



## Ketonization of a nitrile-butadiene rubber by nitrous oxide: Comparison with the ketonization of other type diene rubbers

Sergey V. Semikolenov, Konstantin A. Dubkov\*, Dmitry P. Ivanov, Dmitry E. Babushkin, Mikhail A. Matsko, Gennady I. Panov

Boreskov Institute of Catalysis, Russian Academy of Science, Lavrentieva 5, Novosibirsk 630090, Russian Federation

### ARTICLE INFO

#### Article history:

Received 17 June 2009

Received in revised form 25 September 2009

Accepted 4 October 2009

Available online 13 October 2009

#### Keywords:

Nitrile-butadiene rubber

Diene rubbers

N<sub>2</sub>O

Functional polymers

Functional oligomers

Polyketones

### ABSTRACT

Noncatalytic ketonization of a nitrile-butadiene rubber (21 mol% acrylonitrile units) by nitrous oxide was shown to yield polymeric products functionalized with carbonyl (mainly ketone) groups. The reaction was conducted in a benzene solvent at 180–230° and pressure of 3–6 MPa. An assumed ketonization mechanism includes a 1,3-dipolar cycloaddition of N<sub>2</sub>O to C=C bonds in butadiene units.

According to the NMR and GPC data, the main route of the reaction (ca. 85%) proceeds without cleavage of the C=C bonds and yields ketone groups in the polymer backbone. The minor route (ca. 15%) includes the cleavage of C=C bonds resulting in fragmentation of the macromolecules that leads to a decrease in their molecular weight. The nitrile (–CN) groups remain untouched. The resulting product is a bifunctional low-molecular rubber containing, in addition to originally present nitrile groups, a regulated amount of new ketone groups randomly distributed along the polymer backbone.

The results for nitrile-butadiene rubber are compared with the earlier studied ketonization of butadiene and isoprene rubbers. The molecular structure of monomeric units was shown to be an important characteristic of a parent rubber affecting the reaction rate, degree of fragmentation, and consistency (rubber-like, plastic, or liquid) of the resulting material.

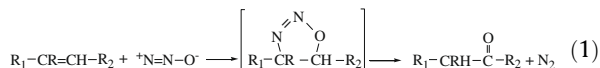
© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

Functionalized polymers are commonly prepared by the copolymerization of dienes with the monomers containing various functional groups, or by the chemical modification (maleinization, epoxidation, chlorination, etc.) that incorporates functional groups into a parent polymer, usually containing double C=C bonds [1–7]. Similar methods allow also for the preparation of liquid rubbers (low-molecular polymers) with functional groups randomly distributed along the polymer backbone [8–10].

Recently nitrous oxide (N<sub>2</sub>O) was shown to perform selective noncatalytic oxidation of polymer C=C bonds

into carbonyl C=O groups, which was called carboxidation reaction [11–13]. Since the reaction yields mainly the ketone groups, it can also be called “ketonization” following the authors [14,15]. A possibility to apply this reaction for the polymer ketonization was demonstrated earlier with the butadiene rubber (BR) and isoprene rubber (IR) [13,16]. Similar to olefins, ketonization of the diene rubbers most probably proceeds via the 1,3-dipolar cycloaddition of N<sub>2</sub>O to C=C bond [14,17–19]:



where R<sub>1</sub> and R<sub>2</sub> are hydrocarbon radicals, and R is a CH<sub>3</sub> radical or hydrogen atom. The features of N<sub>2</sub>O as an

\* Corresponding author. Fax: +7 383 330 96 87.  
E-mail address: [dubkov@catalysis.ru](mailto:dubkov@catalysis.ru) (K.A. Dubkov).

oxidant were specially studied in the earlier works by the example of different type olefins (aliphatic, cyclic, etc.) [14,20–22] and rubbers [13,16]. It was shown that  $N_2O$  has a remarkable ability to react solely with  $C=C$  bonds and is inert toward other bonds ( $C-C$ ,  $C-H$ ,  $C-OH$ ,  $C=O$ ,  $C\equiv N$ , etc.).

Previous studies revealed that ketonization is accompanied by cleavage of a certain part of reacting  $C=C$  bonds. Availability of the cleavage route may lead to a considerable decrease in the initial rubber molecular weight resulting in low-molecular functional rubbers called unsaturated liquid polyketones [13,16].

These polymeric materials are distinguished from the known saturated polyketones, which are synthesized by copolymerization of carbon monoxide with olefins catalyzed by palladium complexes [23–26]. The presence of  $C=O$  groups and  $C=C$  bonds provides an additional opportunity for the useful application of unsaturated polyketones as well as a possibility for their subsequent chemical modifications [4,7,25–27].

