

Abstract

The so-called ketonization reaction of nitrous oxide (N₂O) with butadiene rubbers Buna CB25 and Buna CB35 having different contents of 1,2-units was studied. The ketonization of rubbers (5 g) by N₂O (0.185 mol) was performed batchwise in a Parr reactor (100 ml) in a benzene solvent (80 ml) at 200–230°C and elevated pressure. The reaction products were characterized by gel-permeating chromatography, ¹³C NMR, and ¹H NMR spectroscopy. A series of functionalized polymers and oligomers of a new type, unsaturated polyketones, with varying molecular weights and contents of carbonyl, mainly ketone, groups was obtained. GPC measurements demonstrated that molecular weight of polymers decreases with increasing conversion of C=C bonds and amount of the oxygen introduced from N₂O. According to NMR data, upon ketonization of both rubbers, mainly ketone groups randomly distributed along the backbone are formed by the reaction of N₂O with internal C=C bonds in 1,4-units.

Butadiene rubbers [-CH₂-CH=CH-CH₂]_n

Main route of ketonization by N₂O ⇒ formation of ketone groups in the backbone:

$$\sim\text{CH}=\text{CH}\sim + \text{N}_2\text{O} \rightarrow \sim\text{CH}(\text{C}=\text{O})\text{CH}_2\sim + \text{N}_2$$

Introduction

In the last decades, nitrous oxide (N₂O) attracts much attention as a donor of active oxygen for selective catalytic oxidation, in particular, for the direct hydroxylation of benzene to phenol over FeZSM-5 zeolites [1]. Beside catalytic reactions, of great interest is non-catalytic oxidation with N₂O of olefins to ketones and aldehydes (the so-called ketonization reaction). In the temperature range of 150–280°C and at a pressure of 2–8 MPa, such oxidation proceeds in the liquid phase with high selectivity often exceeding 90%. Thus, ketonization of olefins provides a promising way for the synthesis of various carbonyl compounds [1, 2]. A remarkable feature of N₂O is its ability to react solely with the olefinic C=C bonds, being inert toward other bonds. That is why the reaction products do not undergo further oxidation. The ketonization proceeds by a non-radical mechanism involving the 1,3-dipolar cycloaddition of N₂O to the C=C bond via the formation of an unstable 1,2,3-oxadiazoline intermediate:

$$\text{R}_1-\text{CH}=\text{CH}-\text{R}_2 + \text{N}=\text{N}-\text{O} \rightarrow \text{R}_1-\text{CH}(\text{N}=\text{N})-\text{CH}(\text{O})-\text{R}_2 \rightarrow \text{R}_1-\text{CH}_2-\text{C}(=\text{O})-\text{R}_2 + \text{N}_2$$

Another promising approach is the use of N₂O for selective oxidation of C=C double bonds in polymers. Earlier, we have shown that ketonization of diene rubbers by N₂O opens a synthetic route for obtaining a new type of functionalized polymers and oligomers - unsaturated polyketones (UPKs) [1, 2]. This reaction is applicable to various types of diene rubbers and allows obtaining UPKs with different structure of monomeric units, controllable molecular weight, and specified concentration of carbonyl groups. In this work, we have studied the ketonization of butadiene rubbers Buna CB25 and Buna CB35 with different contents of 1,2-units.

References

1. Parmon V.N., Panov G.I., Uriarte A., Noskov A.S., Catal. Today, 2005, 100, 115-131.
2. Dubkov K.A., Panov G.I., Parmon V.N., Russ. Chem. Rev., 2017, 86, 510-529.

¹H NMR of ketonized CB35 samples

1 - CB35 parent
2 - CB35-200-10
3 - CB35-230-6
4 - CB35-230-12

- Decrease in C=C bonds concentration
- Formation of -CHO groups

Ketonization of Buna CB25 with N₂O

Buna CB25: Mn = 180000 (Mw/Mn = 2.1), 0.4 % 1,2-units, 99.6 % 1,4-units (97.2 % cis-1,4-units, 2.4 % trans-1,4-units)

Effect of Reaction conditions on ketonization of Buna CB25

#	Sample	Reaction conditions	N ₂ O conversion (%)	C=C bonds conversion (%)	Oxygen content (wt. %)	Appearance
1	CB25-parent	-	0	0	0	rubber
2	CB25-200-6	200°C, 6 h	1.9	4.2	1.2	soft polymer
3	CB25-215-6	215°C, 6 h	4.4	9.5	2.7	fluid polymer
4	CB25-230-6	230°C, 6 h	8.0	17.4	4.9	viscous liquid
5	CB25-230-12	230°C, 12 h	14.1	29.6	8.1	viscous liquid

