POLYMER PRODUCTS and CHEMICAL PROCESSES

Techniques, Analysis and Applications

Editors
Richard A. Pethrick, PhD, DSc
Eli M. Pearce, PhD
Gennady E. Zaikov, DSc

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Edited by

**Richard A. Pethrick, PhD, DSc, Eli M. Pearce, PhD,
and Gennady E. Zaikov, DSc**

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Eli M. Pearce, PhD

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LIST OF ABBREVIATIONS

AC	activated complex
AdometDC	S. adenosylmenthionine decarboxylase
AI	aromatization index
ALA	α-linolenic acid
BBIC	bioluminescent bioreporter integrated circuit
BSR	butadiene-stirene rubber
CANARY	Cellular Analysis and Notification of Antigen Risks and Yields
CdTe	cadmium telluride
CIGS	Copper Indium/Gallium Di Selenide
CNT	carbon nanotubes
CVD	chemical deposition method
DCI	disubstituted CI
DCP	dicumeneperoxide
DHA	docosahexaenoic acid
DMF	dimethylformamide
DSC	differential scanning calorimetery
DSSC	dye-sensitized solar cells
EDG	electron-donating groups
EFA	essential fatty acids
EPA	eicosapentaenoic acid
EWG	electron-withdrawing groups
FF	fill factor
FTIR	Fourier transform infrared spectroscopy
GFP	green fluorescent protein
GPi	graphitized polyimide
HAART	highly active retroviral therapy
IRMOFs	isoreticular metal-organic frameworks
ITO	indium tin oxide
LA	linoleic acid

MCI	monosubstituted CI
MMD	mass-molecular distribution
MOFs	metal-organic frameworks
MPP	maximum power point
MWCNTs	multi walled carbon nanotubes
ONRL	Oak Ridge National Laboratory
PAHs	polycylic aromatic hydrocarbons
PAN	polyacrylonitrile
PAni	polyaniline
PET	poly thyleneterphthalate
PKS	polyketide synthase
PO	primary ozonide
PP	poly propylene
PSM	post-synthetic modification
PV	photovoltaic
PZT	Plumbum Zirconate Titanate
RF	remote frequency
RT	reverse transcriptase
SBUs	secondary building units
SDA	stearidonic acid
SEM	scanning electron microscopy
TC	technical carbon
TSC	textile solar cell
UV	ultraviolet
VLCPUFA	very long chain polyunsaturated fatty acids
XRD	X-ray diffraction

LIST OF SYMBOLS

a	lower linear scale of fractal behavior
c	concentration of the monomeric units
d	Euclidean space
D_f	fractal dimension
E_a	activation energy
E_{max}	maximum field amplitude
E_n and E_m	elasticity moduli of nanocomposite and matrix polymer
F	free energy
I_{sc}	short-circuit current
k	Boltzmann constant
l_0	skeletal bond length
l_n	linear length scale
N	number of particles with size ρ
P_{in}	incident light power density
P_{max}	maximum electrical power
R_g	gyration radius
R_p	nanofiller particle
S_i	quadrate area
S_u	nanoshungite particles specific surface
t	ozonation time (s)
T_g	glass transition temperature
V_{oc}	open-circuit voltage
Y	total ozonide yield

Greek Symbols

α	Henry's coefficient
γ	globe swelling
γ_L	Grüneizen parameter
η_{rel}	relative viscosity

φ	reacted ozone
φ_{if}	interfacial regions
ν	Poisson ratio
ρ_n	nanofiller particles aggregate density

PREFACE

Polymer Products and Chemical Processes presents leading-edge research in the rapidly changing and evolving field of polymer science as well as on chemical processing. The topics in the book reflect the diversity of research advances in the production and application of modern polymeric materials and related areas, focusing on the preparation, characterization, and applications of polymers. The book also covers various manufacturing techniques. The book will help to fill the gap between theory and practice in industry.

Polymer Products and Chemical Processes is a collection of 11 chapters that highlights many important areas of current interest in polymer products and chemical processes. It is also gives an up-to-date and thorough exposition of the present state of the art of polymer analysis. There are many chapters that will familiarizes the reader with new aspects of the techniques used in the examination of polymers, including chemical, physico-chemical and purely physical methods of examination.

