Synthesis of Functionalized Liquid Rubbers from Polyisoprene

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ABSTRACT: Noncatalytic transformation of *cis*-1,4-polyisoprene rubber (M_n = 320,000) into functionalized liquid rubbers containing various amounts of carbonyl groups was studied. The process is performed via selective carboxidation of the polymer C=C bonds by nitrous oxide (N_2O) in the temperature range of 180–230°C and under 3–6 MPa pressure. The carboxidation proceeds by the nonradical type mechanism involving the 1,3-dipolar cycloaddition of N_2O to the C=C bond. The main route of the reaction (ca. 65%) proceeds without cleavage of the internal C=C bonds and leads to the formation of ketone groups in the polymer backbone. The second route (ca. 35%) includes the cleavage of C=C bonds, yielding the molecules of a smaller size. This route results in a manifold decrease of the molecular weight, which, depending on the carboxidation degree, may be more than two orders of magnitude less than that of the parent rubber. A series of functionalized liquid rubbers having M_n value from 1000 to 19,000, and the oxygen content from 0.3 to 3.9 wt % was obtained in the form of the liquid unsaturated polyketones. Similar polyketones can also be prepared by carboxidation of the natural rubber. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1241–1249, 2009

Key words: functionalization of polymers; polyisoprene; natural rubber; oligomers; nitrous oxide

INTRODUCTION

The polymers containing functional groups are used for the production of materials having such important characteristics as high adhesion, chemical and thermal stability, etc.[1–4] Such polymers are commonly synthesized by the copolymerization of dienes with the monomers containing functional groups or by the chemical modification of suitable initial polymers.[2–6] The latter approach is most widely used with polydienes containing C=C bonds.

Liquid rubbers having the terminal or randomly distributed functional groups constitute an important type of the functionalized polymers.[7–9] Because of their technological advantages, they are widely employed as adhesives, coatings, additives to composite materials, etc. The development of new types of functionalized polymers and improved methods for preparing such materials are of great importance.

In the last two decades, nitrous oxide (N_2O) has attracted much attention as a selective oxygen donor for the oxidation of hydrocarbons.[10–12] Beside catalytic reactions, noncatalytic N_2O oxidation of alkenes into carbonyl compounds (ketones and aldehydes) is of great interest.[13–15] The oxidation proceeds with high selectivity, which in many cases exceeds 90%. A remarkable feature of N_2O is its ability to react solely with the alkene C=C bonds, being inert toward all other bonds.[15] Since the carbonyl groups are formed by an oxidation process, this reaction type was called the "carboxidation."[12,16,17] The carboxidation proceeds by a nonradical mechanism via the 1,3-dipolar cycloaddition of N_2O to the alkene double bond with intermediate formation of 1,2,3-oxadiazoline cycle (reaction 1)[13,14,18]:
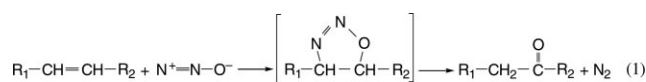
where R_1 and R_2 are the alkyl radicals or hydrogen atoms. This mechanism was convincingly supported by the quantum-chemical modeling of the N_2O interaction with some alkenes.[19–21] The carboxidation can be applied to alkenes of different types (aliphatic, cyclic, heterocyclic, etc.), opening a new way for the preparation of carbonyl compounds.[15,21,22]

Beside individual alkenes, many polymers also have the double carbon–carbon bonds. This makes it possible to apply the carboxidation for functionalizing such unsaturated polymers by converting some

C=C bonds into carbonyl groups. Earlier, this approach has been demonstrated with a low-molecular polyethylene containing terminal C=C bonds,[23] and cis-1,4-polybutadiene (poly-BD) rubber having a high concentration of internal double bonds.[17] In the latter case, especially interesting results were obtained. It was shown that carboxidation of poly-BD may provide a manifold decrease of the initial molecular weight. This leads to a new type of functionalized liquid rubbers, which were called "unsaturated polyketones" as far as they contain both C=C bonds and carbonyl groups.

This polymer type is different from the well-known saturated polyketones. The latter materials can be prepared by several methods including the copolymerization of carbon monoxide with alkenes,[24–27] the polymerization or copolymerization of unsaturated ketones, or the oxidation of poly-BD by t-BuOOH in the presence of Pt(II) complexes.[28] The both types of polyketones exhibit a high adhesion and are a promising type of functionalized polymers. They can serve as a starting material for producing other types of functionalized polymers, since the carbonyl groups are readily subjected to chemical modification.[24,26,29]

This work is devoted to the carboxidation of polyisoprene (poly-IP) rubber and its structural analog, the natural rubber. In distinction to poly-BD, the monomeric unit of poly-IP has a methyl substituent at the double bond. In the case of individual alkenes, the presence of such a substituent, on the one hand, changes the reactivity of the double bond, and on the other hand, makes it more inclined to cleavage upon the interaction with N_2O. One of the goals of this work is to elucidate how much the structure of monomeric unit affects the carboxidation of the rubber as well as the properties of polyketones.

