with the low molecular olefins. The only difference is that the polymer substituents at the C=C bonds are less mobile which influences the sp^2-sp^3 transition and the ozonides formation. In the first stage, when primary ozonide (Scheme 1, reaction 1) are formed, the lower mobility of the polymer substituents requires higher transition energy, the rate being respectively lower as compared to that with low molecular olefins and the arising strain accelerates the PO decomposition to zwitterion and carbonyl compound. The lower mobility of the polymer parts impedes the further ozonide formation and brings about the zwitterion leaving the cage and going into the volume

which in its turn accelerates the degradation process. The latter is associated with either its monomolecular decomposition or its interaction with low molecular components in the reaction mixture. The efficiency of degradation is determined by the C=C bonds location in the macromolecule, for example, at C=C bond location from the macromolecule center to its end, it is in the range from 2 to 1.

$$M_1 = (1/\gamma) \cdot M_0 \qquad (Eq.5)$$

where: $M_2 = M_0 - M_1$; $1 \leq \gamma \leq 2$ – coefficient pointing the C=C-bond location; M_0, M_1 and M_2 – the molecular weights of the initial macromolecule and the two degradated polymer parts, respectively.

At $\gamma=2$, i.e. when the broken C=C bond is located in the macromolecule center, the values of M_1 and M_2 will be exactly equal to $M_0/2$, at $\gamma \to 1$, i.e. at terminal C=C bond in the polymer chain, the value of M_1 will approximate to M_0 and thus the value of M_2 will be practically insignificant. For example, M_2 may be 50-1000 which is of 3-4 order less than that of the macromolecule and in fact degradation process will not occur. The viscosimetric determination of the molecular weight which we have applied in our experiments is with accuracy of ±5 % and does not allow the differentiation of molecular weights of 22700, 19000 and 9000 for the corresponding rubbers. This suggests that the cleavage of C=C bonds located at a distance of 420, 280 and 100 units from the macromolecule end would not affect the measured molecular weight.

Since the reaction of elastomers ozonolysis proceeds in the diffusion and diffusion-kinetic region, at low conversions each new gas bubble in the reactor would react with a new volume of the solution. From the other hand, the reaction volume is a sum of the liquid layers surrounding each bubble. It is known that the depth of the penetration from the gas into the liquid phase is not proportional to the gas concentration and thus the rise of ozone concentration would increase the reaction volume to a considerably lower extent than the ozone concentration. This leads to the occurrence of the following process: intensive degradation processes take place in the micro volume around the bubble and one macromolecule can be degraded to many fragments while the macromolecules out of this volume, which is much greater, may be not changed at all. Consequently with increase in ozone concentration, one may expect a reduction of coefficient MMD and increase of the oligomeric phase content. This will result in apparent decrease of ϕ at the viscosimetric measurements. The discussion above makes possible the correct interpretation of the data in Fig.3.

In the spectra of the ozonized polybutadienes the appearance of bands at 1111 and 1735 cm^{-1}, that are characteristic of ozonide and aldehyde groups, corespondingly, is observed [22, 31]. It was found out that the integral intensity of ozonide peak in the 1,4-*cis*-polybutadiene (E-BR) spectrum, is greater and of the aldehyde one is considerably smaller in comparison with the respective peaks in the Diene 35 NFA (BR) spectrum, at one and the same ozone conversion degree of the double bonds. The mentioned differences in the aldehyde yields indicate that, according to IR-analysis, the degradation efficiency of the BR solutions is greater.

The ^{1}H-NMR spectroscopy provides much more opportunities for identification and quantitative determination of functional groups, formed during ozonolysis of polybutadienes [32]. Fig. 4 shows spectra of ozonized E-BR. The signals of the ozonolysis products are decoded in Table 3 on the basis of Fig. 5. The ozonide: aldehyde ratio, determined from NMR spectra, was 89:11 and 73:27 for E-BR and BR, correspondingly. The peak at 2.81 ppm is present only in the spectra of ozonized Diene 35 NFA. It is usually associated with the occurrence of epoxide groups [33]. The integrated intensity of that signal compared to the signal of aldehyde protons at 9.70-9.79 ppm was about 10%. Similar signal at 2.75 ppm has been registered in the spectra of ozonized butadiene-nitrile rubbers, where the 1,4-*trans* double bonds are dominant [31].

According to [2, 10] two isomeric forms of 1,2,4-trioxolanes exist. The ratio between them is a function of the double bond stereochemistry, steric effect of the substituents and the conditions of ozonolysis. It was fond out only on the low molecular weight alkenes [19, 21]. The ^{1}H-NMR spectroscopy is the most powerfull method for determination of the *cis/trans* ratio of ozonides (in the case of polymers it is practically the only one method that can be applied). The measuring is based on the differences in the chemical shifts of the methine protons of the two isomers: the respective signal of the *cis* form appears in lower field compared to the *trans* one [19, 21]. The multiplet on Fig. 3 in the area of 5.1-5.18 ppm could be interpreted as a result of partial overlapping of triplets of *trans*- and *cis*-ozonides: 5.12 ppm (t, J≈5 Hz, 2H) and 5.16 ppm (t, J≈5 Hz, 2H), respectively. It is interesting to note that the *cis/trans* ratio of the E-BR 1, 2, 4-trioxolanes is practically equal to that obtained from *cis*-3-hexene [19, 34]. The resolution of the respective BR spectrum does not allow consideration in detail of the multiplicity of the signals at 5.10 and 5.15 ppm. In this case the area of the signals is widened, most probably due to the presence of ozonide signals of the 1,2-monomer units [20].