In chapter 1, some new aspects of ozone and its reactions on diene rubbers are presented. The importance of nanocomposites in today's modern science is highlighted in chapter 2, in which different types of polymer nanocomposites structures are studied in detail. The simulation of nanoelements' formation and interaction is explained in chapter 3. Chapter 4 is divided into three sections to introduce new points of views on advanced polymers. The stabilization process of PAN nanofibers is studied in detail in chapter 5. In chapter 6, carbon nanotubes' structure in polymer nanocomposites is updated for our readers. Exploring the potential of oilseeds as a sustainable source of oil and protein for aquaculture feed is presented in chapter 7. Microbial biosensors are introduced in chapter 8. New development of solar cloth by electrospinning technique is well defined in chapter 9. Applications of metal-organic frameworks in textiles are described in chapter 10 and chapter 11 and are divided into 3 sections in present important topics related to the book's objectives.

This book describes the types of techniques now available to the polymer chemist and technician, and discusses their capabilities, limitations, and applications and provides a balance between materials science and mechanics aspects, basic and applied research, and high technology and high volume (low cost) composite development

**— Richard A. Pethrick, PhD, DSc, Eli M. Pearce, PhD,
and Gennady E. Zaikov, DSc**

SOME NEW ASPECTS OF OZONE AND ITS REACTIONS WITH DIENE RUBBERS

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E. M. PEARCE, and G. KIRSHENBAUM

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1.1   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].

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 favorable 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.

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 nonozonide 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.

1.2   EXPERIMENTAL METHODS

1.2.1   MATERIALS

Commercial samples of 1,4-*cis*-polybutadiene (SKD; E-BR); polybutadiene (Diene 35 NFA; BR); 1,4-*cis*-polyisoprene (Carom IR 2200; E-IR) and polychloroprene (Denka M 40; PCh) 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 precipitation from CCl_4 solutions in excess of methanol. The above mentioned elastomer structures were confirmed by means of ^{1}H-NMR spectroscopy. *Ozone* was prepared by passing oxygen flow through a 4–9 kV electric discharge.

TABLE 1   Some characteristics of polydiene samples.

Elastomer	Monomeric unit	Unsaturation degree,%	1,4-*cis*, %	1,4-*trans*-, %	1,2-, %	3,4-, %	$M_v.10^{-3}$	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

1.2.2   *OZONATION OF THE ELASTOMER SOLUTIONS*

The ozonolysis of elastomers was performed by passing an ozone-oxygen gaseous mixture at a flow rate of $v=1.6\times10^{-3}\pm0.1$ l.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, mole) was calculated by the Eq. (1):

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

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].

Note: m$_v$ is the average molecular weight, determined viscosimetrically from equation $[\eta]=k.M_v^{\alpha`}$, where $[\eta]=(\eta_1/C)(1+0.333\eta_1)$, $\eta_1=\eta_{rel-}1$, $\eta_{rel-}$ is the intrinsic viscosity; C-solution concentration; $k=1.4.10^{-4}$ – Staudinger's constant and $\alpha` = 0.5–1.5$ – 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].

1.3   RESULTS AND DISCUSSION

Florry [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 more slowly, compared with their low molecular analogs (catalytic hydrogenation). The folded or unfolded forms of the macromolecules provide 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 any 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 the reactivity. The theory predicts that the properties of the system: polymer-solvent can be described by the parameter of so called globe swelling (γ), which defines the free energy (F) of the system and thus the rate constant of the reaction. For a reversible reaction, i.e., polymerization – depolymerization, the dependence of the rate constant of the chain length growing on the molecular weight is expressed by the following equation:

$$\ln k_{pj}/k_p = - \text{const.}(5\gamma - 3/\gamma).(d\gamma/dM).M_0 \qquad (2),$$

Where m_o 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 effects. 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].

Table 2 summarises the rate constants of the ozone reactions with some conventional elastomers and polymers and their low molecular analogs, synthesized by us. It is seen that the reactivities of elastomers and polymers and their corresponding low molecular analogs, as it is 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: for

example 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 reactions with polymers and low molecular analogs in CCl$_4$, 20°C.