EXPERIMENTAL

Carboxidation of rubber

Most experiments were carried out using a synthetic stereoregular cis-1,4-poly-IP rubber of a trademark SKI-3 ($M_n^0 = 320,000$, $M_w/M_n = 2.8$), produced by Nizhnekamsk Petrochemical Plant (Nizhnekamsk, Russian Federation). According to the ^{1}H- and ^{13}C-NMR analysis, the rubber contained 98.5% cis-1,4-units, 1.1% trans-1,4-units, and 0.4% 3,4-units. Additionally, carboxidation of natural rubber, NR, (cis-1,4-poly-IP, $M_n^0 = 170,000$, $M_w/M_n = 2.3$) was studied.

The rubbers were carboxidized with nitrous oxide in a high-pressure Parr reactor of 100 cm^3 capacity equipped with a manometer and stirrer. The setup used in these experiments was described in detail earlier.[17] After loading 5 g rubber and 60 cm^3 benzene, air was evacuated from the reactor for 1 min

with a vacuum pump. Medical-grade N_2O (Cherepovets Azot, Cherepovets, Russian Federation) was fed into the reactor on stirring (250 rpm). In all the experiments, the initial amount of N_2O was 0.186 mol, which exceeds 2.5 times the amount of double C=C bonds in the loaded rubber sample (0.074 mol). The reactor was hermetically closed, heated at a 6°C/min ramp to the reaction temperature (180–230°C) and kept for 6–12 h. Depending on the temperature, the reaction pressure varied from 3 to 6 MPa.

After termination of the reaction, the reactor was cooled to room temperature, and the gas phase composition (N_2O, N_2, O_2, CO, CO_2, low hydrocarbons) was analyzed using the GC method.[17] In all cases, molecular nitrogen was a sole reaction product detected in the gas phase, and CO_x concentration did not exceed 0.01 mol %.

After the analysis, the pressure was slowly released. The carboxidized polymer sample was recovered from the solution by evaporating the benzene solvent under vacuum at 20–50°C.

The conversion of N_2O (X_{N_2O}), the conversion of C=C bonds ($X_{C=C}$), and the concentration of oxygen introduced into the polymer ($C_{(O)}$) were calculated from the GC data as follows:

$$X_{N_2O} = \frac{N_{N_2}}{N_{N_2O}^0} \cdot 100 (\%) \quad (2)$$

$$X_{C=C} = \frac{N_{N_2}}{N_{C=C}^0} \cdot 100 (\%) \quad (3)$$

$$C_{(O)} = \frac{16 N_{N_2}}{g^0 + 16 N_{N_2}} \cdot 100 (wt\%) \quad (4)$$

where N_{N_2} is the amount of nitrogen (mol) formed by reaction (1), $N_{N_2O}^0$ is the initial amount of N_2O (mol), $N_{C=C}^0$ is the initial amount of C=C bonds (mol), and g^0 is the initial weight of the rubber (g).

NMR analysis

The composition and structure of the polymer samples were studied with both ^{1}H and ^{13}C NMR spectroscopy. The spectra were recorded at room temperature with a Bruker MSL-400 spectrometer at 400.13 and 100.61 MHz, respectively, with solutions of samples in CCl_4. Other details of NMR analysis are given earlier.[17]

Quantitative ^{13}C NMR analysis was performed with the spectra recorded with the inverse-gated proton decoupling (IGATED) and long pulse delays to provide full relaxation of ^{13}C nuclei. Under these conditions, integral intensity of ^{13}C-NMR signals is proportional to the number of carbon atoms of a certain type. In the parent poly-IP, integral signal

TABLE I
Reaction Conditions and Characteristics of Carboxidized Poly-IP Rubber Samples

No.	Sample	Reaction conditions (temperature and time)	N_2O conversion, X_{N_2O} (%)	Reaction rate, W_{N_2O} (mmol/h)	Conversion of C=C bonds, $X_{C=C}$ (%)			Amount of oxygen introduced, $C_{(O)}$ (wt %)			Sample consistency
					GC	NMR	Average	GC	NMR	Average	
1.	PI-parent	–	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	Rubber
2.	PI-180-12	180°C, 12 h	0.5	0.08	1.2	1.1	1.2	0.3	0.3	0.3	Viscous liquid
3.	PI-200-12	200°C, 12 h	1.3	0.20	3.4	3.2	3.3	0.8	0.7	0.8	Viscous liquid
4.	PI-215-12	215°C, 12 h	2.3	0.36	5.9	6.4	6.2	1.4	1.4	1.4	Viscous liquid
5.	PI-230-6	230°C, 6 h	2.8	0.87	7.1	7.6	7.4	1.6	1.8	1.7	Viscous liquid
6.	PI-230-12	230°C, 12 h	7.3	1.13	18.4	16.2	17.3	4.2	3.7	3.9	Viscous liquid

intensity of C atoms having double bond ($I_{C=C}$) makes up 2/5 of the total intensity of the rubber carbon (I_Σ). This ratio correlates with the theoretical value, since a monomeric unit of poly-IP includes one C=C bond per five carbon atoms. The content of ketone groups in carboxidized samples was calculated from the ratio $I_{C=O}/I_\Sigma$, where $I_{C=O}$ is the integral signal intensity of ketone groups. The content of other groups was calculated in a similar way.