The basic route of the reaction – the formation of normal ozonides does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature (by analogy with Scheme 1 of polyisoprenes, see it below) [31, 32]. The most favorable conditions for ozone degradation emerge when the cage interaction (Scheme 1, reaction 3) does not proceed. Therefore, the higher ozonide yield the lower the intensity of ozone degradation of the polybutadienes and vice versa. As it was already determined the ozonide yields for the 1,4-*cis*- and 1,2- monomer units are close to 83-90%, whereas that for the 1,4-*trans* units is about
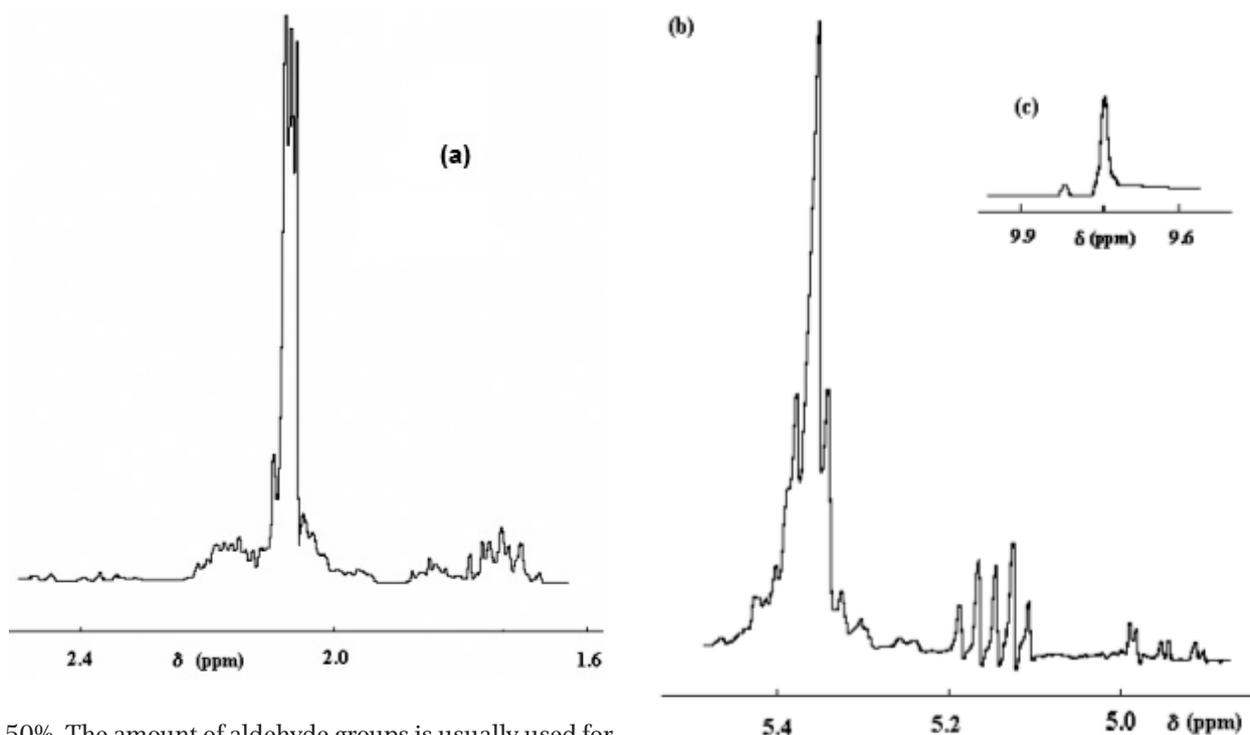
50%. The amount of aldehyde groups is usually used for evaluation of the intensity and efficiency (number of chain scissions per molecule of reacted ozone) of ozone degradation of elastomers. In this case it should be taken into account that the dominant route of degradation leads to the formation of 1 mol of aldehyde from 1 mol of ozone [32].

Fig. 4 (a,b,c). *^{1}H-250 MHz NMR spectra of E-BR solutions (0.89 g / 100 ml CCl$_4$) ozonized to 18% conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 20°C)*
Rys. 4 (a, b, c). *Widmo ^{1}H – 250 MHz roztworów E-BR (0.89 g/100 ml CCl$_4$) poddanego ozonowaniu do osiągnięcia 18% konwersji podwójnych wiązań (wzorzec zewnętrzny TMS; rozdzielczość cyfrowa 0,4 Hz, 20°C)*

4.2. Polyisoprenes

The positive inductive effect of the methyl group in polyisoprene enhances the rate of ozone addition to the double bonds from $6 \cdot 10^4$ for SKD to 4.10^5 M$^{-1} \cdot$s^{-1} for Carom IR 2200. The infrared spectra of ozonized

