

Ozonolysis of Polybutadienes with Different Microstructure in Solution

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ABSTRACT: The reaction of ozone with 1,4-*cis*-polybutadiene and polybutadiene having the following linking of the butadiene units: 1,4-*cis* (47%), 1,4-*trans* (42%), 1,2 (11%) was investigated in CCl₄ solution. It was found out by means of IR-spectroscopy and ¹H-NMR spectroscopy that the basic ozonolysis products of both elastomers are ozonides and aldehydes. 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, and their yield was about 10% of that of the aldehydes. On the basis of BR ozonolysis it was established that the ozonide yield from 1,4-*trans* units is

about 50%. By using the aldehyde yields, an evaluation was made of the efficiency of ozone degradation of the two polybutadienes, according to which the respective value of BR is considerably higher than that of E-BR. A reaction mechanism is proposed, which explains the formation of the identified functional groups and the differences in the ozone degradation of the studied elastomers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 427–433, 2007

Key words: ozonolysis; polybutadienes; solution; ozone degradation

INTRODUCTION

It is well known that there exist some differences in the kinetics and in the mechanism of ozonolysis of the respective *cis*- and *trans*-alkenes.^{1–3} It is established that as a rule the values of the rate constants for the *trans*-alkenes are about 1.5–2 times higher than those of the *cis*-forms.^{4–9} On the other hand the yield of the basic reaction product in the so-called “nonparticipating solvents”-ozonide is usually greater in the case of *cis*-alkenes.^{2,10,11} The ozone reaction with polydienes in solution is used for determination of the elastomers structure,^{12,13} their modification,¹⁴ and especially for investigations on the kinetics and mechanism of ozone degradation.^{15,16} The degradation, observed in solution, is due to the proceeding of nonozonide routes of ozonolysis, which are accompanied by formation of terminal carbonyl groups.^{17–19} Our comparative study of the ozonolysis of 1,4-*cis*- and 1,4-*trans*-polyisoprenes did not find considerable differences in the yields of ozonides and carbonyl compounds, and in the efficiency of ozone degradation of the two elastomers.²⁰

In the present article an attempt is made to examine some peculiarities of the ozonolysis of *cis*- and *trans*-polymeric double bonds of two polybutadienes with different microstructure.

EXPERIMENTAL

Materials

Ozone

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

Rubbers

Commercial samples of 1,4-*cis*-polybutadiene rubber (SKD) and polybutadiene (Diene 35 NFA), produced by AOA Nizhnekamskneftekhim and Firestone Tire and Rubber Co., respectively, were used in the experiments. The molecular masses of the elastomers were determined by the GPC method on a Waters instrument. The weight and number-average molecular mass were 413,000 and 154,700 for the SKD (E-BR)-samples and 298,000 and 113,300 for the Diene 35 NFA (BR), respectively.²¹ The corresponding polydispersity indices were 2.67 and 2.63. All rubbers were purified by a threefold precipitation from CCl₄ solutions with excess of methanol.

The microstructure of the polymers (in %), determined from respective ¹H-NMR spectra, was as follows: SKD (1,4-*cis*: > 96) and Diene 35 NFA (1,4-*cis*: 47; 1,4-*trans*: 42; 1,2: 11).

Procedures and apparatus

Ozonation of polymer solutions

The experiments were performed in a bubbling reactor, equipped with a thermostatic water jacket and a

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viscometer. An ozone–oxygen mixture with ozone concentration in the range of $0.1\text{--}1.2 \times 10^{-4}$ mol/L was passed through the reactor at a rate of $1.5 \pm 0.15 \times 10^{-3}$ L/s. The ozone concentrations in the gas phase at the reactor inlet and outlet were measured spectrophotometrically at 254 nm.³ The volume of the polymer solutions was 15 mL for the viscometric measurement and 10 mL for the rest of measurements. The changes in the molecular mass during ozonolysis were registered viscometrically. The algorithm for determination of the characteristic viscosity and of the degradation efficiency, defined by the number of viscometrically detected chain scission acts with respect to one molecule of reacted ozone, is described elsewhere.²² All the viscometric measurements were performed at 25°C.

Infrared spectra were acquired on a Carl Zeiss Spectord IR-71 dispersive spectrophotometer. ¹H-nuclear magnetic resonance spectra were recorded on a Bruker WM 250 MHz instrument.