Compound	M.w.	$k.10^{-4}$, M^{-1}.s^{-1}
Polychloroprene	8.10^5	0.42 ± 0.1
Vinylchloride	62.45	0.18
2-bromopropene	121	0.28 ± 0.05
Polybutadiene	$3.3.10^5$	6.0 ± 1
Cyclododecatriene-1,5,9	162	35 ± 10
Poly(butadiene-costirene)	8.10^4	6 ± 1
Gutta-percha	3.10^4	27 ± 5
Natural rubber	1.10^6	44 ± 10
2-me-pentene-2	85	35 ± 10
Squalene	410	74 ± 15
Polystirene	5.10^5	$0.3.10^{-4}$
Cumene	120	$0.6.10^{-4}$
Polyisobutylene	$1.7.10^5$	$0.02.10^{-4}$
Cyclohexane	84	$0.01.10^{-4}$

It has been found out that the effects, related either to the change in the macromolecule length or to the folding degree, do not affect the ozonolysis in solution. Probably this is due to the fact that the reaction is carried out in elastomeric solutions, in which the macromolecules are able to do free intramolecular movements and they do not react with adjacent macromolecules. Moreover, the rate of macromolecules reorganization is probably higher than the rate of their reaction with ozone as the experiment does

not provide any evidence for the effects of the change in the parameters pointed earlier [29].

However, it should be noted that k values of the elastomers are about 2–6 times lower that those of the low molecular analogs. The accuracy of activation energy (E_a) determination does not allow to estimate the contribution of the two parameters: preexponential factor (A) or E_a for the decrease in k. If we assume that the mechanism of ozone reaction with monomers and elasomers is similar, i.e., the reactions are isokinetic, then $A_{mon} = A_{pol}$. At k_{mon}/k_{pol} = 2÷6 the difference in E_a at 20°C will be 0.5–1.0 kcal/mole. At the low experimental values of E_a, these differences will become commensurable and thus the determination of E_a is not sufficiently accurate. In this case two assumptions could be made which can give a reasonable explanation for the lower values of k_{pol}: (1) the 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 movements of the polymer susbstituents during the formation of activated complex (AC) 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.

Table 2 shows some examples of ozonolysis of saturated polymers – polystirene 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 of magnitude lower.

1.3.1   POLYBUTADIENES

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

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

where $[O_3]$ is the ozone concentration at a distance δ; α – Henry's coefficient; $[O_3]_0$ – equilibrium ozone concentration in the gas phase at the

reactor inlet; δ – penetration depth of ozone from the interphase surface [22]; k – rate constant of the ozone reaction with double bonds; c – concentration of the monomeric units; D – diffusion coefficient of ozone in the liquid phase.

It was found out 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 should be described by first or pseudo first order kinetics.
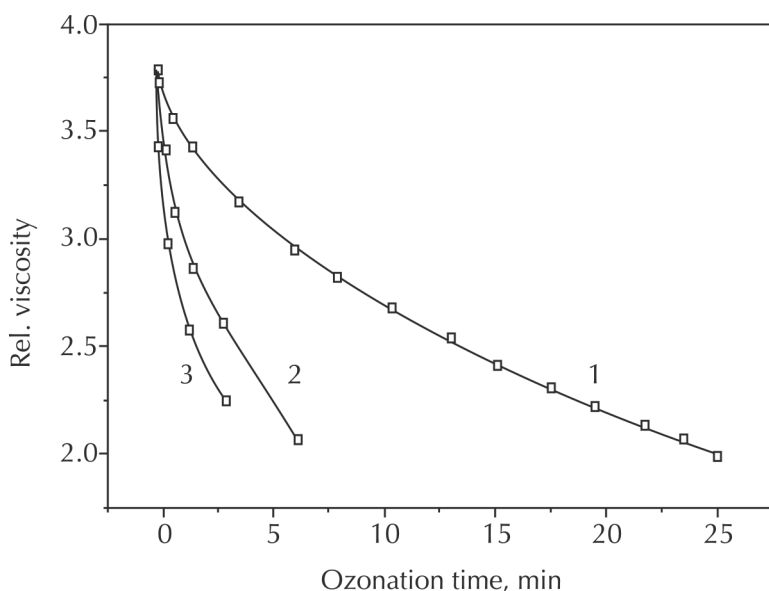

FIGURE 1   Dependence of the relative viscosity (η_{rel}) of SKD solutions (0.6 g in 100 ml CCl$_4$) on reaction time at ozone concentrations of: 1–1.10^{-5} M; 2–4.5.10^{-5} M; 3–8.25.10^{-5} M.