GPC analysis

Molecular weight (MW) and molecular-weight distribution (MWD) of polymers were determined by the high-temperature gel permeation chromatography (GPC) with a Waters Model 150C instrument additionally equipped with a differential viscometer Viscotek 100. Chromatograms were taken using four mixed-bed TSK-gel columns (GMHXL-HT, Tosoh Corp.). The measurements were conducted at 140°C with a 1,2,4-trichlorobenzene solvent. The chromatograms were processed with a universal calibration curve obtained with polystyrene standards having a narrow MWD in a broad range of molecular weights (from 1×10^3 to 13.2×10^6).

RESULTS AND DISCUSSION

Carboxidation of synthetic polyisoprene

The reaction conditions and the samples obtained after carboxidation of the rubber by nitrous oxide are presented in Table I. Designations of the samples include the reaction temperature and time. For instance, sample PI-200-12 was prepared by the carboxidation of synthetic poly-IP rubber at 200°C for 12 h.

As seen from the table, the reaction rate is very low at 180°C. The N_2O conversion (X_{N_2O}) attains only 0.5% for 12 h. As the temperature is raised to 230°C, the X_{N_2O} increases by more than an order of magnitude, attaining 7.3% for 12 h. The reaction rate based on the N_2O conversion was calculated with eq. (5):

$$W_{N_2O} = N_{N_2O}^0 \cdot X_{N_2O} \cdot t^{-1} \tag{5}$$

where t is the reaction time. The activation energy determined from the temperature dependence of the rate is 23 kcal/mol. This value is close to the activation energy for the carboxidation of poly-BD rubber[17] and 2-butene,[30] comprising 24 and 22 kcal/mol, respectively.

Since N_2O is consumed only for carboxidation of the rubber, the conversion of C=C bonds ($X_{C=C}$) in the parent poly-IP and the amount of oxygen introduced into the polymer ($C_{(O)}$) can be calculated from the GC data on N_2O conversion. Table I also presents the $X_{C=C}$ and $C_{(O)}$ values determined from the NMR data on the total concentration of carbonyl groups (ketone and aldehyde) in the rubber samples. The results obtained by the two methods agree well with each other. For further calculations, we shall use the average $X_{C=C}$ and $C_{(O)}$ values. The data presented in Table I show that the average values of $X_{C=C}$ and $C_{(O)}$ increase considerably with increasing the reaction temperature and time and attain 17.3 and 3.9 wt %, respectively, for the most carboxidized sample PI-230-12.

Previously,[17] it was shown that thr reactivity of C=C bonds in poly-BD rubber toward N_2O is close to that of individual linear alkenes.[13,15] Thus, after the carboxidation of poly-BD at 230°C for 12 h, the C=C bonds conversion attained 34.3%.[17] A comparison with the average $X_{C=C}$ value (17.3%) for sample PI-230-12 obtained under similar conditions indicates that the reactivity of C=C bonds in poly-IP is approximately two times lower when compared with poly-BD. In our opinion, this difference is related to the presence of a methyl substituent at the double bond in a monomeric unit of poly-IP. This may cause higher steric hindrances to the double bond attack by N_2O in poly-IP when compared with poly-BD, thus decreasing the reactivity.

It is important that the carboxidation strongly affects the outward appearance and consistence of the resulting samples. In distinction to poly-BD, the introduction of even a small oxygen amount (0.3 wt

%) into poly-IP transforms it into a liquid rubber. All carboxidized poly-IP samples are viscous transparent liquids. As the amount of introduced oxygen increases, viscosity of the samples decreases. As shown later, these changes are related to a manifold decrease in the MW of the rubber caused by carboxidation.

NMR study

The NMR spectroscopy is one of the most informative methods for reliable identification of functional groups that form during the carboxidation of rubber. The signals assigned to the following main moieties are identified in the ^{13}C spectrum of the parent polymer: internal double bonds ($>$C$=$CH$-$) of 1,4-units (135.2 and 125.67 ppm), ($-$CH$_2$$-CH_2$$-$) moieties (26.88 and 32.72 ppm), and ($-$CH$_3$) groups (24.04 ppm). In addition, there are weak signals at 112.29 and 147.32 ppm assigned to terminal double bonds in vinylidene groups ($>$C$=$CH$_2$) of 3,4-units. The [1]H spectrum of the parent rubber reveals the corresponding signals of protons in the same moieties: ($>$C$=$CH$-$) at 5.22 ppm, ($-$CH$_2$$-CH_2$$-$) at 2.16 ppm ($-CH_3$) groups at 1.81 ppm, and weak signals of ($>$C$=$CH$_2$) moieties at 4.81, 4.87, and 5.81 ppm.