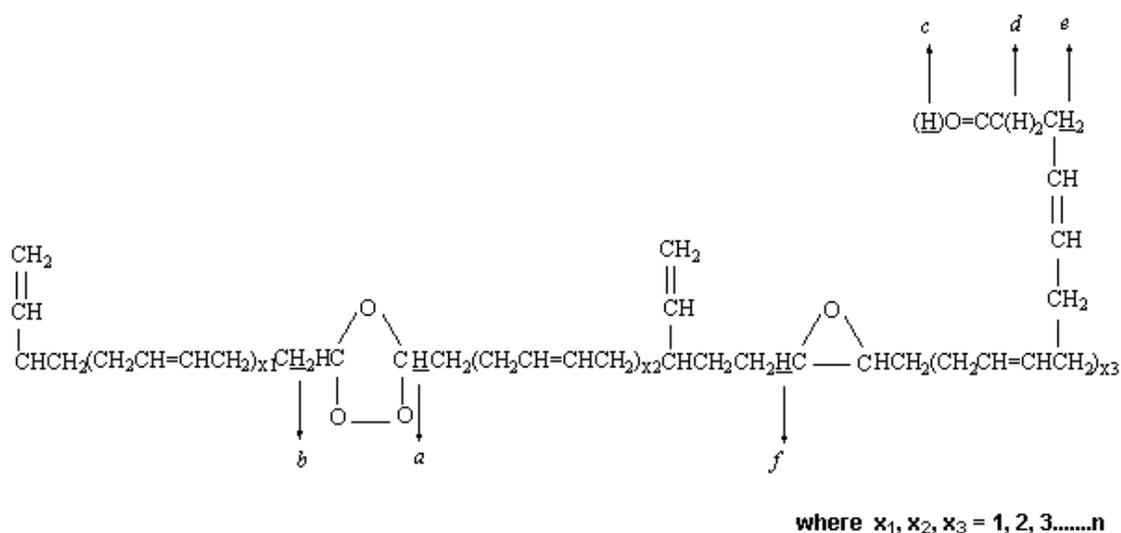

where x$_1$, x$_2$, x$_3$ = 1, 2, 3.......n

Fig. 5. *Selection of protons with characteristic signals in the ^{1}H-250 MHz NMR spectra of partially ozonized polybutadiene macromolecules*
Rys. 5. *Selekcja protonów z charakterystycznymi sygnałami w widmie ^{1}H-250 MHz NMR makrocząsteczek polibutadienu poddanych częściowemu ozonowaniu*

1,4-*trans*-polyisoprene (Z-IR) show two intense bands at 1100 and 1725 cm^{-1}, characteristic of ozonide and keto groups, respectively [19, 35]. These spectra are identical with the well-known spectra of 1,4-*cis*-polyisoprenes (E-IR), as far as ozonide and carbonyl bands are concerned [22, 36]. It was found that the integrated intensity of the peak at 1100 cm^{-1} in the E-IR and Z-IR spectra is equal for one and the same amount of reacted ozone. By analogy with the peak at 1110 cm^{-1}, the integral intensity of the peak at 1725 cm^{-1} is also one and the same. The latter show that, according to the infrared spectra, the degradation efficiencies of E-IR and Z-IR with respect to the amount of consumed ozone do not practically differ.

Table 3. *Assignment of the signals in the ^{1}H-NMR spectra of partially ozonized E-BR and BR rubbers*
Tabela 3. *Przyporządkowanie sygnałów w widmie ^{1}H-NMR kauczuków E-BR i BR poddanych częściowemu ozonowaniu*

Assignment of the signals (according Fig. 4)	Chemical shifts (ppm)		Litera-ture
	E-BR	BRA	
a	5.10 – 5.20 max 5.12, 5.16	5.05 – 5.18 max 5.10, 5.15	[19, 34]
b	1.67 – 1.79 max 1.72, 1.76	1.66 – 1.80 max 1.73	[7, 19]
c	9.75	9.74	[33]
d	2.42 – 2.54 max 2.47	2.42- 2.54 max 2.50	[33]
e	2.27 – 2.42 max 2.35	2.27 – 2.42 max 2.35	[33]
f		max 2.81	[33]

The ^{1}H-NMR spectroscopy affords much more opportunities for identification and quantitative determination of functional groups formed on ozonolysis of polyisoprenes. Fig. 6 shows spectra of non-ozonized and ozonized E-IR. Changes in the spectra of ozonized elastomers are decoded in Table 4 on the basis of Fig.7. It is seen that besides ketones, aldehydes are also formed as a result of ozonolysis. A comparison between methylene and methine proton signals of the non-ozonized polyisoprenes and the corresponding ozonide signals indicates a considerable overlap in the ranges 1.60-1.90 and 4.5-5.5 ppm. A signal overlap is also registered in the 2.00-2.20 ppm region, characteristic of methyl protons of keto groups. Because of the reasons mentioned above, the ozonides and aldehydes were quantified by using the integrated intensity of the signals at 1.40 (a) and 9.70-9.79 (g) ppm, respectively. Ketone amounts were determined as a difference between the total intensity of the methylene signals from aldehydes and ketones, 2.40-2.60 and 2.35-2.60 ppm, respectively, and the doubled intensity of the aldehyde signal at 9.70-9.79

ppm. Thus the obtained ozonide: ketone:aldehyde ratio was 40:37:23 and 42:39:19 for 1,4-*cis*-polyisoprene and 1,4-*trans*-polyisoprene, correspondingly. The peak at 2.73 ppm, present in the spectra of both ozonized elastomers, is associated with the occurrence of epoxide groups [33, 37]. The integrated intensity of that signal compared to the signal at 9.70-9.79 ppm was 21 and 15 % for E-IR and Z-IR, respectively.

Current ideas about the mechanism of C=C double bond ozonolysis in solution are summarized in Schemes 1 and 2 [19, 21, 34]. As a result of the decomposition of the initial reaction product, primary ozonide (PO), zwitterionic species is formed, termed as Criegee's intermediates or carbonyl oxides (hereafter referred to as CI) (Scheme 1, reactions 2 and 2'). Two intermediates are formed from asymmetric olefins: monosubstituted CI (MCI) and disubstituted CI (DCI), if their *syn* and *anti* stereoisomers are not taken into account. It is known that carbonyl oxides are predominantly formed at carbon atoms with electron-donating substituents [19]. Excellent correlations of the regioselectivities of M_o fragmentation with electrondonation by substituents (as measured by Hammett and Taft parameters) have been obtained, consistent with the effects expected for stabilisation of a zwiterionic carbonyl oxide [20]. According to ref. [23], for polyisoprenes the ratio between the two intermediates, DCI and MCI, is 64:36.