The value of ϕ, corresponding to 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:

$$\phi = 0.5\,[(M_{vt})^{-1} - (M_{v0})^{-1}].P/G, \tag{4}$$

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

The dependence of ϕ on G is a straight line for a given reactor and it depends on the hydrodynamic conditions in the reactor. It is seen from Fig. 2 that the ϕ values are increasing linearly with the reaction time and decreasing 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.

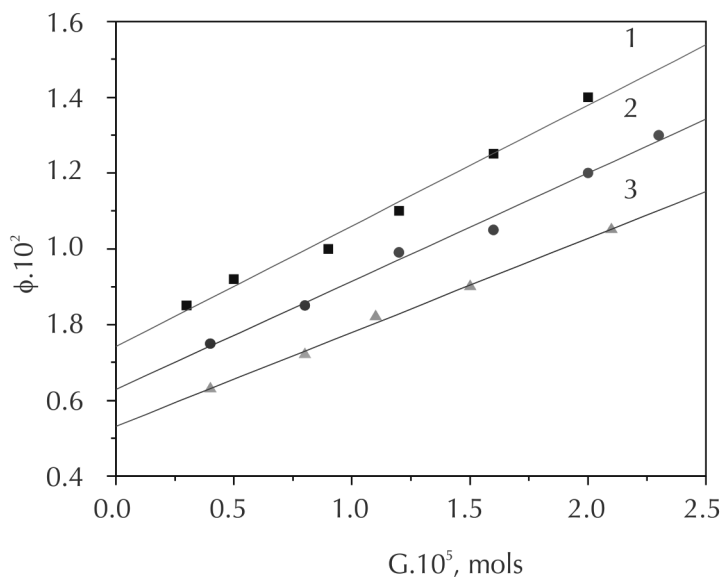**FIGURE 2**   Dependence of ϕ on G for SKD (0.6/100) at various ozone concentrations: 1–1.10^{-5} M; 2–$4.5.10^{-5}$ M; 3–$8.25.10^{-5}$ M.

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 Eq. (3) we have obtained δ within the range of 1.10^{-3}–2.10^{-4} cm, which indicates that the reaction is taking place in the volume around the bubbles, and hence in the diffusion region.

The ozonolysis of polydienes in solutions is described by the Criegee's mechanism. The C=C bonds in the macromolecules are isolated as

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, also affect the polymer reactivity; similarly they do this in case of 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 ozonides (PO) (Scheme 1, reaction 1) are formed, the lower mobility of the polymer substituents requires higher transition energy, the rate being respectively lower, compared to that with low molecular olefins and the existing strain accelerates the PO decomposition to 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 pass into the volume, which in its turn accelerates the degradation process. The latter is associated either with its monomolecular decomposition or with 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.

$$M_1 = (1/g).M_0, \tag{5}$$

where $m_2 = M_0 - M_1$; $1 \leq g \leq 2$ – coefficient pointing the C=C-bond location; M_0, M_1 and M_2 – the molecular weights of the initial macromolecule and of the two degradated polymer parts, respectively.

At g=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 g®1, i.e., at terminal C=C bond in the polymer chain, the value of M_1 will be approximated to M_0 and thus the value of M_2 will be practically insignificant. For example, M_2 may be 50–1000, which is 3–4 orders of magnitude 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, has accuracy of ±5% and does not allow the differentiation of molecular weights of 22,700, 19,000 and 9,000 for the corresponding types of rubbers. This suggests that the cleavage of C=C bonds, located at distances of 420, 280 and 100 units from the macromolecule end, would not affect the measured molecular weight.