After the reaction with N_2O, the spectra show significant changes taking place in the rubber. [13]C spectra of carboxidized samples indicate a decrease in the intensity of signals from both the internal and terminal C$=$C bonds. Concurrently, three signals of ketone groups ($>$C$=$O) appear in the 204–211 ppm region (Fig. 1, spectra 1–4). The most intense signal at 210.7 ppm can be attributed to isolated C$=$O groups in the polymer backbone, which have a methyl group at carbon atom in the α-position (ketone K1, Fig. 1). Signal with a lower intensity at 204.5 ppm can be assigned to methyl-ketone groups (ketone K2, Fig. 1) located at the ends of a polymer chain. The third low intense signal in the range of 208.5 ppm can be attributed to ketone having the chain branching at carbon in the α-position (ketone K3, Fig. 1). The intensity of all these signals attains maximum level for the most carboxidized sample PI-230-12 (Fig. 1, spectrum 4).

According to the ^{1}H-NMR analysis of carboxidized samples, a small amount of aldehyde groups of several types is also formed in the course of the reaction. Their signals are observed in the 9.5–10 ppm region. ^{13}C-NMR spectrum of the most carboxidized sample PI-230-12 also indicates very weak signals of aldehyde groups near 187.9, 188.5, 199.0, and 203.4 ppm. Assignments of these signals to aldehyde moieties were confirmed using gated decoupled spectra, which show C$-$H couplings (doublets with [1]J_{CH} near 170 Hz) because of the single aldehyde proton. Unfortunately, the low intensity of these sig-
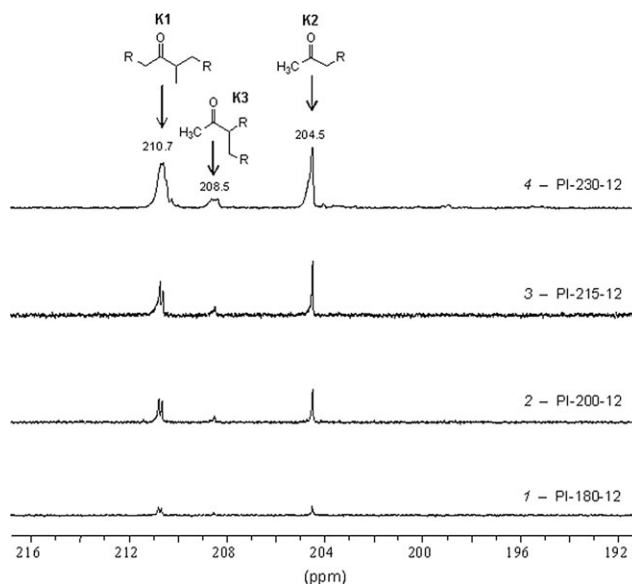

Figure 1 ^{13}C-NMR spectra of carboxidized poly-IP samples (Tables I–III) in the C$=$O signals region.

nals prevents detailed interpretation of the aldehydes formed. No hydroxyl or other oxygen-containing groups were detected in the samples.

The results of quantitative analysis of the NMR spectra are presented in Table II. One may see that a decrease in the fraction of monomeric units containing double bonds ($C_{C=C}$) is accompanied by an equivalent increase in the concentration of the units containing C$=$O groups ($C_{C=O}$). In all cases, the sum ($C_{C=C} + C_{C=O}$) exceeds 97%. This indicates that within the NMR accuracy, the interaction of poly-IP rubber with N_2O leads to a quantitative transformation of C$=$C bonds into carbonyl groups. As seen from Table II, the reaction results in the formation of functionalized polymers containing mainly ketone groups. Their total fraction exceeds 95% of the total amount of carbonyl groups.

It seems interesting that the aldehydes fraction (1.8–4.8%) considerably exceeds the expected value, which should not be higher than the initial fraction (0.4%) of the terminal C$=$C bonds in 3,4-units of the rubber. This indicates that aldehyde groups are formed at carboxidation of not only the terminal but also the internal double bonds because of their cleavage upon interaction with N_2O.

The cleavage of C$=$C bonds is also evidenced by the ratio of internal and terminal double bonds in the carboxidized samples. Our earlier study[30] on carboxidation of 1- and 2-butenes has shown that the reactivity of terminal C$=$C bonds is $\sim$ 1.5 times higher than the reactivity of internal bonds. Hence, one might expect that the fraction of terminal bonds in the samples should decrease with increasing the carboxidation degree. However, this fraction, on the contrary, increases from 0.4 to 3.5% (Table II). This