Polyfunctional polymers containing functional groups of different types are of particular interest. In this work, we investigated a possibility of preparing bifunctional polymers by ketonization of  $C=C$  bonds of nitrile-butadiene rubber (NBR). The resulting material was expected to have two types of functional groups, i.e. the original nitrile and the new ketone groups. The results are compared with the previous studies on the BR [13] and IR [16] to elucidate some similarities and differences in ketonization of diene rubbers.

## 2. Experimental

The study was carried out with NBR of a trademark BNKS-18AMN ( $M_n = 58,000$ ,  $M_w/M_n = 6.9$ ) produced by Krasnoyarsk Synthetic Rubber Plant (Krasnoyarsk, Russian Federation). By the NMR data, the rubber contains 65.4 mol% of butadiene 1,4-units, 13.3 mol% of 1,2-units, and 21.3 mol% of acrylonitrile units.

The ketonization of rubber with nitrous oxide was performed in a setup equipped with a high-pressure Parr reactor of 100 cm<sup>3</sup> capacity [13]. The reactor was loaded with 5 g rubber, 60 cm<sup>3</sup> benzene (a solvent) and 0.186 mol  $N_2O$  by a method described elsewhere [13,21]. The amount of  $N_2O$  was ca. 2.5 times greater than the amount of  $C=C$  bonds in the loaded polymer (0.073 mol). The reactor was heated at a 6 °C/min ramp to the reaction temperature (180–230°) and kept for 6–12 h. Depending on the temperature, the reaction pressure varied from 3 to 6 MPa.

After the termination of the reaction, the reactor was cooled to room temperature, and the gas phase composition ( $N_2O$ ,  $N_2$ ,  $O_2$ ,  $CO_x$ , and low hydrocarbons) was analyzed using the gas chromatography (GC) method [13,21]. In all the experiments, nitrogen was the only reaction product detected in the gas phase, and  $CO_x$  concentration did not exceed 0.01 mol%.

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:

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

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

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

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). The reaction rate was calculated by equation:

$$r_{N_2O} = N_{N_2O}^0 \cdot X_{N_2O} \cdot t^{-1} \cdot V^{-1} \quad (5)$$

where  $t$  is the reaction time (h), and  $V$  is the initial volume of liquid phase in the reactor (0.065 l).

After the analysis, the pressure was slowly released and the reactor was opened. The ketonized polymer sample was recovered from the solution by evaporating the solvent under vacuum at 50°.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of the polymer samples dissolved in 1,4-dioxane were recorded at room temperature with a Bruker AVANCE spectrometer at 400.13 and 100.61 MHz, respectively. <sup>13</sup>C NMR spectra were referenced to the signal of 1,4-dioxane at 67 ppm. Quantitative NMR analysis was performed with the <sup>13</sup>C spectra, which were recorded with inverse gated proton decoupling (IGATED) and long pulse delays to provide full relaxation of <sup>13</sup>C nuclei.

Molecular weight (MW) and molecular weight distribution (MWD) of polymers were determined by high-temperature gel permeation chromatography (GPC) with a Waters 150C instrument equipped with differential viscometer Viscotek 100. Other details of NMR and GPC analysis are given earlier [13].

## 3. Results and discussion

### 3.1. Ketonization of NBR rubber and identification of the products

The data on ketonization of NBR are presented in Table 1. Designations accepted for the resulting polymer samples include the temperature and time of the reaction. For instance, NBR-230-12 denotes the sample obtained after the reaction at 230° for 12 h. As seen from the table, the reaction proceeds rather slowly at 180°. During 12 h,  $N_2O$  conversion attains only 0.8% and the reaction rate  $r_{N_2O}$  is 2 mmol/l h. As the temperature rises to 230°, the corresponding values increase more than an order of magnitude, attaining 9.5% and 24.3 mmol/l h. The activation energy determined from the Arrhenius plot is 23 kcal/mol. This value is typical for ketonization of both rubbers [13,16] and olefins [21,28].

Table 1 shows also conversion of the rubber double bonds ( $X_{C=C}$ ) and amount of oxygen introduced into the polymer ( $C_{(O)}$ ). These values were calculated by two methods: from GC data on the amount of nitrogen formed by reaction (1), and from NMR data on the concentration of carbonyl groups in ketonized samples. Both methods give

Download English Version:

<https://daneshyari.com/en/article/1396221>

Download Persian Version:

<https://daneshyari.com/article/1396221>

[Daneshyari.com](https://daneshyari.com)