- Deep ketonization ⇒ functionalized liquid oligomers

Quantitative NMR data for Buna CB25 samples

#	Sample	C=C bonds conversion (%)	Distribution of carbonyl products (%)			Fraction of cleaved C=C bonds, F _{cleav} (%)
			Ketones, >C=O	Linear aldehydes, -CH ₂ -CHO	Branched aldehydes, >CH-CHO	
1	CB25-parent	0	0	0	0	-
2	CB25-200-6	4.2	95.3	3.1	0.7	25.1
3	CB25-215-6	9.5	95.9	3.4	0.7	23.4
4	CB25-230-6	17.4	95.1	4.2	0.7	19.4
5	CB25-230-12	29.6	94.9	4.4	0.7	18.6
		Average	95.3	4.0	0.7	4.0

- Decrease in C=C bonds concentration
- An equivalent increase in the concentration of >C=O and -CHO groups
- Preferred formation of ketone >C=O groups
- Ketonization of CB25 rubber ⇒ unsaturated polyketones

Quantitative NMR data for Buna CB35 samples

#	Sample	C=C bonds conversion (%)		Ketones/aldehydes ratio
		into ketone	into aldehyde	
1	CB35-parent	0	0	-
2	CB35-200-5	2.8	0.8	3.5
3	CB35-200-10	6.7	1.5	4.4
4	CB35-230-6	15.7	3.3	4.8
5	CB35-230-12	23.7	4.7	5.1

- Decrease in C=C bonds concentration
- An equivalent increase in the concentration of >C=O and -CHO groups
- Preferred formation of ketone >C=O groups
- Higher concentration of aldehydes (lower ketones/aldehydes ratio) than for CB25

¹³C NMR of ketonized CB25 samples (olefinic carbons region)

5 - CB25-230-12
4 - CB25-230-6
3 - CB25-215-6
2 - CB25-200-6
1 - CB25 parent

- Decrease in C=C bonds concentration
- Formation of new vinyl end groups (-CH₂-CH=CH₂)

Molecular weight distribution of ketonized CB25 samples

#	Sample	C=C bonds conversion (%)	Mn	Mw	Mz	Mw/Mn
1	CB25-parent	0	180000	370	700	2.1
2	CB25-200-6	4.2	32000	74	140	2.3
3	CB25-215-6	9.5	15000	38	68	2.5
4	CB25-230-6	17.4	6000	16	36	2.6
5	CB25-230-12	29.6	3300	8.5	17	2.6

- Ketonization of CB25 ⇒ MW decrease
- Deep ketonization ⇒ liquid polyketones
- Regulated amount of C=O groups and controllable molecular weight

Molecular weight distribution of ketonized CB35 samples

#	Sample	C=C bonds conversion (%)	Mn	Mw	Mz	Mw/Mn
1	CB25-parent	0	105000	230	446	2.2
2	CB25-200-6	3.6	8100	20	36	2.5
3	CB25-215-6	8.2	3900	9.8	18	2.5
4	CB25-230-6	19.0	1550	3.3	6.0	2.1
5	CB25-230-12	28.4	860	1.7	3.0	2.0

- Ketonization of CB35 ⇒ MW decrease
- A more rapid decrease in MW than for CB25 rubber
- Formation of liquid polyketones
- Regulated amount of C=O groups and controllable molecular weight

¹³C NMR of ketonized CB25 samples (>C=O region)

5 - CB25-230-12
4 - CB25-230-6
3 - CB25-215-6
2 - CB25-200-6
1 - CB25 parent

- Formation of >C=O and -CHO groups

Ketonization of Buna CB35 with N₂O

Buna CB35: Mn = 105000 (Mw/Mn = 2.2), 9.6% 1,2-units, 90.4% 1,4-units (37.7% cis-1,4-units, 52.7% trans-1,4-units)

Effect of Reaction conditions on ketonization of Buna CB35

#	Sample	Reaction conditions	N ₂ O conversion (%)	C=C bonds conversion (%)	Oxygen content (wt. %)	Appearance
1	CB35-parent	-	0	0	0	rubber
2	CB35-200-5	200°C, 5 h	2.4	3.6	1.3	fluid polymer
3	CB35-200-10	200°C, 10 h	4.8	8.2	2.6	liquid
4	CB35-230-6	230°C, 6 h	10.2	19.0	5.5	liquid
5	CB35-230-12	230°C, 12 h	17.2	28.4	8.5	liquid

- Ketonization ⇒ functionalized liquid oligomers

Schemes of butadiene rubbers ketonization

Ketonization of internal C=C bonds in 1,4-units (CB25 and CB35 rubbers):