Table 4. *Assignment of the signals in the ^{1}H-NMR spectra of partially ozonized 1,4-cis- and 1,4-trans- polyisoprenes*
Tabela 4. *Przyporządkowanie sygnałów w widmie ^{1}H-NMR 1,4-cis- i 1,4-trans-poliizoprenów poddanych częściowemu ozonowaniu*

Assignment of the signals (according Fig. 4)	Chemical shifts (ppm)		Litera-ture
	E-IR	Z-IR	
a	max 1.41	max 1.40	37, 38
b	1.70 – 1.78	1.68 – 1.82 max 1.71	37
c	2.10 – 2.20	2.10 – 2.20	33
d	2.22 – 2.40 max 2.33, 2.36	2.22 – 2.35 max 2.29, 2.33	33
e	2.40 – 2.60 max 2.47	2.35 – 2.55 max 2.48, 2.46	33
f	max 2.73	max 2.73	33
g	max 9.76	max 9.77	33

Ozonides are the basic product of polyisoprene ozonolysis in non-participating solvents. It is known that the dominant part of ozonides is formed through the interaction between CI and the corresponding carbonyl group, which originate from the decomposition of one and the same PO, i.e. a solvent cage effect is operating (Scheme 1, reactions 3 and 3') [19, 34]. With simple

olefins the so-called normal ozonides are over 70 % [26]. Cross-ozonide formation is also observed (Scheme 1, reactions 5 and 5'). The amount of cross-ozonides is dependent upon the structure of the double bonds, their concentration in the solution, temperature and solvent nature. Reference data indicate that the cross-ozonide yield is strongly reduced at C=C bond concentrations of the order of 0.1 M, with non-polar solvents, and at temperatures over 0 °C [19]. It is reasonable to expect that the polymeric nature of the double bonds in the polyisoprenes would additionally impede the formation of cross-ozonides. Our estimates showed that the amount of cross-ozonides, formed on ozonolysis of both elastomers, is less than 10% of their total quantity. A very small percentage in the overall balance of reacted ozone is the share of the reaction of polymeric ozonides formation (Scheme 1, reactions 4 and 4') [22].

In the presence of two types of intermediates, DCI and MCI, it is interesting to follow their further conversion with a view to the reaction products determined by ^{1}H-NMR spectroscopy. The reaction between CI and carbonyl groups is usually considered to be 1,3-cycloaddition [20, 34]. In this connection the CI-aldehyde interaction is the most effective one: it readily precedes with high ozonide yields. Ketones are considerably less dipolarophilic and good yields of ozonides are limited to special conditions involving particularly reactive ketones, intramolecular reactions, or where ketone is used as the reaction solvent and is therefore present in large concentration [19-21]. In order to evaluate the contribution of reactions 3 and 3' (Scheme 1), it is useful to discuss two hypotheses: i) no reaction proceeds between MCI and ketone, the registered amount of ozonides being formed in reaction 3; ii) because of the solvent cage effect already mentioned, both the reactions can be considered with practically equal rate constants. Then the ozonide yields would be proportional to the ratio between the two zwitterions (64:36). In this case the corresponding yields of the reactions DCI + aldehyde and MCI + ketone can be calculated from the following system of equations:

$$Y = x + y \qquad\qquad (Eq.6)$$
$$x/y = 64/36 \qquad\qquad (Eq.7)$$

where Y is the total ozonide yield, x and y are the corresponding ozonide yields with the former and the latter reactions, respectively. Results are given in Table 5. A comparison between the aldehyde amounts from both hypotheses and NMR data shows that the former hypothesis leads to results that are much closer to the experimental data.

More complicated is the question of the other conversion routes with carbonyl oxides outside the solvent cage. It is generally accepted that the deactivation of DCI from low molecular olefins normally takes place via a bimolecular reaction mechanism. At low temperatures (below -70 °C) dimeric peroxides are formed (Scheme 2, reaction 1) whereas higher temperatures give rise to the formation of carbonyl compounds and evolution of oxy-

gen (Scheme 2, reaction 2) [20]. However, on comparing the yields of keto groups, determined from ^{1}H-NMR spectra, with the amounts of ketones and DCI, presented in Table 5, it is seen that reaction 2, if occurring at all, is not dominating during DCI conversion. From kinetic evaluations of CI concentrations in solution it follows that under comparable experimental conditions these concentrations are 4-6 orders of magnitude lower than those of the C=C bonds [23]. Very likely, interac-
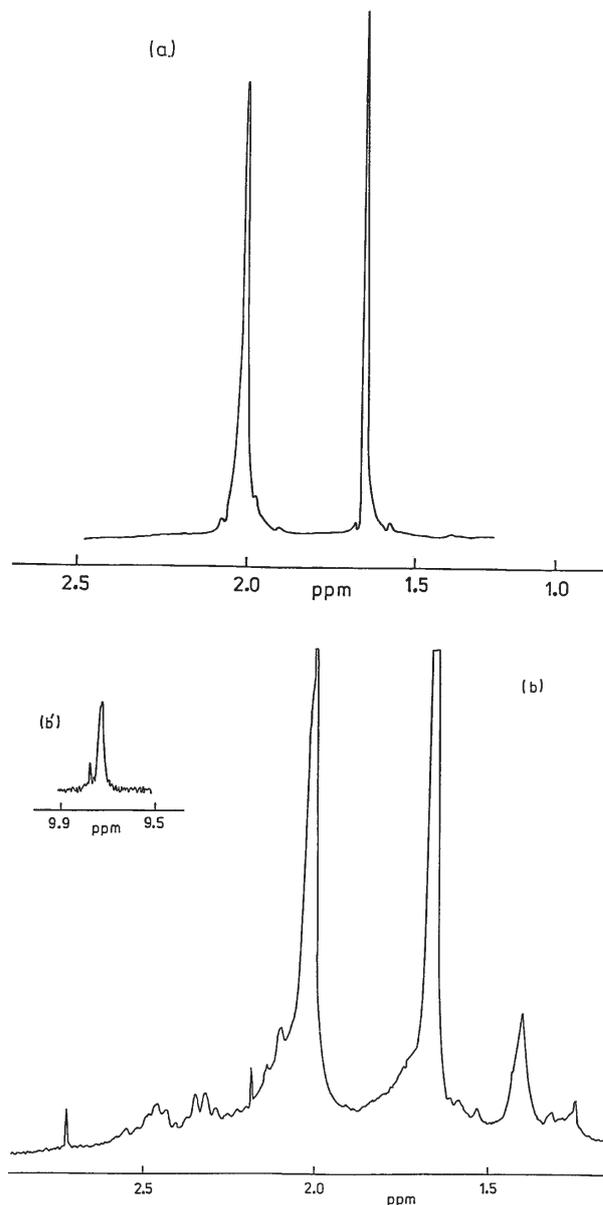

Fig. 6. *^{1}H-250 MHz NMR spectra of 1,4-cis-polyisoprene solutions (1 g / 100 ml CCl₄): (a) non-ozonized; (b) ozonized to 23% conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 20°C)*
Rys. 6. *Widma ^{1}H-250 MHz NMR roztworów 1,4-poliizoprenu (1 g / 100 ml CCl₄): (a) niepoddanego ozonowaniu; (b) poddanego ozonowaniu do osiągnięcia 23% konwersji podwójnych wiązań (wzorzec zewnętrzny TMS; rozdzielczość cyfrowa 0,4 Hz, 20°C)*
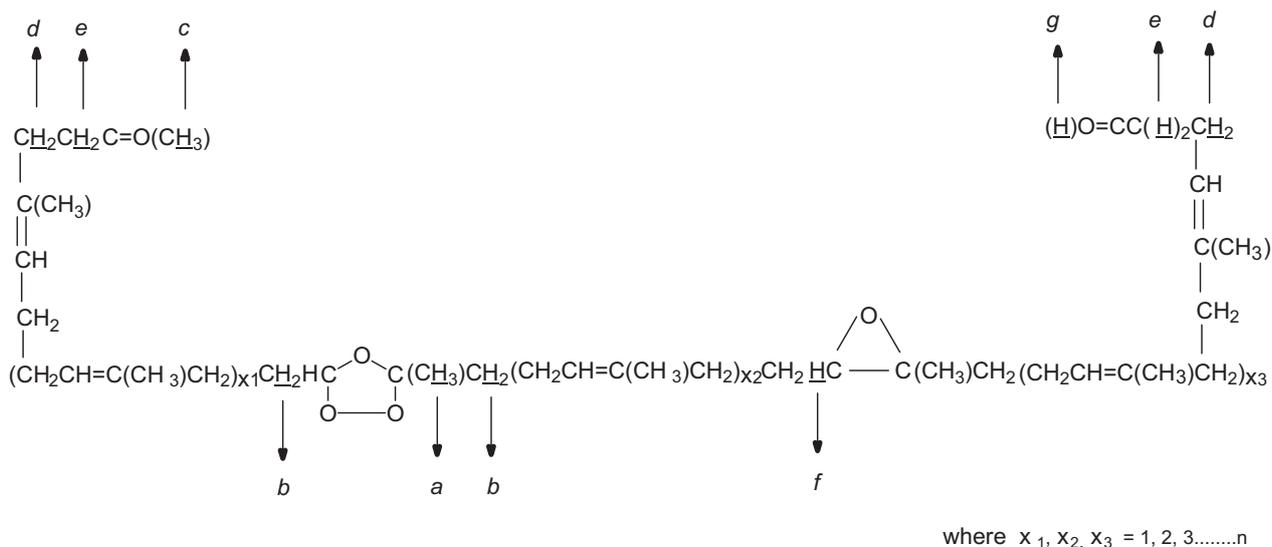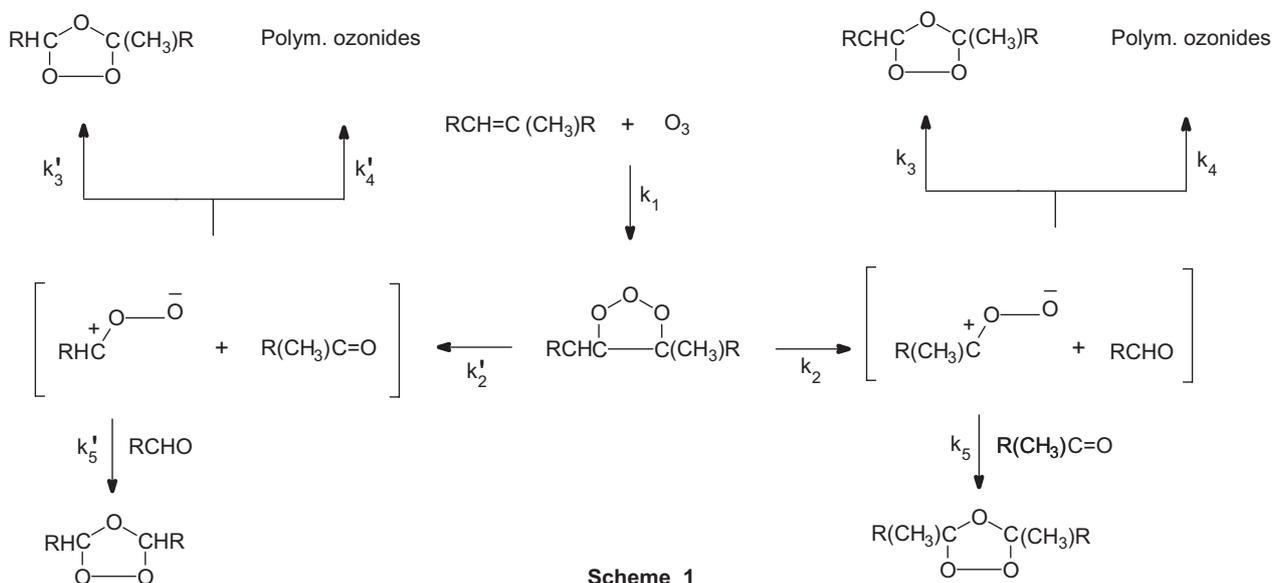
Fig. 7. *Selection of protons with characteristic signals in the ^{1}H-250 MHz NMR spectra of partially ozonized poly-isoprene macromolecules*
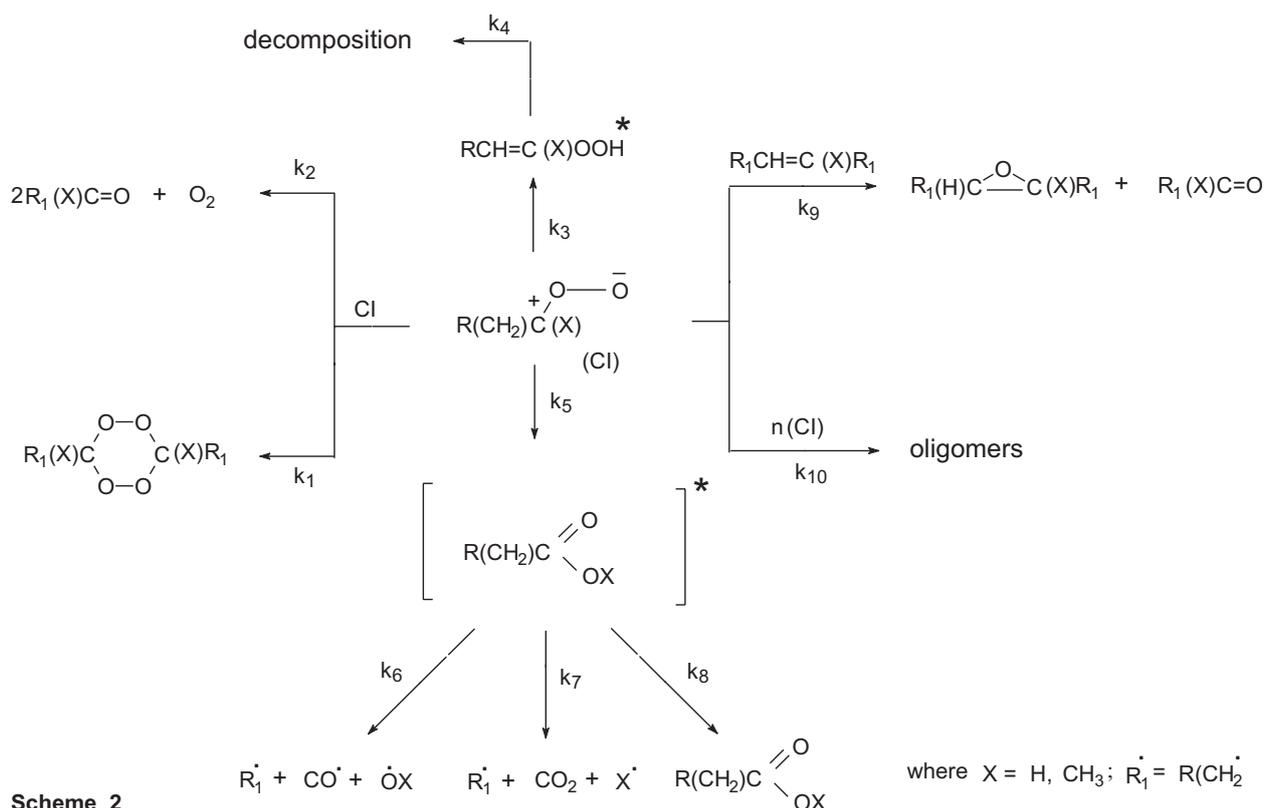
Rys. 7. *Selekcja protonów z charakterystycznymi sygnałami w widmie ^{1}H-250 NMR makrocząsteczek poliizoprenu poddanego częściowemu ozonowaniu*

Table 5. *Intermediates and products of the ozonolysis of 1,4-cis-, and 1,4-trans- polyisoprenes*

Tabela 5. *Związki pośrednie i produkty ozonolizy 1,4-cis- i 1,4-trans-poliizoprenów*

	DCI + aldehydes (64 %)			MCI + ketones (36 %)		
	ozonides (%)	aldehydes (%)	DCI (%)	ozonides (%)	ketones (%)	MCI (%)
hypothese (i)						
E – IR	40	24	24	0	36	36
Z – IR	42	22	22	0	36	36
hypothese (ii)						
E – IR	26	38	38	14	22	22
Z – IR	27	37	37	15	21	21

Scheme 1

decomposition   ← k_4

$RCH=C(X)OOH$ * $R_1CH=C(X)R_1$ $R_1(H)C\!\!-\!\!\overset{O}{\underset{}{}}\!\!-C(X)R_1$ + $R_1(X)C=O$

$2R_1(X)C=O + O_2$ k_2 k_9

  k_3

CI $R(CH_2)\overset{+}{C}(X)\overset{O-\bar{O}}{}$ (CI)

$R_1(X)C\overset{O-O}{\underset{O-O}{}}C(X)R_1$ k_1 k_5 n(CI)   oligomers k_{10}

$[R(CH_2)C\overset{\diagup O}{\diagdown OX}]$ *

k_6 k_7 k_8

$\dot{R_1} + \dot{CO} + \dot{O}X$ $\dot{R_1} + CO_2 + \dot{X}$ $R(CH_2)C\overset{\diagup O}{\diagdown OX}$ where $X = H, CH_3$; $\dot{R_1} = R(\dot{CH_2})$

Scheme 2

tions between two or more DCI are hindered by extremely low values of CI concentration and mostly by the polymeric nature of substituent R_1. Under these conditions, DCI tautomerization followed by decomposition of hydroperoxides, formed in the excited state (Scheme 2, reactions 3 and 4), seems most probable.

On going into MCI conversion routes one should have in mind the lower stability and lifetime of these intermediates compared to DCI. Reference data on the proceeding of reactions 1 and 2 (Scheme 2) during ozonolysis of low-molecular olefins in solution are missing [34]. On ozonolysis of 1,4-*trans*-polychloroprene the share of CI of the MCI type is over 80%, in agreement with the induction effect of the chlorine atom [23]. However, no aldehyde groups in the ozonized polymer solution were found [39]. It follows that the interaction between MCI entites, if any, is not the dominating deactivation reaction with these intermediates. The most probable MCI monomolecular deactivation route is assumed to be the isomerization of the MCI intermediates via hot acid to radicals (Scheme 2, reactions 5, 6, 7), because no acid groups were detected (Scheme 2, reaction 8). According to the literature reaction 5 (Scheme 2) does not occur with DCI intermediates [21].

Another route of carbonyl oxide deactivation is double bond epoxidation. Various schemes of olefin epoxidation during ozonolysis have been suggested but the epoxidation via CI (Scheme 2, reaction 9) is presumed to be the most probable with the C=C bonds in polyisoprenes [20, 21]. Since a peak at 2.73 ppm has also been observed under similar conditions on ozonolysis of acrylonitrile-butadiene copolymers [31], as well as dur-

ing ozonolysis of polybutadienes, it can be assumed that the epoxidation reaction takes place with the participation of both types of CI.

4.3. Polychloroprene

The electronaccepting properties of the chlorine atom at the polychloroprene double bond reduces the reactivity of Denka M40 as demonstrated by its relatively low rate constant, i.e. $k=4\cdot10^3$ $M^{-1}\cdot s^{-1}$. In this reaction the ratio between the zwitterions A and B, according to theoretical calculations, is in favour of A, the ratio being A/B = 4.55. The A formation is accompanied by choroanhydride group formation and that of B with aldehyde one. In both cases the ozonides formation is insignificant and the zwitterions react predominantly in the volume resulting in enhancement of the degradation process. The intensive band detected at 1795 cm^{-1} in the IR spectrum of ozonized Denka M40 solutions (Fig.8) is characteristic of chloroanhydride group [39]. This fact correlated well with the conclusion about the direction of the primary ozonide decomposition. The band at 955 cm^{-1} is also typical of chloroanhydrides. Two other bands – at 1044 and 905 cm^{-1} may be attributed to the C-O vibrations. The valent vibrations characteristics of HO-groups are observed in the region of 3050-3500 cm^{-1}.

The iodometrical analysis of active oxygen in the ozonized Denka M40 solutions shows that the amount of O-O groups is ca. 43%. It is of interest to note that the HI reaction with ozonized polychloroprene solutions occurs quantitatively for 3-4 h, while in SKD the same proceeds only to 20% after 24 h. The above data, however,
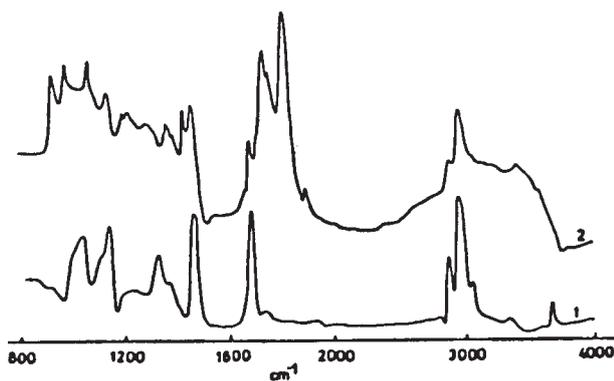
Fig. 8. *Infra-red spectra of Denka M40 solutions: 1 – non-ozonized; 2 – ozonized to 40% conversion*
Rys. 8. *Widma IR roztworów Denka M40: 1 – niepoddanego ozonowaniu; 2 – ozonowanego do 40% konwersji*

Fig. 9. *DSC curve of Diene 35 NFA rubber (BR)*
Rys. 9. *Krzywa DSC kauczuku Diene 35 NFA (BR)*

provide insufficient information for the preferable route of the zwitterions deactivation (via dimerization, polymerization of zwitterions or secondary processes).The DSC analysis of the products of Denka M40 ozonolysis reveals that the chloroprene rubber ozonolysis yields polyperoxide as the enthalpy of its decomposition is found to be very close to that of dicumene peroxide (DCP), The higher value of E_a (ca. two times of that of DCP) testifies the possible formation of polymer peroxides [4].

4.4. DSC study of thermal decomposition of partially ozonised diene rubbers

The thermal decomposition of the ozonized diene rubbers can exercise influence on the ageing processes as an initiator of the oxidation reactions [40]. On the other hand it is of interest for the elastomers modification and oligomerization [6]. The importance of the DSC method to the investigation of 1,2,4-trioxolanes is based on high values of the enthalpy of the reaction of ozonide thermal decomposition and on the temperature range in
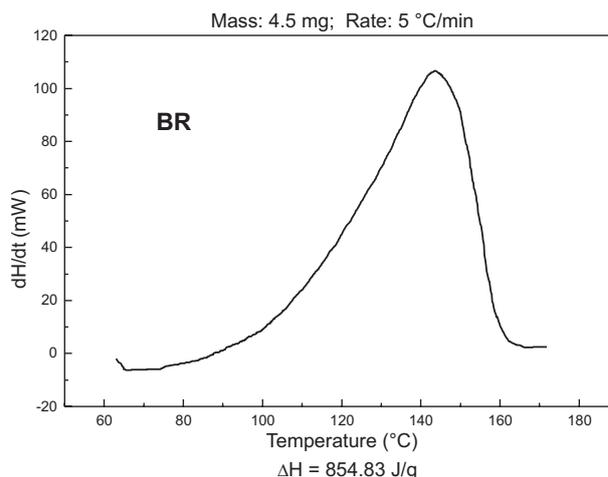
which it takes place [41-43]. An intense and relatively broad exothermic peak is characteristic for the thermograms of the partially ozonated 1,4-*cis*-polybutadiene (E-BR), Diene 35 NFA (BR), 1,4-*cis*-polyisoprene (E-IR), 1,4-*trans*-polyisoprene (Z-IR) and 1,4-*trans*-polychloroprene (PCh), recorded in 60–200°C range (Fig. 9). Practically no thermal effects are detected in the respective thermograms of the nonozonized samples.

For an objective consideration on the enthalpy changes it is necessary to normalize ΔH values with respect to the amount of consumed ozone (G). It is distributed on the whole mass of the ozonated sample. The whole mass is a sum of the mass of nonozonated rubber and mass of the incorporated in diene macromolecules oxygen atoms, grouped as a moles ozone. Determination of the amounts of the incorporated ozone (G_{inc}) in rubber samples is performed in [43]. The corresponding values of the coefficient of incorporation of ozone (c_{inc}), defined as a ratio of the amounts of incorporated (G_{inc}) and consumed (G) ozone is presented in Table 6. Using $ΔH_1$ values and ratio of the functional group, deduced from the NMR spectra, the enthalpy of the ozonide thermal decomposition ($ΔH_2$) has been evaluated. The data of Table 6 clearly show tendency of increasing of $ΔH_2$ values with the number of alkyl substituents of the ozonides.

Table 6. *Enthalpy changes on the thermolysis of partially ozonated diene rubbers*
Tabela 6. *Zmiany entalpii podczas termolizy kauczuków dienowych poddanych częściowemu ozonowaniu*

Sample	ΔH (J/g)	c_{inc}	$ΔH_1$ (kJ/mol O₃)	Ozonide (mol)/ Incorp. ozone (mol)	$ΔH_2$ (kJ/mol ozonide)
E-BR	954.07	0.93	332	0.96	373
BR	854.83	0.87	271	0.89	350
E-IR	576.19	0.62	182	0.65	453
Z-IR	576.62	0.62	178	0.67	426
PCh	704.57	0.81	254		
1-Decene ozonide					349 [7]

Table 7. *DSC analysis of the ozonized rubbers decomposition [43]*
Tabela 7. *Analiza DSC produktów rozpadu ozonowanych kauczuków*

	*T_m (°C)	α_s	E (kJ/mol)	n
E-BR	147	0.67	125	1.0
BR	145	0.68	117	0.96
E-IR	160	0.68	111	1.04
Z-IR	149	0.68	113	1.08
PCh	96	0.55	70	1.25
1-Decene ozonide	117	0.63	132	1.0

*T_m and α_s values at heating rate of 5 °C/min; T_m and α_s are temperature and degree of conversion at the DSC peak maximum.

There are no considerable differences between the values of the activation energy (E) and reaction order (n) of the ozonide thermal decomposition with E-IR and Z-IR (Table 7). The smaller E values of the polyisoprene ozonides in comparison with those of E-BR ozonides and 1-decene ozonide are, most probably, due to the lower thermal stability of small amounts of oligomeric peroxides, which are present among the reaction products of E-IR and Z-IR ozonolysis [36].

5. Conclusions

The ozone reaction with a number of polydienes with different configurations of the double bonds and various substituents was investigated in CCl$_4$ solution.

The changes of the viscosity of the polymer solutions during the ozonolysis were characterized by the determination of the number of chain scissions per molecule of reacted ozone (φ). The influence of the conditions of mass-transfer of the reagents in a bubble reactor on the respective φ values were discussed.

The basic functional groups-products from the rubbers ozonolysis were identified and quantitatively characterized by means of IR-spectroscopy and ^{1}H-NMR spectroscopy. The aldehyde:ozonide ratio was 11:89 and 27:73 for E-BR and BR, respectively. In addition, epoxide groups were detected, only in the case of BR, their yield was about 10 % of that of the aldehydes. On polyisoprenes the ozonide:ketone:aldehyde ratio, was 40:37:23 and 42:39:19 for E-IR and Z-IR, respectively. Besides the already specified functional groups, epoxide groups were also detected, their yields being 8 and 7 % for E-IR and Z-IR, respectively, with respect to reacted ozone. In the case of 1,4-*trans*-polychloroprene the chloroanhydride group was found to be the basic carbonyl product.

A reaction mechanism, that explains the formation of all identified functional groups, was proposed. It has been shown that the basic route of the reaction of ozone with elastomer double bonds – the formation of normal ozonides does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature. The most favorable conditions for ozone degradation emerge when the cage interaction between Crigee's intermediates and respective carbonyl groups does not proceed. The amounts of measured different carbonyl groups have been used as a alternative way for evaluation of the intensity and efficiency of the ozone degradation.

The thermal decomposition of partially ozonated diene rubbers was investigated by DSC. The respective values of the enthalpy, the activation energy and the reaction order of the 1,2,4-trioxolanes were determined.

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