TABLE II
NMR Analysis of Carboxidized Poly-IP Rubber Samples

		Double bonds (C=C)			Carbonyl groups (C=O)							
		Fraction of monomeric units having C=C bonds, $C_{C=C}$ (%)	Distribution of C=C bonds (%)		Fraction of monomeric units having C=O groups, $C_{C=O}$ (%)	Distribution of C=O groups (%)						$C_{C=C} + C_{C=O}$ (%)
						Ketones						
No.	Sample		Internal	Terminal		K1	K2	K3	Σ_{ket}	Aldehydes		
1.	PI-parent	100	99.6	0.4	0.0	–	–	–	–	–		100
2.	PI-180-12	98	99.5	0.5	1.1	50.9	38.2	9.1	98.2	1.8		99.1
3.	PI-200-12	95	99.1	0.9	3.2	52.4	36.0	8.8	97.2	2.8		98.2
4.	PI-215-12	91	98.1	1.9	6.4	52.4	34.9	8.6	95.9	4.1		97.4
5.	PI-230-6	90	98.1	1.9	7.6	50.1	37.3	8.7	96.1	3.9		97.6
6.	PI-230-12	81	96.5	3.5	16.2	50.1	34.8	10.3	95.2	4.8		97.2

indicates an additional formation of terminal C=C bonds in the course of the reaction. Actually, the ^{13}C-NMR analysis confirms the formation of new vinyl end groups (R-CH=CH$_2$), which are observed at 36.89, 115.71, and 136.26 ppm. A carboxidation mechanism involving the cleavage of internal C=C bonds in poly-IP yielding vinyl groups will be considered further.

The NMR data on the amount of C=O groups in the carboxidized samples allow calculating the double bonds conversion and the content of oxygen introduced. The corresponding $X_{C=C}$ and $C_{(O)}$ values are presented in Table I. For the most carboxidized sample PI-230-12, the oxygen content is 3.7 wt % and the C=C bonds conversion is 16.2%. It means that each sixth C=C bond of the initial poly-IP macromolecule is converted to C=O group.

Molecular weight distribution

Figure 2 shows MWD curves for the parent rubber and the carboxidized samples. One can notice that by increasing the carboxidation degree, the MWD peaks shift to the region of a lower molecular weight. The values of the number-average (M_n) and the weight-average (M_w) molecular weights as well as their ratio (M_w/M_n) calculated from these data are presented in Table III. The carboxidation of poly-IP leads to a progressive decrease in M_n and M_w values. Even at the most low C=C conversion ($X_{C=C} = 1.2\%$), the M_n decreases nearly 17 times when compared with the initial MW. As the conversion increases, the decrease in the MW becomes more pronounced. Thus, for the most carboxidized sample PI-230-12 with $X_{C=C} = 17.3\%$, the MW decreases more than 300-fold, down to $M_n = 1000$. The polydispersity ratio M_w/M_n for all samples falls in the range of 1.6–1.9.

At elevated temperatures, poly-IP rubber may be subjected to thermal transformations,[31] which may affect the results of carboxidation. To estimate the influence of such transformations on the MW, we conducted a reference experiment. In this experiment, a solution of the parent poly-IP was kept at 230°C for 3 h in helium in the absence of N$_2$O. A homogeneous polymeric product was obtained. According to GPC analysis, the product had a nearly five times lower MW ($M_n = 65,000$) than the starting rubber. However, the data presented in Table III allow one to conclude that the effect of thermal transformations is insignificant, since in the presence of N$_2$O, the MW decreases at least by an order of magnitude faster than in the reference experiment.

Based on the MW data, an average number of cleavages (N_{cleav}) in the initial poly-IP macromolecule can be calculated by eq. (6):

$$N_{cleav} = \frac{M_n^0}{M_n} \cdot \frac{m}{m^0} - 1 \qquad (6)$$

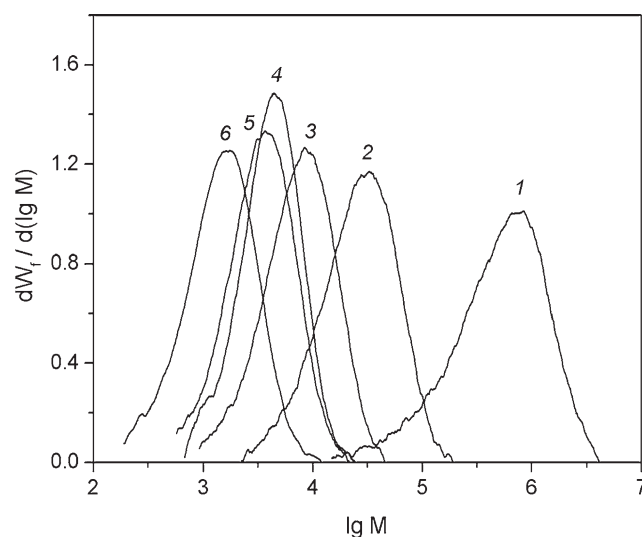where M_n^0 and M_n are the number-average MWs of the parent and carboxidized samples and m^0 and m

Figure 2 MWD curves for carboxidized poly-IP samples. The curve numbers correspond to the sample numbers in Tables I–III.