    Since the reaction of elastomers ozonolysis proceeds either in the diffusion or in 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 phase 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 smaller extent than 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 not be changed at all. Consequently with increase in ozone concentration, one may expect a reduction of coefficient MMD and increase in the oligomeric phase content. This will result in apparent decrease of f in case of the viscosimetric measurements. The discussion above enables the correct interpretation of the data in Fig. 3.
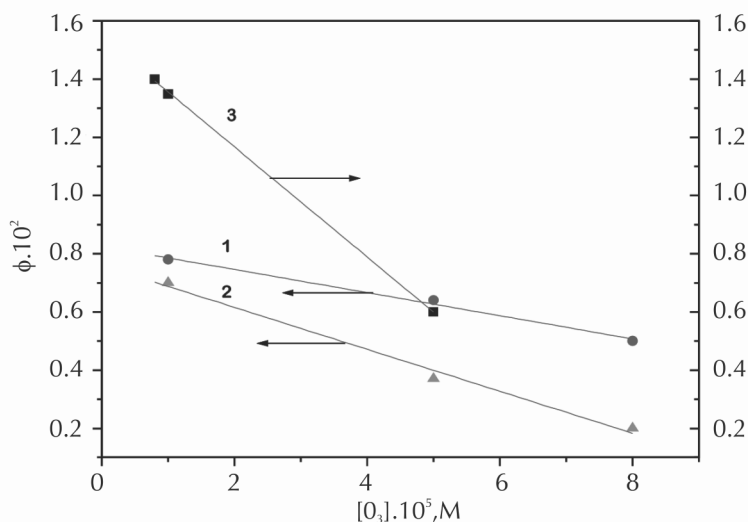

FIGURE 3   Dependence of f on ozone concentration for elastomer solutions: 1 – SKD (0.6/100); 2 – Carom IR 2200 (0.6/100); 3 – Denka M40 (1/100).

In the spectra of the ozonized polybutadienes the appearance of bands at 1111×1735 cm⁻¹, that are characteristic for ozonide and aldehyde groups, respectively, 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 that of the aldehyde 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 ¹H-NMR spectroscopy provides much more opportunities for identification and quantitative determination of functional groups, formed during ozonolysis of polybutadienes [32]. Figure 4 shows spectra
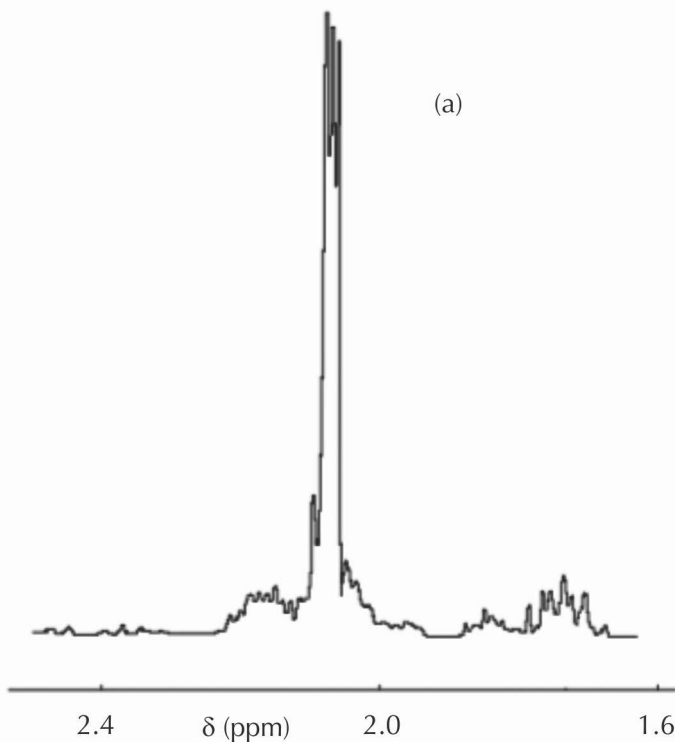

FIGURE 4 (a–c)   1H-250 MHz NMR spectra of E-BR solutions (0.89 g / 100 ml CCl4) ozonized to 18% conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 20°C).

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].

TABLE 3   Assignment of the signals in the ^{1}H-NMR spectra of partially ozonized E-BR and BR rubbers.

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

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 powerful 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: