

# Ozonolysis of Polydienes

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Received 9 December 2002; accepted 9 July 2003

## INTRODUCTION

Interest<sup>1</sup> in the ozone reaction with polydienes is closely related to the problem of ozone degradation of rubber products. The reaction kinetics is found to be strongly dependent on the polymeric state, a question which has attracted special interest in the recent years.<sup>1</sup>

Flory<sup>2</sup> showed that the reactivity of 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 analogs (catalytic hydrogenation). At the same time, many fermentative reactions with polymers take place rapidly while similar reactions with low molecular compounds do not occur at all.<sup>3</sup> The folded or unfolded form of the macromolecules provides various conditions for contact of the reagents with the reacting parts.<sup>4</sup> By using the modified version of this principle,<sup>5</sup> it was possible to explain the proceedings 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 (MW) and reactivity. The theory predicts that the properties of the polymer–solvent system can be described by the parameter of globe swelling ( $\gamma$ ) which defines the free energy ( $F$ ) of the system and, thus, the rate constant of the reaction. For a reversible reaction, that is, polymerization–depolymerization, the dependence of the rate constant of the chain length growth on the molecular weight is expressed by the following equation:

$$\ln k_{pj}/k_{p\infty} = -\text{const} \cdot (5\gamma - 3/\gamma)(d\gamma/dM)M_0 \quad (1)$$

where  $M_0$  is the molecular weight of the studied sample and  $k_{p\infty}$  is the rate constant for infinitely long macromolecules. A good correlation between the the-

oretical and experimental data for polystyrene solutions in benzene is found in ref. 6.

The study of polymer degradation is complicated by a polymer's structural peculiarities on the molecular and supra-molecular level and diffusion characteristics. It is difficult to find simple model reactions for the 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.<sup>7</sup>

## KINETIC DATA

Table I summarizes the rate constants of the ozone reaction with some conventional elastomers and polymers and their low molecular analogs.

It is seen that the reactivity of elastomers and polymers and their corresponding low molecular analogs, 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 such as the  $k$  of polychloroprene being higher than that of vinyl chloride due to the presence of two donor substituents and (2) the dependence of  $k$  on the configuration of the C=C bond in a *trans*-isomer (gutta-percha) and a *cis*-isomer (natural rubber).

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 that the reaction is carried out with thermodynamical elastomer solutions in which the macromolecules can do free intramolecular movements and do not react with adjacent macromolecules. Moreover, the rate of macromolecule 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 out above.<sup>8,9</sup>

TABLE I  
Rate Constants of Ozone with Polymers and Low  
Molecular Analogs in CCl<sub>4</sub>, 20°C

Compound	MW	$k \times 10^{-4} M^{-1} s^{-1}$
Poly(vinyl chloride)	$8 \times 10^5$	$0.42 \pm 0.1$
Vinyl chloride	62.45	0.18
2-Bromopropene	121	$0.28 \pm 0.05$
Polybutadiene	$3.3 \times 10^5$	$6.0 \pm 1$
Cyclododecatriene-1,5,9	162	$35 \pm 10$
Polybutadienestyrene	$8 \times 10^4$	$6 \pm 1$
Gutta-percha	$3 \pm 10^4$	$27 \pm 5$
Natural rubber	$1 \times 10^6$	$44 \pm 10$
2-Me-pentene-2	85	$35 \pm 10$
Squalene	410	$74 \pm 15$
+Polystyrene	$5 \times 10^5$	$0.3 \times 10^{-4}$
Cumene	120	$0.6 \times 10^{-4}$
Polyisobutylene	$1.7 \times 10^5$	$0.02 \times 10^{-4}$
Cyclohexane	84	$0.01 \times 10^{-4}$

However, it should be noted that the  $k$  of the elastomers are about two to six times lower than those of the low molecular analogs. The accuracy of the  $E_a$  determination does not allow one to estimate, because it is not known which of the two parameters  $A$  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, that is, the reactions are isokinetic, then  $A_{\text{mon}} = A_{\text{pol}}$ . At  $k_{\text{mon}}/k_{\text{pol}} = 2 \div 6$ , 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 accurate enough. In this case, two assumptions could be made which can give a reasonable explanation for the lower values of  $k_{\text{pol}}$ : (1) reorientation of the macromolecules is a slower process than that of olefins, which would result in an  $A_{\text{pol}}$  lower than  $A_{\text{mon}}$  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 substituents during AC formation will be more restricted than those in olefins mainly because of their greater molecular mass and size. This will ultimately result in a decrease of the rate constant.

Table I shows also some examples of the ozonolysis of saturated polymers—polystyrene and polyisobuty-

lene. 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.

## POLYBUTADIENE

Some industrial samples of rubbers have been the object of investigation (Table II). The polymers were purified by triple extraction with methanol in a Soxhlet extractor. The experiments were conducted in a bubbling reactor containing a polymer solution (0.06–1%) in tetrachloromethane. The progress of the ozonation are followed viscosimetrically, gel-chromatographically, IR and NMR spectrally, and iodometrically and through triphenylphosphine reduction.

Because of the high viscosity and large rate constants, the reaction takes pace in the diffusion and mixed region. To obtain correct kinetic data, we used the theory of the boundary surface<sup>10</sup>:

$$[O_3] = \alpha[O_3]_0 \exp[-\delta(kcD)^{1/2}] \quad (2)$$

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

It was found that the relative viscosity decreases exponentially upon ozonation of SKD and SKI-3S solutions (Fig. 1). The dotted lines denote the theoretical exponential functions. As the viscosity is proportional to the molecular weight, it follows that the polydiene consumption is described by first or pseudo-first-order kinetics.

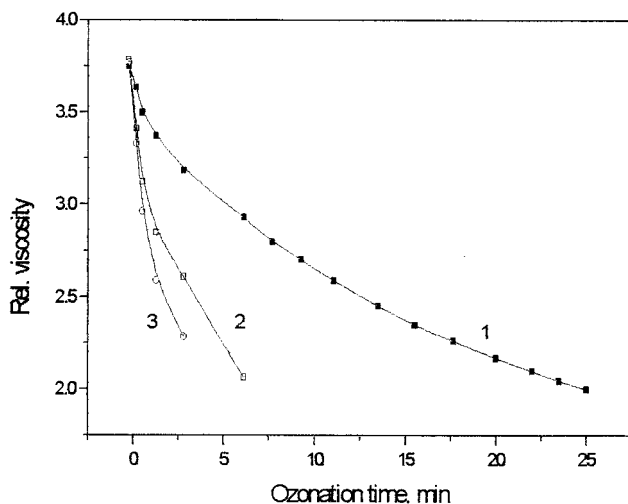
The value of  $\phi$ , standing for the number of degraded polymeric molecules per one absorbed ozone molecule, can be used to calculate the degradation intensity. The value of this parameter ( $\phi$ ) may be estimated using the following equation:

$$\phi = 0.5[M_v^t]^{-1} - (M_v^0)^{-1} P/G \quad (3)$$

TABLE II  
Some Characteristics of Polydiene Samples

Elastomer	Monomeric unit	Unsaturation degree (%)	1,4- <i>cis</i> (%)	1,4- <i>trans</i> (%)	1,2- (%)	3,4- (%)	$M_v \times 10^{-3}$	$N$
SCD	—CH=CH—	95–98	87–93	3–8	3–5	—	454	2.1
SKI-3S	—C(CH <sub>3</sub> )=CH—	94–98	94–97	2–4	—	1–2	380	2.0
Denka M40	—C(Cl)=C—	94–98	5	94	—	—	180	1.8

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



**Figure 1** Dependence of the relative viscosity ( $\eta_{rel}$ ) of SKD solutions (0.6 g in 100 mL  $\text{CCl}_4$ ) on reaction time at ozone concentrations of (1)  $1 \times 10^{-5} M$ , (2)  $4.5 \times 10^{-5} M$ , and (3)  $8.25 \times 10^{-5} M$ .

where  $M_v^t$  is the molecular weight at time  $T$ ;  $M_v^0$  is the initial molecular weight;  $P$ , the polymer amount; and  $G$ , the amount of consumed ozone. The dependence between  $\phi$  and  $G$  is a straight line for a given reactor and depends on the hydrodynamic conditions in the reactor.

It is seen from Figure 2 that the  $\phi$  values increase linearly with the reaction time and decrease with increase in the ozone concentration. The corresponding  $\phi$  values for SKI-3S and Denka M40 ozonolysis are similar. The  $\phi$  values for  $G \rightarrow 0$  were used to avoid the effect of hydrodynamic factors on them. The values of  $\phi$  found for SKD, SKI-3S, and Denka M40 at  $[\text{O}_3] = 1 \times 10^{-5} M$  amount to  $0.7 \times 10^{-2}$ ,  $0.78 \times 10^{-2}$ , and 0.14, respectively, and the slopes are  $-40$ ,  $-70$ , and  $200 M^{-1}$ , respectively. By substituting the known values for the parameters in eq. (2), we obtained  $\delta$  within the range of  $1 \times 10^{-3}$ – $2 \times 10^{-4} \text{ cm}$ , which indicates that the reaction takes place in the volume around the bubbles and, hence, in the diffusion region.

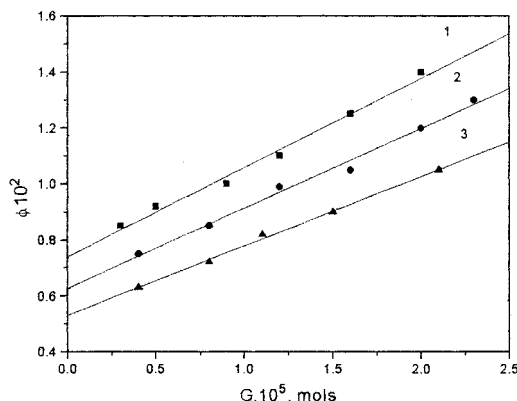
The ozonolysis of polydienes in solutions is described by the Criegee mechanism. The  $\text{C}=\text{C}$  bonds in the macromolecules are isolated since they are separated by three simple  $\text{C}-\text{C}$  bonds. According to the classical concepts, the  $\text{C}=\text{C}$  bonds' configuration and the electronic properties of the groups bound to them affect also the polymer reactivity, similarly as they do the low molecular olefins. The only difference is that the polymer substituents at the  $\text{C}=\text{C}$  bonds are less mobile, which influences the  $sp^2$ – $sp^3$  transition and the ozonide formation. In the first stage, when PO is formed, the lower mobility of the polymer substituents requires a higher transition energy, the rate being, respectively, lower as compared to that with low mo-

lecular olefins and the arising strain accelerates the PO decomposition to a zwitterion and carbonyl compound. The lower mobility of the polymer parts impedes the further ozonide formation and causes the zwitterion to leave the cage and go into the volume, which, 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  $\text{C}=\text{C}$  bonds' location in the macromolecule; for example, at the  $\text{C}=\text{C}$  bond location from the macromolecule center to its end, it is in the range from 2 to 1:

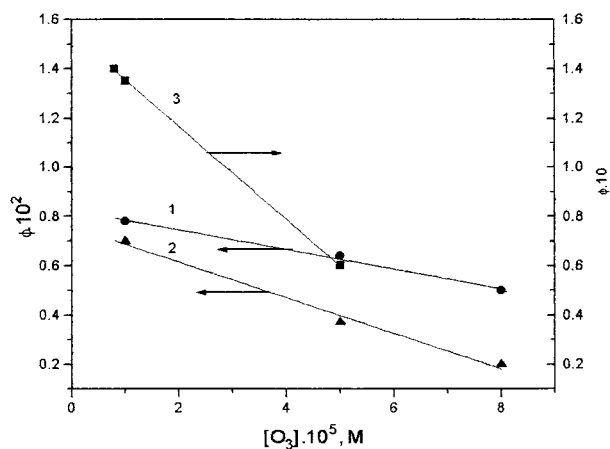
$$M_1 = (1/\gamma)M_0 \quad (4)$$

where  $M_2 = M_0 - M_1$ ;  $1 \leq \gamma \leq 2$  is the coefficient pointing the  $\text{C}=\text{C}$ -bond location, and  $M_0$ ,  $M_1$ , and  $M_2$  are the molecular weights of the initial macromolecule and the two degraded polymer parts, respectively.

At  $\gamma = 2$ , that is, when the broken  $\text{C}=\text{C}$  bond is located in the macromolecule center, the values of  $M_1$  and  $M_2$  will be exactly equal to  $M_0/2$ , at  $\gamma \rightarrow 1$ , that is, at the terminal  $\text{C}=\text{C}$  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 three to four orders less than that of the macromolecule and, in fact, the degradation process will not occur. The viscosimetric determination of the molecular weight which we have applied in our experiments is with the accuracy of  $\pm 5\%$  and does not allow the differentiation of the molecular weights of 22,700, 19,000, and 9000 for the corresponding rubbers. This suggests that the cleavage of  $\text{C}=\text{C}$  bonds located at a distance of 420, 280, and 100 units from the macromolecule end would not affect the measured molecular weight.



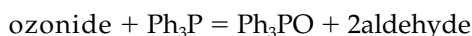
**Figure 2** Dependence of  $\phi$  on  $G$  for SKD (0.6/100) at various ozone concentrations: (1)  $1 \times 10^{-5} M$ ; (2)  $4.5 \times 10^{-5} M$ ; (3)  $8.25 \times 10^{-5} M$ .



**Figure 3** Dependence of  $\phi$  on ozone concentration for elastomer solutions: (1) SKD (0.6/100); (2) SKI-3S (0.6/100); (3) Denka M40 (1/100).

Since the reaction of elastomer 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. On 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 increase of the ozone concentration would increase the reaction volume to a considerably lower extent than that of the ozone concentration. This leads to the occurrence of the following process: Intensive degradation processes take place in the microvolume 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 an increase in the ozone concentration, one may expect a reduction of the MMD and increase of the oligomeric phase content. This will result in an apparent decrease of  $\phi$  at the viscosimetric measurements. The discussion above makes possible the correct interpretation of the data in Figure 3.

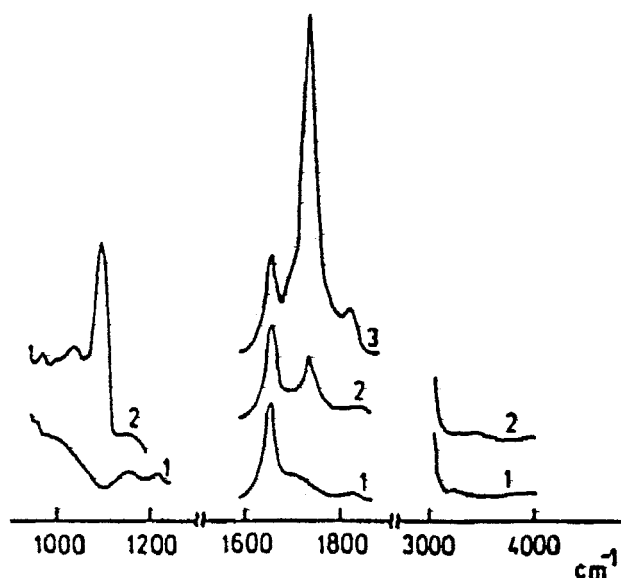
On ozonation of the SKD solution (1/100), at 10% conversion, an intensive band of C—O in the ozonides<sup>9,11</sup> was observed at 1115  $\text{cm}^{-1}$  in the IR spectrum. A less intensive band at 1735  $\text{cm}^{-1}$ , characteristic of C=C vibrations in aldehydes and esters (Figs. 2 and 4), was also registered. Since the ozonides did not react quantitatively with HI, their reaction with triphenylphosphine ( $\text{Ph}_3\text{P}$ ) was used for the determination<sup>12</sup>:



The amount of ozonide as estimated from the band intensity at 1735  $\text{cm}^{-1}$  (Figs. 3 and 4) was  $70 \pm 5\%$  with respect to the amount of the absorbed ozone.

It was found that the amount of C=O groups as estimated from the band intensity at 1735  $\text{cm}^{-1}$  that appears prior the  $\text{Ph}_3\text{P}$  treatment is to 11% of the absorbed ozone (the extinction coefficient is taken from the calibration to  $>\text{C}=\text{O}$  in butyric aldehyde). These functional groups are formed as a result of the proceeding of reactions parallel with those of ozonide formation. Control experiments have demonstrated the relatively high thermal stability of SKD ozonide.<sup>13,14</sup> Usually, it is assumed that the zwitterion isomerization into acid is responsible for the degradation of macromolecules. However, absorption in the 1710–1716  $\text{cm}^{-1}$  range was not detected, although the extinction coefficient for the  $>\text{C}=\text{O}$  bonds in the acids is two to three times higher than that of  $>\text{C}=\text{O}$  in aldehydes and ketones.<sup>11,12</sup> The acid groups may react with the zwitterions, so that their concentration in solution remains below the threshold sensitivity of the spectroscopic method. This assumption is supported by the fact that butyric acid added to the SKD solution is consumed during the reaction (Fig. 5).

The higher band intensity at 1735  $\text{cm}^{-1}$ , obtained on ozonolysis in the presence of acid, as compared with that of the same band in its absence, reveals overlapping of the  $>\text{C}=\text{O}$  absorption in carbonyl and ester groups.<sup>12</sup> The interaction between the zwitterion and the carboxylic group is also confirmed by the appearance of a band at 3480  $\text{cm}^{-1}$  at 50% conversion (Fig. 5). The latter may be attributed to vibrations of the hydroperoxide OH groups. Thus, it can be concluded that the decay of the excited acid molecule resulting from the zwitterion isomerization to free radicals<sup>13</sup> is not the only route for their consumption. Degradation



**Figure 4** Infrared spectra of SKD solutions (1/100): (1) nonozonized; (2) ozonized to 10% conversion; (3) solution after  $\text{Ph}_3\text{P}$  treatment.

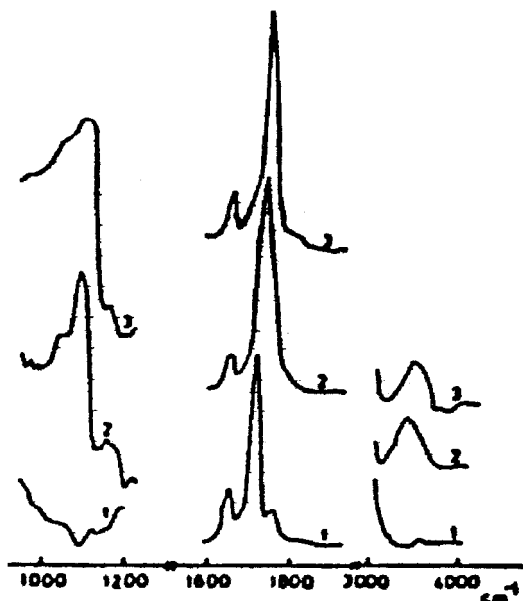


Figure 5 Infrared spectra of SKD solutions (1/100): (1) nonozonized + butyric acid; (2) ozonized to 20% conversion; (3) ozonized to 50% conversion without butyric acid.

may also result from the interactions between zwitterions, leading to di- and polyperoxides which are very unstable and readily decompose into polymer carbonyl compounds with lower molecular weight and an oxygen molecule. It has been found that the most efficient way for the reduction of the molecular weight is provided by the interaction of zwitterions formed in the chain center with low molecular compounds and oligomers.

The thermal decomposition data (DSC spectra) of ozonized rubber (SKD) in an inert atmosphere (Ar) in the temperature range of 323–453 K were processed using the equation suggested by Gorbachev et al.<sup>14–16</sup>:

$$\ln h/h_1 / [\ln(1 - \alpha)/(1 - \alpha_s)] = \{(E_a/RT_s) \times [(T - T_s)/T - 1/\ln(1 - \alpha)/(1 - \alpha_s)]\} + n \quad (5)$$

where  $\alpha$  is the conversion degree;  $H$ , the peak height;  $T$ , the temperature;  $s$ , an index standing for the values of the DSC peak maximum; and  $n$ , the reaction order.

The expression of Julai and Grinhau<sup>16</sup>:

$$\alpha_s = 1 - 1.062n^{1/(1-n)} \quad (6)$$

where  $\alpha_s$  accounts for the transformation degree in the DSC maximum. The results from the study on the thermal degradation of SKD and Diene 35 NFA rubbers are summarized in Table III.

#### CIS-1,4-POLYISOPRENE

The positive inductive effect of the methyl group in polyisoprene enhances the rate of ozone addition to

TABLE III  
DSC Analysis of Products Obtained from Ozonolysis of Polybutadiene Rubbers SKD and Diene 35 NFA

Measurement	Heating rates (°C/min)		
	1	2	5
$\Delta H_1$ (kJ/mol ozonide)	274/216	338/260	355/276
$\Delta H_2$ (kJ/mol $O_3$ )	—/—	370/—	370/—
$T$ (K)	402.3/398.7	409.3/406.2	420/417
$\alpha_s$	0.65/0.70	0.67/0.70	0.68/0.75
$E$ (kJ/mol)	99.9/91.2	105.5/93.7	121/109.6
$n$	0.7/0.73G60	0.73/0.73	0.79/0.73

the double bonds from  $6 \times 10^4$  for SKD to  $4 \times 10^5 M^{-1} s^{-1}$  for SKI-3S. The asymmetry double bond allows the formation of two zwitterions: one as in butadiene (A) and the corresponding ketone, and the other in which one of the hydrogen atoms is substituted by a methyl group (B) and the corresponding aldehyde. Since the stabilization of the zwitterion depends on the electron-donor properties of the substituents, the ratio of zwitterions A/B < 1 and is equal to  $-0.56$ . The interaction between zwitterions and aldehydes leads predominantly to ozonide formation, while that with ketone is more difficult, although there are conflicting literature opinions on the latter.<sup>17–22</sup> The band at  $1725 \text{ cm}^{-1}$  observed in the spectrum of the ozonized SKI-3S solutions (Fig. 6) may be attributed to the absorption of the keto group in the ketone formed together with the zwitterion (A).<sup>23</sup> By means of a calibration using methyl ethyl ketone, it was calculated that the amount of ketone is about 40% of that of the absorbed ozone.

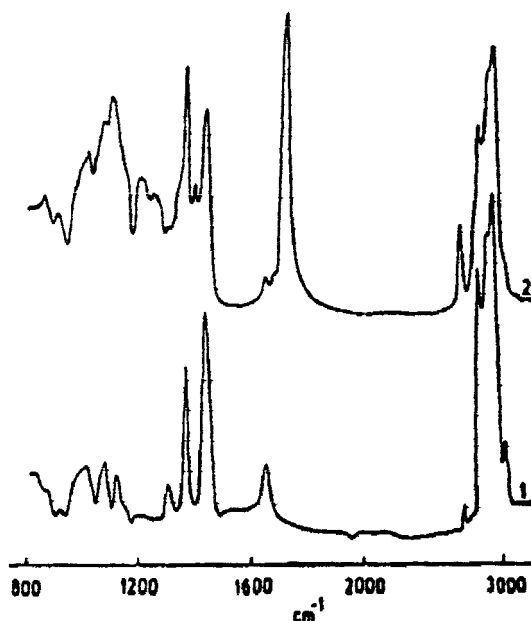


Figure 6 Infrared spectra of SKI-3S solutions: (1) nonozonized; (2) ozonized to 50% conversion.

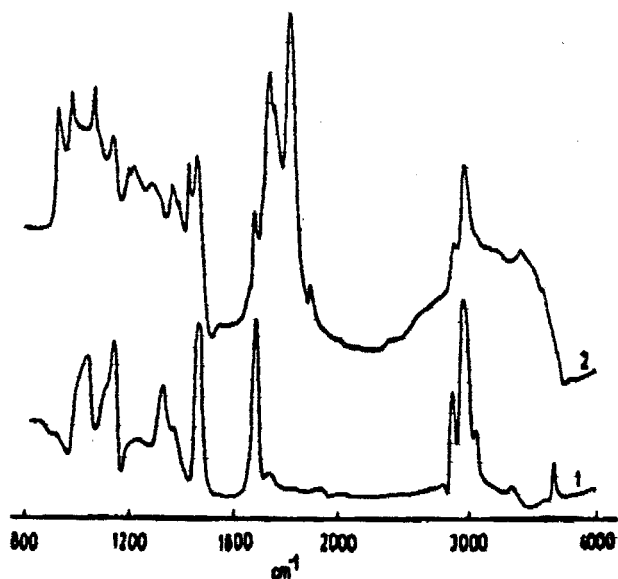


Figure 7 Infrared spectra of Denka M40 solutions: (1) nonozonized; (2) ozonized to 40% conversion.

Consequently, the higher degree of SKI-3S degradation compared with that of polybutadiene is due to the impeded zwitterion A interaction with the corresponding ketone, resulting in its insignificant conversions according to reactions leading to decrease of the molecular weight. The ozonide formation was demonstrated by the occurrence of IR bands at 1110 and 1070  $\text{cm}^{-1}$  (Figs. 2 and 6).

### POLYCHLOROPRENE

The electron-accepting properties of the chlorine atom at the polychloroprene double bond reduces the reactivity of Denka M40 as demonstrated by its relatively low rate constant, that is,  $k = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . In this reaction, the ratio between zwitterions A and B, according to theoretical calculations, is in favor of A, the ratio being  $A/B = 4.55$ . The A formation is accompanied by chloroanhydride group formation and that of B with an aldehyde one. In both cases, the ozonide formation is insignificant and the zwitterions react predominantly in the volume, resulting in enhancement of the degradation process. The intensive band detected at  $1795 \text{ cm}^{-1}$  in the IR spectrum of ozonized

TABLE IV  
DSC Analysis of Denka M40 Ozonolysis

Parameter	Denka M40	SKD	Cumene peroxide
Conversion (%)	28	18	—
Weight loss (%)	7–13	6–11	—
$\Delta H_1$ (kJ/mol $\text{O}_3$ )	239	337	—
$\Delta H_2$ (kJ/mol)	—	—	215
$E_a$ (kJ/mol)	70	128	140
$T_i$ ( $^{\circ}\text{C}$ )	51	86	—
$T_m$ ( $^{\circ}\text{C}$ )	96	147	—
$T_e$ ( $^{\circ}\text{C}$ )	132	175	—

$\Delta H_1$  is the enthalpy related to 1 mol ozone;  $\Delta H_2$ , the enthalpy of cumene peroxide;  $E_a$ , the decomposition activation energy; and  $T_b$ ,  $T_m$ , and  $T_e$ , the temperatures at the beginning, maximum, and end of DSC curves, respectively.

Denka M40 solutions (Fig. 7) is characteristic of the chloroanhydride group.<sup>23</sup> This fact correlated well with the conclusion about the direction of the primary ozonide decomposition. It also reveals insignificant conversion of chloroanhydride to monomer and polymer ozonides. It is difficult to ascribe the absorption maximum at  $1735 \text{ cm}^{-1}$  to a definite functional group because, besides aldehydes and esters, chloroanhydrides also absorb in this region. However, the band at  $955 \text{ cm}^{-1}$  is typical of chloroanhydrides. Two other bands—at  $1044$  and  $905 \text{ cm}^{-1}$ —may be attributed to the C—O vibrations. The valent vibrations characteristic of HO groups are observed in the  $3050$ – $3500 \text{ cm}^{-1}$  range.

The iodometrical analysis of active oxygen in the ozonized Denka M40 solutions shows that the amount of ozonides is about 43%. It is of interest to note that the HI reaction with ozonized polyisoprene solutions occurs quantitatively for 3–4 h, while in SKD, the same reaction proceeds only to 20% after 24 h. The above data, however, provide insufficient information for the preferable route of the ozonide formation (via dimerization polymerization of zwitterions, or secondary processes).

The DSC analysis of the products of Denka M40 ozonolysis together with those of SKD and cumene peroxide as a reference are presented in Table IV. The data of Table IV reveals that the chloroprene rubber ozonolysis that yields polyperoxide is the enthalpy of its decomposition is found to be very close to that of dicumyl peroxide. The higher value of  $E_a$  (ca. twice)

TABLE V  
Characteristics of the Investigated Butadiene–Nitrile Rubbers

Elastomer	Acrylonitrile (%)	1,4-trans (%)	1,4-cis (%)	1,2- (%)	$M_v \times 10^{-3}$	$M_w/M_n$
SKN-18	20	64	21	15	380	3.0
SKN-28	28	65	24	11	300	3.0
SKN-40	39	72	22	6	230	2.7

TABLE VI  
Distribution of the Triad Sequence of 1,4-Butadiene (B)  
and Acrylonitrile (A) Using <sup>1</sup>H-NMR Data

Triads	SKN-18	SKN-26	SKN-40
BBB	73	56	33
BBA	9	14	18
ABA	18	30	49

testifies to the possible formation of polymer peroxides. Moreover, the SKD ozonolysis leads predominantly to the formation of ozonide (89% yield), its enthalpy being significantly higher than that of Denka M40.

### BUTADIENE NITRILE RUBBERS

The most important characteristics of the nitrile rubbers under study are shown in Table V. The results from the NMR study of the nitrile rubbers structure are listed in Table VI.

It was shown that the viscosimetric measurements provide lower values for the ozone degradation level as compared with those obtained from the IR data. This observation may be attributed to the fact that the reaction between ozone and the rubber is localized in a very thin layer around the gas bubbles, while the major part of the macromolecules do not undergo degradation in the solution volume. The intensive progress of the reaction in a very small volume provides conditions for the formation of significant amounts of low molecular products without a significant change of the molecular weight. Nevertheless, the viscosimetric determinations of a series of samples confirm some tendencies of the degradation process. The results from the viscosimetric studies of three nitrile rubbers are shown in Table VII. From Table VII, one can see that  $\phi$  depends on three factors: (1) the ozone concentration, (2) the nature of the solvent, and (3) the rubber structure.

Under the experimental conditions of the bubbling method, the influence of ozone concentration is associated with an insignificant increase of the reaction volume and, thus, to the number of interactions of one macromolecule. The role of the solvent is associated with

- Providing conditions for higher equilibrium ozone concentrations, due to the different values of Henry's coefficients for different solvents ( $\text{CCl}_4 = 2$  and  $\text{CHCl}_3 = 2.8$ );
- Creation of new conformation conditions for the macromolecules and the effect on the electronic properties of the reaction center and the free access of ozone to it and thus on the degradation degree; and
- Participation in the ozonolysis process (which has not been experimentally registered during nitrile rubbers ozonolysis).

It is seen that the increase in the acrylonitrile content in the elastomers studied reduces the probability of the formation of low molecular fragments and, consequently, the degradation degree should increase. Indeed, such a dependence has been experimentally observed (columns 3–5).

It should be noted that during the ozonolysis of SKN-18 (for  $\text{CHCl}_3$  solutions to 25%) gel formation is practically not observed to 30% conversion. Thus, it can be assumed that, under the employed experimental conditions, the contribution of crosslinking reactions (interaction between the zwitterions and aldehydes with high molecular fragments or other structural reactions between macromolecules resulting in an increase of the molecular weight) to the overall balance of the reacted ozone is very small. It was shown that the degradation of macromolecules is a result of the zwitterions' reaction with low molecular compounds in the bulk solution, monomolecular isomerization of the former to acids, and di- and polyperoxides' decomposition with oxygen evolution.<sup>24–26</sup>

Several significant features were found in the <sup>1</sup>H-NMR spectra of the ozonized  $\text{CCl}_4$  solutions of SKN-18: a signal due to the aldehyde proton at 9.75 ppm and a few signals in the 4.97–5.20 ppm region<sup>26,27</sup> ascribed to methine protons and a multiplet at 2.75 ppm with an integral intensity of about 40% of that of the aldehyde peak. The ratio of the aldehyde to the ozonide groups calculated from the integral intensities is about 40:60.

As SKN-26 and SKN-40 are not dissolved in  $\text{CCl}_4$ , the ozonolysis and the <sup>1</sup>H-NMR spectra were recorded in  $\text{CHCl}_3$  and  $\text{CDCl}_3$  solutions. The insoluble

TABLE VII  
No. Chain Scissions Per Molecule of Reacted Ozone ( $\phi$ ) for Ozone Degradation of Nitrile Rubbers at Various Ozone Concentrations in  $\text{CCl}_4/\text{CHCl}_3$  Solvents

Elastomer	Concentration (g/100 mL)	$\phi \times 10^2$ (0.0025 mM $[\text{O}_3]_0$ )	$\phi \times 10^2$ (0.005 mM $[\text{O}_3]_0$ )	$\phi \times 10^2$ (0.01 mM $[\text{O}_3]_0$ )
SKN-18	0.45	2.5/4.8	0.9/2.1	0.6/1.6
SKN-28	0.49	—/7.0	—/5.4	—/1.7
SKN-40	0.40	—/7.5	/6.2	—/2.5

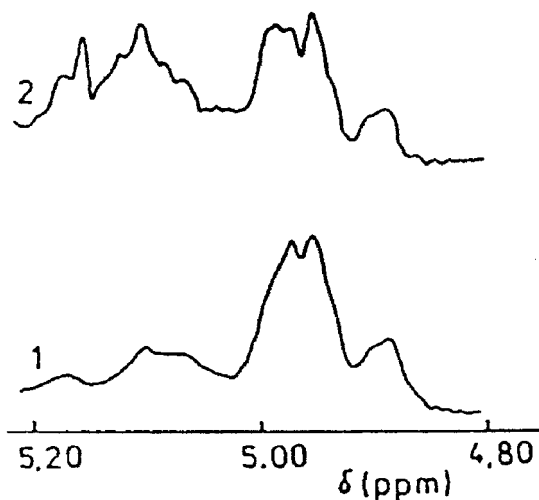


Figure 8  $^1\text{H-NMR}$  spectra of SKN solutions (0.75/100): (1) nonozonized; (2) ozonized to 20% conversion.

gel after ozonation was separated by filtration and  $\text{CDCl}_3$  was added. The following peaks were detected in the  $^1\text{H-NMR}$  spectra: 9.76 ppm (s), 4.97–5.20 ppm (n.d.), 2.73 ppm (m), and a series of very weak peaks in the 3.12–4.20 ppm range.

Simultaneously, the IR spectra (Fig. 9) of nitrile rubbers before and after ozonation were registered. The IR spectra of SKN-26 and SKN-40 are very similar to that of SKN-18 shown in Figure 9. The kinetics of ozonide and aldehyde group formation for the three rubbers was studied by monitoring the changes in the optical density at 1110 and  $1731\text{ cm}^{-1}$ , respectively. The effect of the reacted ozone and the type of solvent, that is,  $\text{CCl}_4$  or  $\text{CHCl}_3$ , was investigated. It may be seen that, in all cases, the kinetic curves are linear to 20% conversion. The slopes of the dependence for the solution of DSN-18 depend on the solvent nature and it amounts to  $2.4 \times 10^{-2}\text{ M}$  aldehyde/ $2 \times 10^{-4}\text{ mol}$  absorbed ozone in  $\text{CHCl}_3$  and is 1.2 times higher than

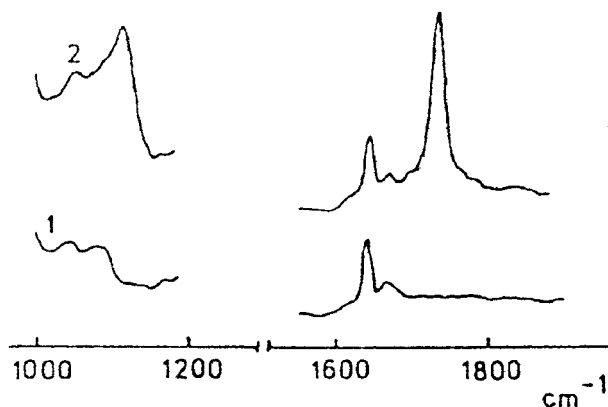


Figure 9 Infrared spectra of SKN-18 solutions (0.75/100): (1) nonozonized solution; (2) ozonized to 20% conversion.

TABLE VIII  
Activation Energy for the Formation of Aldehydes and Ozonides in SKN-18 Ozonolysis

Solvent	$E_a$ (kJ/mol, ozonides)	$E_a$ (kJ/mol, aldehydes)
$\text{CCl}_4$	-0.8	4
$\text{CHCl}_3$	-0.4	0.8

that in  $\text{CCl}_4$ . The registered optical density of the ozonides do not depend on the solvent, but the slope of the curve is found to be twice lower than that of the aldehydes in  $\text{CHCl}_3$ . The slopes of the kinetic curve for aldehyde formation for the solutions of SKN-26 and SKN-40 ( $\text{CHCl}_3$ ) are identical. However, the accumulation of aldehydes takes place with a 2.25 times higher rate. The corresponding slopes are about 8% greater than those of SKN-18. Using literature values for the extinction coefficients for ozonides (115, ref. 26) and aldehydes [ $\epsilon$  (230), refs. 26–29], it was possible to evaluate the aldehyde/ozonide ratio for the three rubbers studied (SKN-18, SKN-26, and SKN-40) in  $\text{CHCl}_3$ , which is 1.03, 1.12, and 1.12 at ambient temperature and 20% conversion. For SKN-18 in  $\text{CCl}_4$ , this ratio amounts to 0.85. The difference in the values of this ratio obtained in the two solvents is probably due to the stabilization of the zwitterion in the more polar solvent, that is, chloroform, and the differences between the various rubbers is associated with the various amounts and sizes of the polymer fragments containing 1,2-double bonds in them. The role of nitrile groups is demonstrated by the electronic effects of the strong electroaccepting CN group and its inductive effect transferred via two  $\sigma$  bonds.

The quantitative interpretation of the NMR spectra of SKN-18 ozonized in  $\text{CHCl}_3$  gives the value of 0.82 for the aldehyde/ozonide ratio, which is within the accuracy limits of the extinction coefficient determination and correlates with the IR data. It was found that from 1 mol of absorbed ozone, 0.52 mol of aldehyde, and 0.72 mol of ozonide are formed in SKN-18 ozonolysis in  $\text{CCl}_4$ . Thus, the ratio amounts to 0.72.

The results from the two spectral studies support our suggestions for the important role of zwitterion reactions in the ozone degradation of nitrile rubbers. Their reactions out of the cage lead to the formation of di- and polyperoxides which are converted to aldehydes with the evolution of oxygen.

The effect of the temperature on aldehyde/ozonide ratio is illustrated by the kinetic parameters given in Table VIII. In the ozonolysis of nitrile rubbers, the amount of aldehyde groups formed varies within the range of 50–70%, while on ozonolysis of 1,4-*cis*-polyisoprene, it is about 11%. The significant difference could be explained by the presence of nitrile groups in the polymer molecules and the difference in the con-

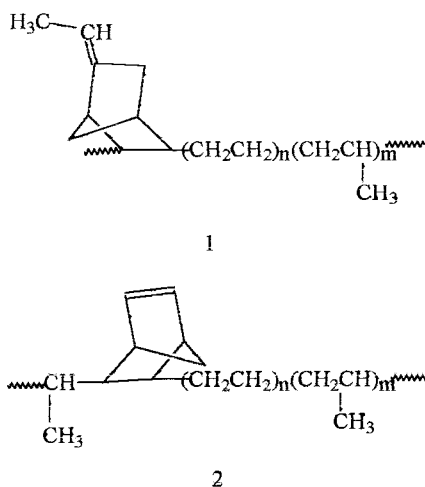


figuration of the C=C bonds: 64–72% *trans* for the nitrile rubbers and 94–97% *cis* for the isoprene rubber. The literature data point out that the ozonide yield from *trans*-olefins is considerably lower than that from *cis*-olefins.<sup>26,27</sup>

### ETHYLENE PROPYLENE RUBBERS

Ethylene propylene rubbers (EPDM) are copolymers of 65–80% ethylene with 35–20% propylene and a third copolymer, diene 1–2% (e.g., cyclopentadiene, 1,4-hexadiene, 2-ethylene norbornene-5). They are characterized by high resistance toward the action of temperature, oxygen, and ozone, mainly because of the extremely low content of C=C bonds. The vulcanizing properties are due to the presence of the diene copolymer. In most cases, the EPDM rubbers are employed alone and only in particular cases in combination with diene elastomers due to their low compatibility with them, for the preparation of efficient antiozonant and antioxidant materials. Their application as antiozonant additives will be discussed further in detail.

The investigations were carried out on Keltan 778 samples (ethylene:propylene:ethylene norbornene = 75.5:23:1.5 with  $M_v = 193,000$  and  $M_w/M_n = 1.84$ ) in  $\text{CCl}_4$  (0.6/100):



The diene copolymer undergoes polymerization both via the vinyl and norbornene double bond (1 and 2) in a 1:4.66 ratio. These structures were identified using <sup>1</sup>H-NMR 250 MHz. The spectra analysis suggests the existence of two preferable conformations for the methyl group, during the polymerization via the norbornene C=C bond. The first one is when the methyl group is oriented toward the polymer chain and the second one when it is oriented in the opposite direction.

Upon ozonolysis of EPDM, the reaction centers are the C=C bonds of the diene copolymer, although

their concentration is almost 70 times lower as compared with that of the C—H bonds, which is due to the substantially higher rate constants (to four to six orders).<sup>30</sup> Because of the relatively high viscosity of the solutions, the rate constants of ozonolysis could not be determined accurately. The value of the activation energy estimated from the dependence of the viscosity change of the ozonized EPDM rubber solutions on the temperature is found to be  $E_a = 33$  kJ/mol. Ozone attacks these double bonds, resulting in the formation of two zwitterions in the volume. The interaction between the latter leads, rather, to structurization of the macromolecules and growth of the polymer molecular mass than to its reduction. At low temperatures, this process is more efficient and thus the activation energy has a negative value. The presence of peroxide bridges is easily established. The treatment of the ozonized solution with  $\text{PPh}_3$  gives  $\text{PPh}_3\text{O}$  and the molecular weight is restored.

The thermal decomposition of ozonized Keltan 778 solutions in an inert atmosphere makes possible the estimation of the Arrhenius parameters for the monomolecular decomposition of the crosslinked molecules. The activation energy was estimated as 19 kcal/mol, which is in a very good agreement with other data on the decomposition of compounds containing peroxide bridges.<sup>31,32</sup>

To determine the type of the bridges, the <sup>1</sup>H-NMR spectra of the initial rubber have been recorded. It reveals four doublets assigned to the four methine protons: (1) *cis*-vinylene, 5.08 ppm; (2) *trans*-vinylene, 5.30 ppm; (3) methine proton in norbornene, located in the direction of the polymer matrix, 5.58 ppm; and (4) methine proton orientated in the opposite direction to the polymer chain, 5.70 ppm. The quantitative analysis showed that *trans*-vinyl radicals (2) constitute the major portion of the free radicals, while the norbornene double bond is found to be the most reactive in the polymerization process, due mainly to the highly strained hydrocarbon structure. The latter could not form ozonide at the double-bond rupture but easily leads to polyperoxide formation.

### CONCLUSIONS

First, in the polydiene molecule, ozone attacks the double bonds in it. In general, this reaction proceeds following the Prof. Creege mechanism. Mainly, values of the reaction constants of the ozone reaction with double bonds depend on (i) substituents at the double bonds—their kind, number and volume, and (ii) configuration of the double bonds—*cis* or *trans*. Because this reaction is electrophilic, all substituent donors of electrons will increase the values of the reaction constants (e.g., butadiene and isoprene), whereas these which attract electrons will decrease them (e.g., isoprene and polychloroprene). The observed anomaly

when a *trans*-isomer reacts faster than a *cis* one (e.g., natural rubber and gutta-percha) is explained by the increase of the energy of activation at the *cis*-isomer, because, at the rehybridization of two carbon atoms from  $sp^2$  to  $sp^3$ , substituents start to move opposite to each other and repulsion of their van der Waals radii occurs.

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