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TABLE III
MW Characteristics of Carboxidized Poly-IP Rubber Samples

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#	Sample	Average conversion of C=C bonds, $X_{C=C}$ (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Number of cleavages in the initial molecule, N_{cleav}	Average weight of a monomeric unit, m (g/mol)	Number of monomeric units in a molecule	Number of C=O groups in a molecule
1.	PI-parent	0	320	910	2.8	0	68.0	4706	0
2.	PI-180-12	1.2	19	34	1.8	16	68.2	279	3.3
3.	PI-200-12	3.3	5.8	9.9	1.7	55	68.5	85	2.8
4.	PI-215-12	6.2	3.4	5.8	1.7	94	69.0	49	3.1
5.	PI-230-6	7.4	2.8	4.6	1.6	115	69.2	41	3.0
6.	PI-230-12	17.3	1.0	1.9	1.9	332	70.8	14	2.4

are the corresponding average weights of monomeric units. Table III shows that with increasing the C=C bonds conversion, the N_{cleav} value also increases, attaining 332 for the most carboxidized sample PI-230-12. Accordingly, the resulting macromolecules become progressively smaller with the number of monomeric units decreasing from 4706 to 14.

Figure 3 compares the effect of carboxidation degree on the number of cleavages in poly-IP (curve 1) and poly-BD (curve 2) macromolecules. The poly-BD curve was plotted with the data of Ref. 17. One may see that the increase in the C=C bonds conversion leads to an approximately proportional increase in N_{cleav} value for the both rubbers. However, at the same conversion level, the number of cleavages in poly-IP is nearly by an order of magnitude higher. As a result, with increasing $X_{C=C}$, its MW decreases faster when compared with poly-BD. The reason for this difference will be considered further when discussing the mechanism of poly-IP carboxidation.

Interestingly, the number of C=O groups included in the molecules formed from poly-IP is only slightly changed with carboxidation degree and varies in the range of 2.4–3.3 (Table III).

The molecular characteristics presented in Table III show that carboxidation of poly-IP rubber leads to the formation of oligomeric materials. Thus, a macromolecule of the most carboxidized sample has a M_n of 1000 and includes, on average, 14 monomeric units, of which 2.4 units contain C=O groups and 11.6 units contain C=C bonds. This material is a liquid unsaturated polyketone.

Mechanism of Poly-IP carboxidation

As noted earlier, the mechanism of alkenes carboxidation implies the 1,3-dipolar cycloaddition of the N_2O molecule to the C=C bond and the formation of a five-membered oxadiazoline complex (reaction 1), which decomposition leads to a carbonyl compound. This mechanism well agrees with all results on the carboxidation of various alkene types[13–15,18]

and unsaturated polymers.[17,23] Further analysis of the results on poly-IP carboxidation will be made also within this mechanism.

A scheme of N_2O interaction with internal C=C bonds of poly-IP is presented in Figure 4(a). This type bonds account for 99.6% of the total amount of double bonds in the rubber. Therefore, their carboxidation mainly determines the nature of the resulting products.

Figure 4(a) shows that the intermediate oxadiazoline complex may have configurations I or II. In complex I, the oxygen is bound to the third carbon atom in a monomeric unit of poly-IP. According to the NMR data, complex I decomposes without cleavage of C—C bond by the route (1–1) yielding a ketone group in the polymer backbone (ketone K1). This route does not lead to a decrease in MW.

In complex II, the oxygen is bound to the second carbon atom in a monomeric unit, which bearing no hydrogen atom, since it is additionally bound with the methyl group. This complex decomposes mainly
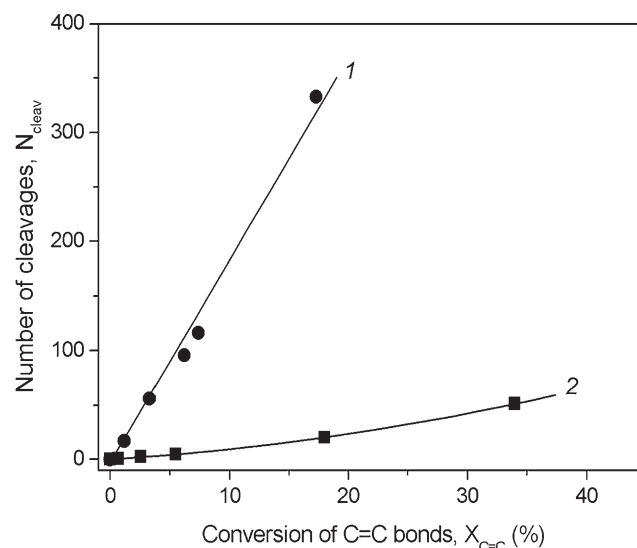

Figure 3 The effect of C=C bonds conversion on the number of cleavages at carboxidation: 1—synthetic poly-IP (by the data of Table III); 2—poly-BD (by the data of Ref. 17).
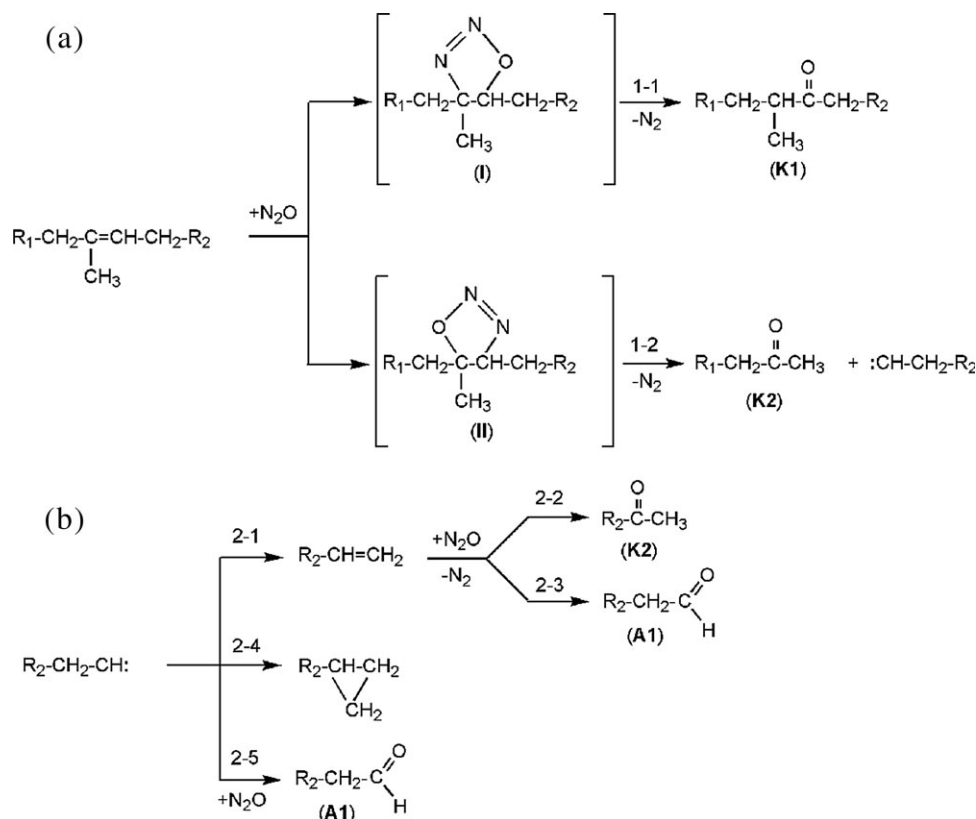
Figure 4 Carboxidation mechanism involving internal C=C bonds of poly-IP rubber: (a) carboxidation of C=C bonds in 1,4-units and (b) transformations of carbene.

with cleavage of the initial C=C bond (route 1–2). This gives two smaller fragments: a methylketone K2 and a stoichiometric amount of the carbene R_2—CH$_2$—CH. This is the route that leads to a decrease in the MW of polymer.

Further transformations of carbene are shown in Figure 4(b). The carbene mainly isomerizes (route 2–1) into a molecule with the end vinyl group (R_2—CH=CH$_2$). As noted earlier, new vinyl groups are actually detected in carboxidized samples by the NMR. The terminal double bonds in such groups may also react with N$_2$O by a scheme similar to the carboxidation of terminal alkenes[21,30] yielding a methylketone of K2 type (route 2–2) and a linear aldehyde A1 (route 2–3) as the main products. A small fraction of carbene may be rearranged by the route (2–4) to form cyclopropane derivatives. Their formation is indicated by the low-intensity signals at 4.53 ppm in ^{13}C spectra of the most carboxidized samples. Relatively large $^1J_{CH}$ constant ($\sim$ 162 Hz) for corresponding triplet, which is observed in ^{13}C-gated decoupled spectra, together with rather low chemical shift are highly characteristic of cyclopropyl ring CH$_2$ carbons. One can assume that besides these route, the carbene may directly interact with N$_2$O, also yielding a linear aldehyde A1 (route 2–5).

By increasing the carboxidation degree, the concentrations of carbene and accordingly that of R_2—CH=CH$_2$ fragments also increase. As a result, route (2–3) and (2–5) involving these fragments lead to a growth of the aldehydes fraction in the products, as it is observed by the NMR (Table II).

Ketone types K1 and K2 constitute the main part, 85–89%, of the carbonyl products (Table II). There are also a small amount (8.6–10.3%) of another type ketone K3 formed upon carboxidation without C=C bond cleavage. A detailed mechanism of its formation is unclear. A part of this type of ketones form upon the N$_2$O interaction with terminal double bonds in 3,4-units.

The ratio between the routes with and without the cleavage of internal C=C bonds can be estimated from the NMR data using the concentrations of corresponding ketones:

$$F_{\text{cleav}} = \frac{K2}{K1 + K2 + K3} \cdot 100(\%) \qquad (7)$$

This ratio characterizes the fraction of the cleavage route (F_{cleav}). Calculation by eq. (7) with the data of Table II gives the average value $F_{\text{cleav}} = 37\%$. This value may be somewhat overstated, because some of the K2-type ketones may form from new vinyl groups by the route (2–2).