RESULTS AND DISCUSSION

Viscometric study of ozone degradation

The ozone bubbling through polybutadienes solutions results in a decrease in their viscosity, and thus, in the corresponding molecular masses (Fig. 1). It was seen that the degradation of BR is more intensive. The number of chain scissions per molecule of reacted ozone (ϕ), derived from Figure 1, was used to measure the efficiency of degradation of the two polybutadienes towards the consumed ozone. The obtained values at

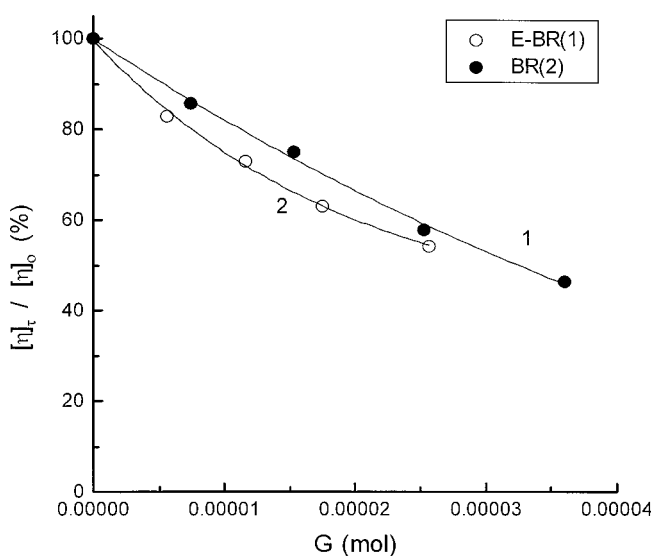


Figure 1 Dependence of $[\eta]_t/[\eta]_0$ (%) on the amount of reacted ozone (G) for carbon tetrachloride solutions (0.6 g/100 mL) of E-BR and BR. Note that $[\eta]_0$ and $[\eta]_t$ are the intrinsic viscosity values prior to and during ozonization, respectively; ozone concentration at the reactor inlet was 5×10^{-5} mol/L.

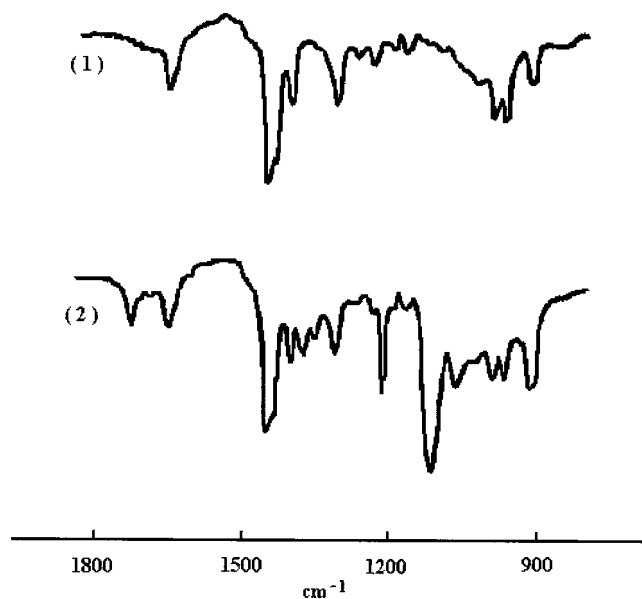


Figure 2 IR-spectra of E-BR solutions (0.89 g/100 mL CCl_4). (1) Nonozonized and (2) ozonized to 18% conversion of the double bonds.

$[\text{O}_3] = 1.2 \times 10^5$ mol/L for SKD and Diene 35 NFA were 0.007 and 0.009, respectively. It has been found that at a degree of ozone conversion of the double bonds higher than 20–25% a gel formation is registered.²² For that reason the ozone degradation of 1,4-*cis*-polybutadiene has been described as a competitive process of degradation and crosslinking routes.²² However, it has been determined that the relative part of the crosslinking reactions in the overall balance of the consumed ozone is very low compared with the share of the degradation routes, especially under conditions of relatively low values of $[\text{O}_3]$.¹⁷

The ϕ values, determined by viscometric measurements, do not correspond to the real extent of the degradation efficiency of the elastomers.^{16,19,22,23} The discrepancy between the viscometric data and those obtained by functional group analysis is a result of uneven distribution of the degradation process in the bubbling reactor. The characteristics of the mass transfer of reagents during ozonolysis in bubbling reactor were discussed in detail in Refs. 16 and 22. In the case of 1,4-*cis*-polybutadiene, because of the very high values of its rate constant with ozone (6×10^4 L mol⁻¹ s⁻¹), the instantaneous volume of the polymeric solution layer in which the reaction takes place is about 1.1×10^{-3} cm³ (0.007% from the total volume)²³; the frequency of replacement of the boundary surface of the liquid phase is about 250 times per second.²² The intensive progress of the reaction in a very small volume determines the formation of significant amount of low-molecular-mass fragments which in practice cannot be viscometrically detected.

The examination of the differences in the ϕ values for E-BR and BR should be based mainly on two

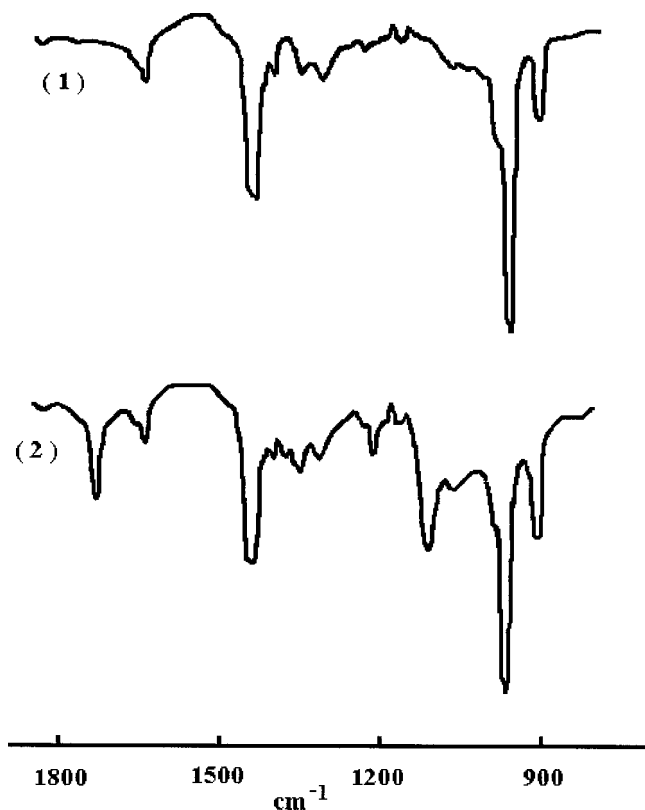


Figure 3 IR-spectra of BR solutions (0.89 g/100 mL CCl_4). (1) Nonozonized and (2) ozonized to 18% conversion of the double bonds.

factors: (i) the conditions of mass transfer of the reagents and (ii) the reaction mechanism. Under other identical conditions the mass transfer parameters are determined by the rate of the reaction. It is usually assumed that the 1,4-trans double bonds react with ozone about two times faster than the respective 1,4-cis-double bonds.³⁻⁹ In this connection the rate of the ozone reaction with BR can be evaluated based on the already mentioned suggestion about respective k value and 42% content of the 1,4-trans double bonds. Our estimation is that the influence of the relatively small difference in the rate values of E-BR and BR could not be significant. As far as the reaction mechanism is concerned, it will be shown further that in the case of BR, the relative share of the routes responsible for degradation in the overall balance of consumed ozone is considerably greater, in comparison with the respective one of E-BR.

Functional group analysis

IR-spectra of nonozonized and ozonized polybutadiene solutions are shown in Figures 2 and 3. In the spectra of the ozonized polybutadienes the appearance of bands at 1111 and 1735 cm^{-1} , characteristic of ozonide and aldehyde groups, correspondingly, is observed.^{2,3,17} It was found that the integral intensity of ozonide peak in the E-BR spectrum is greater and that of the aldehyde one is considerably smaller in comparison

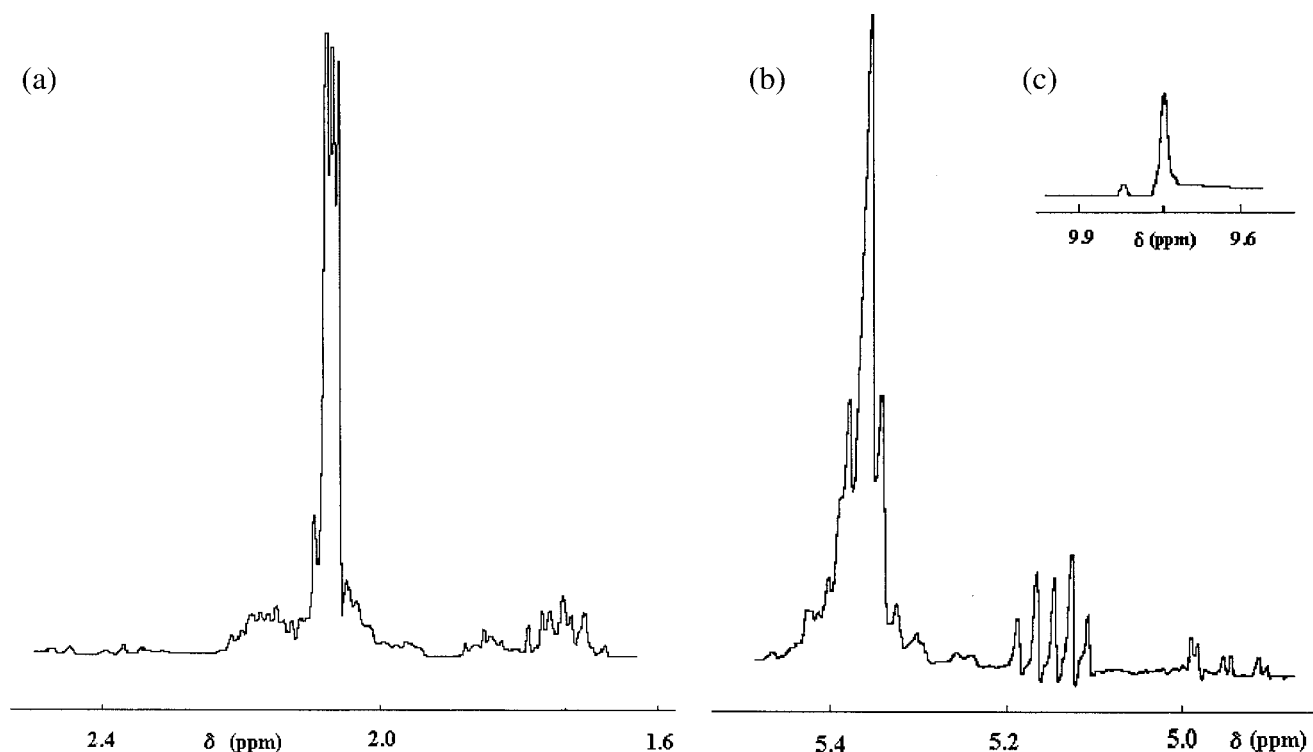


Figure 4 ^1H -250 MHz NMR spectra of E-BR solutions (0.89 g/100 mL CCl_4) ozonized to 18% conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 20°C).

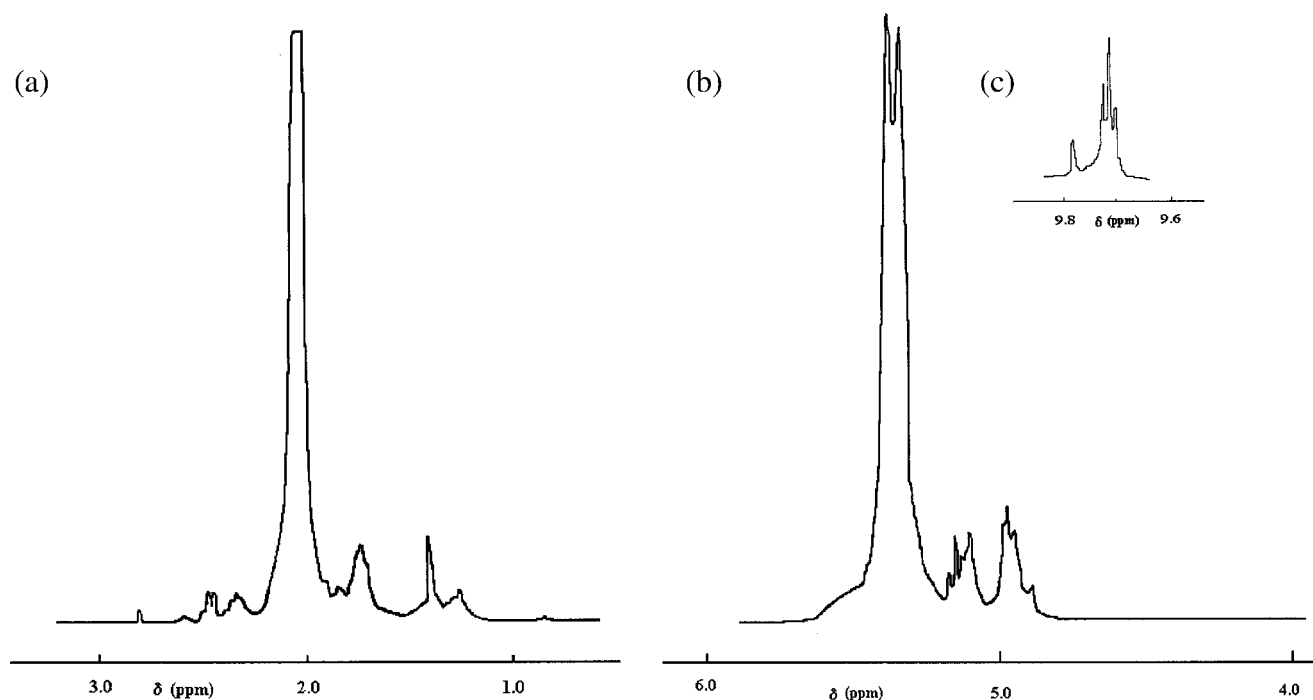


Figure 5 ^1H -250 MHz NMR spectra of BR solutions (0.89 g/100 mL CCl_4) ozonized to 18% conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 20°C).

with the respective peaks in the 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 ^1H -NMR spectroscopy provides much more opportunities for identification and quantitative determination of functional groups formed during ozonolysis of polybutadienes. Figures 4 and 5 show spectra of ozonized E-BR and BR, respectively. The signals of the ozonolysis products are decoded in Table I on the basis of Figure 6. The ozonide:aldehyde ratio, determined from NMR spectra, was 89 : 11 and 73 : 27 for E-BR and BR, respectively. 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.²⁴ The integrated intensity of that signal compared with the signal of aldehyde protons at 9.70–9.79 ppm was about 10%. Similar signal at 2.75 ppm has been regis-

tered in the spectra of ozonized butadiene–nitrile rubbers, in which the 1,4-*trans* double bonds are dominant.²³

There exist two isomeric forms of 1,2,4-trioxolanes.^{2,10} Their ratio is a function of the double bond stereochemistry, the steric effect of substituents, and the conditions of ozonolysis, and it has been studied only for low-molecular-weight alkenes.^{10,25} The ^1H -NMR spectroscopy is the most universal method for determination of the *cis/trans* ratio of ozonides (in the case of polymers it is practically the only 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 with the *trans* one.^{2,10} In accordance with the above-mentioned, the multiplet on Figure 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 (t, $J \approx 5$ Hz, 2H) and 5.16

TABLE I
Assignment of the Signals in the ^1H -NMR Spectra of Partially Ozonized E-BR and BR Rubbers

Assignment of the signals (according to Fig. 4)	Chemical shifts (ppm)		Reference
	E-BR	BR	
a	5.10–5.20 max 5.12, 5.16	5.05–5.18 max 5.10, 5.15	[12, 24]
b	1.67–1.79 max 1.72, 1.76	1.66–1.80 max 1.73	[12, 24]
c	9.75	9.74	[25]
d	2.42–2.54 max 2.47	2.42–2.54 max 2.50	[12, 24]
e	2.27–2.42 max 2.35	2.27–2.42 max 2.35	[12, 24]
f		max 2.81	[25]

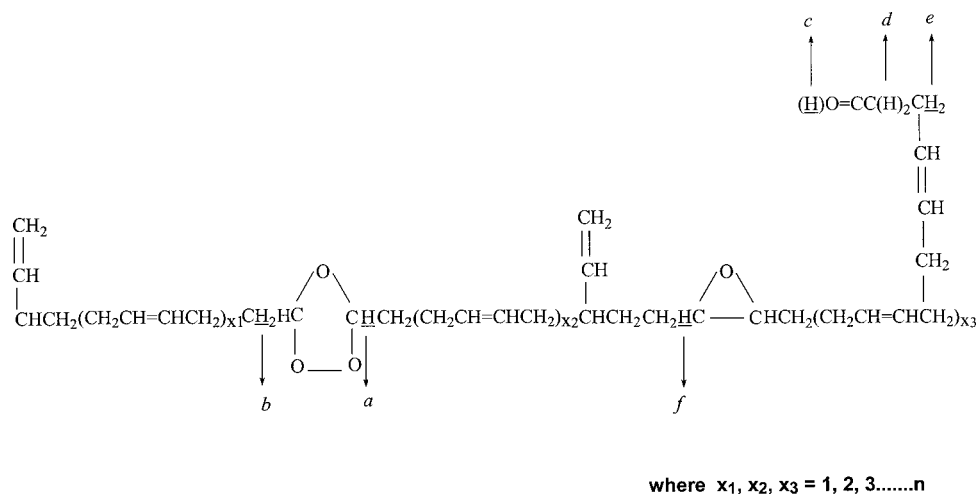


Figure 6 Selection of protons with characteristic signals in the ^1H -250 MHz NMR spectra of partially ozonized polybutadiene macromolecules.

($t, J \approx 5 \text{ Hz}, 2\text{H}$), 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.^{10,26} 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.²⁷

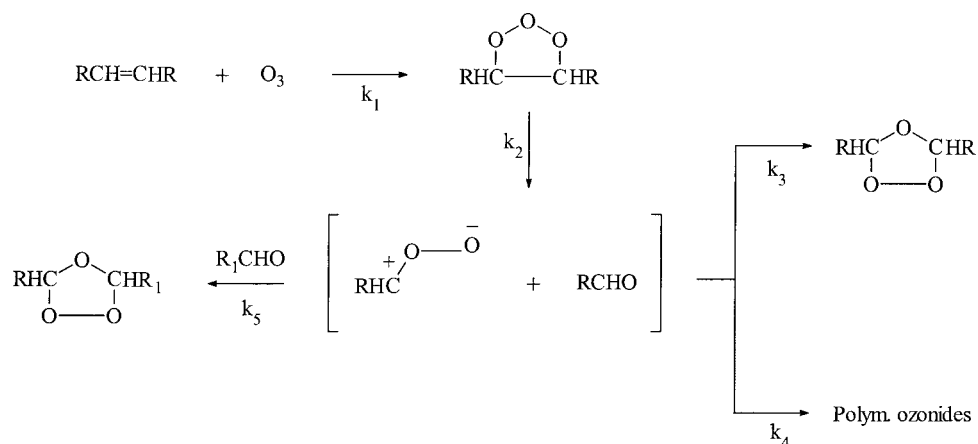
Reaction mechanism

The modern concepts about the mechanism of the reaction of ozone with $\text{C}=\text{C}$ double bonds in solution are summarized in Schemes 1 and 2.^{1,2,25,27,28} The initial reaction product, the *cis*- or *trans*-molozone (MO) is unstable, and at temperatures higher than -150°C for the *cis*-isomer and -90°C for the *trans*-isomer is decomposed to aldehyde and zwitterionic species termed as Criegee's intermediate or carbonyl oxide (hereafter referred to as CI) (Scheme 1, reaction 2).^{25,27} The basic product of double bonds ozonolysis in nonparticipating solvents—the ozonides are obtained in reaction of

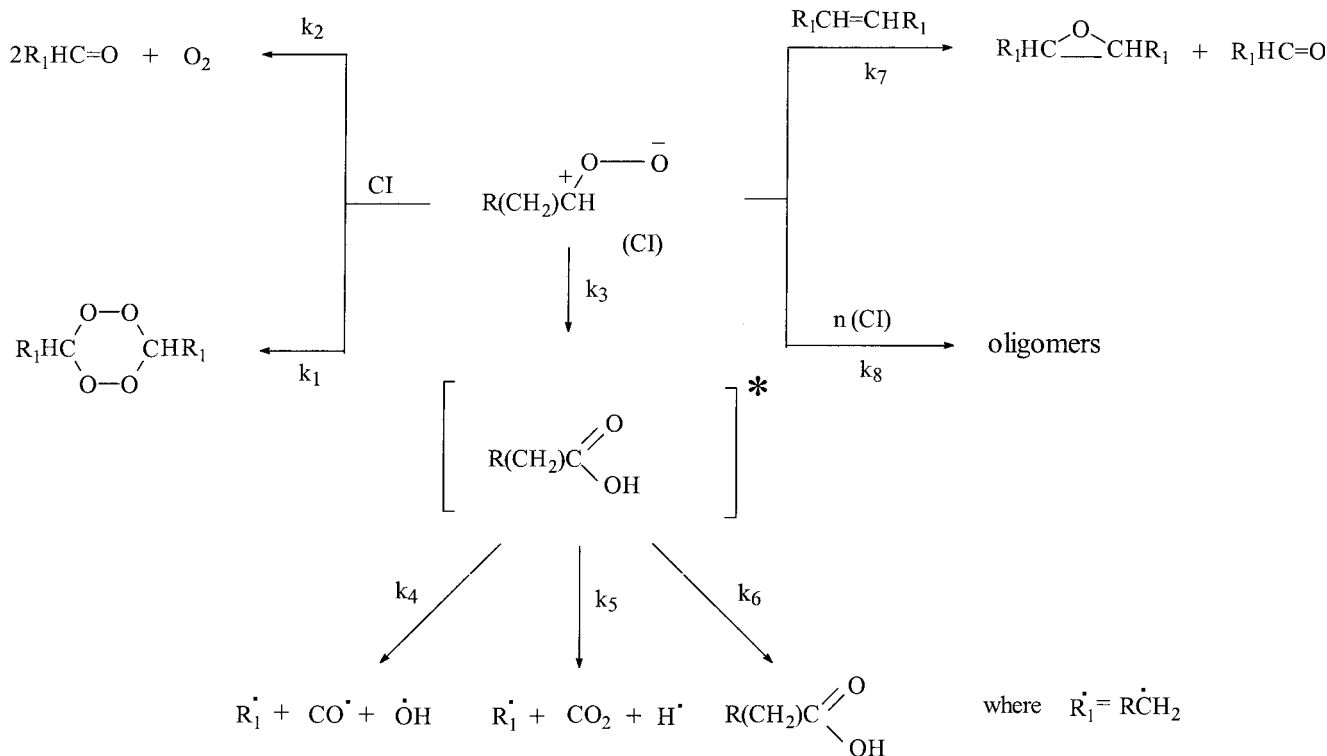
CI with a carbonyl compound. It has been found that the dominant part of ozonides is formed through interaction between carbonyl oxide and the corresponding carbonyl group, which both originate from the decomposition of one and the same MO, i.e., a solvent cage effect is acting (Scheme 1, reactions 3).^{1,25} The yield of the so-called normal ozonides from the simple olefins are usually over 70% from the total ozonide yield.²⁵

The cross-ozonide formation, observed with alkenes,^{1,2,10,11} is possible with polydienes too (Scheme 1, reaction 5). The problem is that the application of ^1H -NMR spectroscopy, in the case of polybutadienes, does not allow differentiation between normal, cross, and polymeric ozonides. Our experimental conditions (respective values of $[\text{C}=\text{C}]$, $[\text{O}_3]$, and temperature) do not favor the proceeding of reaction 5.² It is obvious that the influence of the polymeric nature of the double bond substituents on the cross-ozonide formation also cannot be positive.

As it was already mentioned the ozonide yield of E-BR is considerably higher in comparison to that of



Scheme 1 Formation of ozonides.



Scheme 2 Alternative routes of conversion of CI intermediates.

BR. Upon investigation of the alkene ozonolysis in solution it has been found that the yield of normal and cross 1,2,4-trioxolanes depends on such factors as stereometric structure of the double bonds, nature of the substituents, and of the solvent, temperature, and alkene concentration.^{2,10,26} There exists a general rule that the *cis*-alkenes usually give a higher yield of ozonides (total) and of normal 1,2,4-trioxolanes when compared with the *trans* isomers.^{2,10} For example the maximal ozonide yields of the *cis*- and *trans*-3-hexene are respectively, 88% and 49%, and the minimum values are 81% and 22%.^{2,10} In the case of *cis*- and *trans*-2-butene the maximum values are 72% and 36% and the minimum are 48% and 36% correspondingly.^{2,10} The high selectivity of the reaction towards 1,2,4-trioxolanes is also typical of the ozonolysis of the terminal double bonds which could be considered as analog of the 1,2-monomer units.²⁷ The analysis of the reaction selectivity towards the ozonides shows similarity between the 1,4-*cis*-polybutadiene units and the *cis*-3-hexene, while in the case of *cis*-2-butene the results are lower. An attempt was made to evaluate the yield from 1,4-*trans* units, based on their contents in BR, the data determined by ¹H-NMR for E-BR and assuming the ozonide yield of 1,2-units equal of that of 1,4-*cis* units. We obtained that the selectivity towards ozonides for the 1,4-*trans* units of polybutadiene is about 50%.

As it was reported previously, at 20–25% ozone conversion of polybutadienes, especially of those with high contents of 1,4-*cis* units, a gel formation is observed.^{17,22} It has been found that the crosslinks of

polymers containing double C=C bonds in the side chain have peroxide nature.²⁹ The kinetics of the cross-linking process during ozonolysis of polymers with double bonds has been studied in Refs. 23 and 31. Our expectations are that in the case of the polybutadienes, the predominant part of crosslinks are result of formation of polymeric ozonides (Scheme 1, reaction 4), but their share in the overall balance of reacted ozone is very small, of the order of a few percents.

The second main product of the polybutadiene ozonolysis are the aldehydes. According to the mechanism of the ozone reaction with double bonds in solution, the aldehyde groups are being formed when the conversion of CI intermediates is proceeding through routes, which are an alternative to the carbonyl oxide–aldehyde interaction.^{2,28} The nonozonide routes are illustrated in Scheme 2. In the case when the CI conversion results in formation of carbonyl group, two moles of aldehydes are obtained from one mole of ozone (Scheme 2, reactions 2 and 7). Another route of CI deactivation is its isomerization via hot acid to radicals (Scheme 2, reactions 4 and 5). In this case one mole of ozone produces one mole of aldehyde.³ Acidic groups were not detected among the reaction products (Scheme 2, reaction 6). The stability and the life time of low-molecular-weight CI intermediates with different substituents and their capability to undergo various monomolecular and bimolecular interactions are widely discussed in the literature.^{27,28} The peculiarities of conversion of two intermediates in polyisoprene ozonolysis (one of them is the same as

that obtained from polybutadiene) are considered in Ref. 20. It has been shown that, under our experimental conditions, the dominant "nonozonide" route of conversion of the respective carbonyl oxide intermediate is its isomerization via hot acid.

The epoxide groups may be formed as a result of direct interaction between ozone and a double bond, or by a reaction of a double bond with dioxirane, which could be considered as the cyclic form of the carbonyl oxide intermediate.^{27,28} However, there is no evidence that the above-mentioned reactions or the cyclization of the respective intermediate are taking place with alkenes, which are structural analogs of the polybutadienes, or with the very polybutadienes. The most probable suggestion is that the epoxide groups are products of interaction of the carbonyl oxide with a double bond (Scheme 2, reaction 7). It should be noted that, in contrast to the ozonolysis of *cis*- and *trans*-hexene,²⁶ 1,4-*cis*- and 1,4-*trans*-polyisoprene,²⁰ in the case of polybutadienes the formation of epoxide groups is observed only when the elastomer macromolecules contain 1,4-*trans* monomer units. This phenomenon could be explained with the relatively higher stability of the dominant stereochemical form (*syn* carbonyl oxide) of the respective intermediate that originates from ozonolysis of 1,4-*trans* units.²⁸

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.^{30,31} The most favorable conditions for ozone degradation emerge when the cage interaction (Scheme 1, reaction 3) does not proceed. Therefore the higher the 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 of the order of 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 one mole of aldehyde from one mole of ozone.

CONCLUSIONS

The reaction of ozone with 1,4-*cis*-polybutadiene and polybutadiene containing 1,4-*cis*-; 1,4-*trans*- and 1,2-monomeric units was investigated in CCl₄ solution. 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, and their yield was about 10% of that of the aldehydes. On the basis of the BR ozonolysis, it was established that the ozonide yield from 1,4-*trans* units is about 50%.

The nonozonide routes of deactivation of the Criggé's intermediates were discussed. A supposition is substantiated that monomolecular decomposition to radicals via isomerization to hot acid is the dominant route for CI conversion. Taking into account the aldehyde yields, an evaluation was made of the efficiency of ozone degradation of the two polybutadienes, according to which the respective value of BR is considerably higher than that of E-BR.

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