No.	Sample	Reaction conditions (temperature and time)	Average conversion of C=C bonds, $X_{C=C}$ (%)	Average amount of oxygen introduced, $C_{(O)}$ (wt %)	$M_n \times 10^{-3}$	M_w/M_n	Number of monomeric units in a molecule	Number of C=O groups in a molecule	Sample consistency
1.	NR-parent	–	0.0	0.0	170	2.3	2,500	0	Rubber
2.	NR-230-6	230°C, 6 h	5.6	1.3	4.5	1.8	65	3.7	Viscous liquid
3.	NR-230-12	230°C, 12 h	12.3	2.8	1.6	1.6	23	2.8	Viscous liquid

The F_{cleav} value can be calculated independently from the GPC data using a ratio between the number of cleavages (N_{cleav}) and the number of C=C bonds that reacted with N_2O in the initial macromolecule containing, on average, 4706 monomeric units:

$$F_{cleav} = \frac{N_{cleav}}{4706 \cdot 0.01 \cdot X_{C=C}} \cdot 100 (\%) \qquad (8)$$

With the data of Table III, this method gives the F_{cleav} value in the range of 28–41% for different carboxidation degrees with the average value 34%, which satisfactorily agrees with the NMR estimation. On the basis of the data of the both methods, further we accept this value to be $F_{cleav} = 35\%$.

Note that the fraction of the cleavage route for poly-IP appears much higher than for poly-BD, where $F_{cleav} = 5\%$.[17] We assume that this distinction is related with the different structure of monomeric units in these rubbers. The presence of a methyl substituent at the double bond in poly-IP leads to the decomposition of intermediate complex II [Fig. 4(a)] mainly with the cleavage of C—C bond. The cleavage is necessary to form C=O group at second carbon atom in poly-IP monomeric unit. This is the cause of a more considerable decrease in the MW of poly-IP when compared with poly-BD at a similar carboxidation degree.

The fraction of terminal C=C bonds in 3,4-units of synthetic poly-IP is only 0.4%. So, their interaction with N_2O has no significant effect on the carboxidation products.

Carboxidation of natural rubber

Studied *cis*-1,4-poly-IP rubber is a synthetic analog of the natural rubber (NR). Therefore, one could expect that similar liquid unsaturated polyketones can also be prepared from this natural and renewable feedstock. To verify this idea, we conducted two experiments on carboxidation of the NR using the reaction conditions similar to those of runs 5 and 6 (Table I) with synthetic poly-IP. The results obtained are presented in Table IV.

According to the GC and NMR data, at 230°C for 6 h, the average conversion of C=C bonds in the NR attains 5.6%, and the amount of introduced oxygen is 1.3 wt %. When the reaction time is increased to 12 h, the values of $X_{C=C}$ and $C_{(O)}$ attain 12.3% and 2.8 wt %, respectively. These values are 25–30% lower than the corresponding values for PI-230-6 and PI-230-12 samples (Table I). However, essentially both polymers show a close reactivity. The carboxidized samples NR-230-6 and NR-230-12 are also viscous liquids having the M_n of 4500 and 1600, respectively.

The NMR analysis of the samples revealed similar functional groups as in the case with synthetic poly-IP. For example, with the NR-230-12, the fractions of ketones K1, K2, and K3 among the carbonyl products are 51.2, 34.7, and 9.2%, respectively. Thus, the total fraction of ketones is 95.1%, and the fraction of aldehydes is 4.9%, which is very close to the distribution of carbonyl groups in the PI-230-12 (Table II). The cleavage route for the NR calculated by eq. (7) is $F_{cleav} = 36\%$, which also agrees well with 35% for the synthetic rubber.

So, the carboxidation of both the synthetic poly-IP and the natural rubber allows obtaining the liquid unsaturated polyketones with a regulated MW and controlled concentration of C=O groups.

CONCLUSIONS

The results reported in this work show that carboxidation by nitrous oxide can be successfully applied to the poly-IP for obtaining the functionalized liquid rubbers containing carbonyl groups. A high concentration of C=C bonds in the poly-IP makes it possible to vary the amount of oxygen introduced in a broad range. In this work, it ranges from 0.3 to 3.9 wt % oxygen, which corresponds to 1.2–17.3% conversion of the rubber C=C bonds into C=O groups.

Similar to the case of poly-BD, the 1,3-dipolar cycloaddition mechanism well explains the experimental data obtained with poly-IP rubber. However, different structures of the monomeric units have a significant effect on the carboxidation process. Availability of CH_3-substituent at the poly-IP C=C bonds makes the reaction about two times slower, but strongly intensifies the cleavage route. With the

poly-BD this route is only 5%, while with the poly-IP it attains nearly 35%. Therefore, in the latter case, at the same content of the oxygen introduced, the fragmentation of the parent macromolecules is much higher, and the MW of the resulting products is much lower. Even the introduction of such a small oxygen amounts as 0.3 wt % transforms the poly-IP into a liquid oligomeric material.

To summarize, one can conclude that the carboxidation of various unsaturated polymers provides a possibility for preparing a broad variety of the liquid polyketones having different combinations of important properties such as the MW and the concentration of C=C bonds and C=O groups.

The carboxidation of natural rubber shows that oligomeric unsaturated polyketones can also be readily prepared from this available and renewable feedstock.

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