Scheme 1

$$\sim\text{CH}=\text{CH}\sim + \text{N}_2\text{O} \xrightarrow{\text{R1}} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{N}=\text{N} \\ \parallel \\ \text{O} \end{array} \right] \sim\text{CH}-\text{CH}\sim \xrightarrow{(1)} \sim\text{CH}(\text{C}=\text{O})\text{CH}_2\sim \xrightarrow{(2)} \sim\text{CH}(\text{C}=\text{O})\text{CH}_2\text{CHO} + \sim\text{CH}(\text{C}=\text{O})\text{CH}_2\text{CHO} \xrightarrow{(3)} \text{H}_2\text{C}=\text{CH}\sim$$

- A certain fraction of reacting internal C=C bonds (~4% for CB25 and ~16.8% for CB35) is cleaved (route 2)
- This leads to the decrease in the molecular weight
- CB35 rubber contains mainly 1,4-units (99.6 mol. %)
- Therefore, unsaturated polyketones obtained by ketonization of this rubber contain mainly ketone >C=O groups in the main chain, as well as end aldehyde -CHO groups and end vinyl -CH=CH₂ groups:

$$\text{CH}_2=\text{CH}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_m-(\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2)_n-\text{CH}_2-\text{C}(=\text{O})-\text{H}$$

¹H NMR of ketonized CB25 samples

5 - CB25-230-12
4 - CB25-230-6
3 - CB25-215-6
2 - CB25-200-6
1 - CB25 parent

- Decrease in C=C bonds concentration
- Formation of -CHO groups

¹³C NMR of ketonized CB35 samples (olefinic carbons region)

1 - CB35-160-12
2 - CB35-200-5
3 - CB35-200-10
4 - CB35-230-6
5 - CB35-230-12

- Decrease in C=C bonds concentration
- Formation of new vinyl end groups (-CH₂-CH=CH₂)

Ketonization of terminal C=C bonds in 1,2-units (CB35 rubber):

Scheme 2

$$\text{CH}=\text{CH}_2 + \text{N}_2\text{O} \xrightarrow{\text{R2}} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{N}=\text{N} \\ \parallel \\ \text{O} \end{array} \right] \text{CH}=\text{CH}_2 \xrightarrow{(1)} \text{CH}_2=\text{C}(=\text{O})-\text{CH}_2 \xrightarrow{(2)} \text{CH}_2=\text{C}(=\text{O})-\text{CH}_2\text{CHO} + \text{CH}_2=\text{C}(=\text{O})-\text{CH}_2\text{CHO} \xrightarrow{(3)} \text{CH}_2=\text{C}(=\text{O})-\text{CH}_2\text{CHO} + \text{CH}_2$$

- CB35 rubber contains a significant fraction of 1,2-units (9.6 mol. %)
- Therefore, unsaturated polyketones obtained by ketonization of this rubber additionally contain side -CHO, -CH₂-CHO, and -CO(CH₃) groups (Scheme 2)

¹H NMR of ketonized CB25 samples (-CHO region)

5 - CB25-230-12
4 - CB25-230-6
3 - CB25-215-6
2 - CB25-200-6
1 - CB25 parent

- Formation -CHO groups

¹³C NMR of ketonized CB35 samples (>C=O region)

1 - CB35-160-12
2 - CB35-200-5
3 - CB35-200-10
4 - CB35-230-6
5 - CB35-230-12

- Formation of >C=O and -CHO groups

Conclusion

In this work, the selective oxidation of C=C bonds in butadiene rubbers Buna CB25 and Buna CB35 with nitrous oxide (the so-called ketonization reaction) was studied. The reaction leads to obtaining unsaturated polyketones (UPKs). According to NMR data, upon ketonization of both rubbers, mainly ketone groups randomly distributed along the backbone are formed by the reaction of N₂O with internal C=C bonds in 1,4-units. A certain fraction of reacting internal C=C bonds (~4% for CB25 rubber and ~16.8% for CB35 rubber) is cleaved, leading to the formation of shorter macromolecules containing aldehyde and end vinyl groups. As a result, the molecular weight of polymers decreases with increasing conversion of C=C bonds, and consistency of UPKs varies from a rubber-like form to a viscous liquid.

In the case of CB25 rubber the products of the following structure were obtained:

$$\text{CH}_2=\text{CH}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_m-(\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2)_n-\text{CH}_2-\text{C}(=\text{O})-\text{H}$$

Upon ketonization of CB35 rubber, which contains a significant fraction of 1,2-units (9.6 mol. %), the terminal C=C bonds in such units are additionally oxidized. As a result, the obtained UPKs contain, along with ketone groups in the backbone, additional aldehyde and ketone side groups. Thus, the ketonization with N₂O is applicable to various types of diene rubbers and allows obtaining UPKs with different structure of monomeric units, controllable molecular weight, and specified concentration of carbonyl groups. The method requires neither catalysts nor expensive reagents. Since N₂O reacts solely with olefinic C=C bonds, the reaction proceeds with high selectivity and does not yield any by-products. Due to their properties, oligomeric UPKs can be used as components of polymeric materials and adhesives [3, 4].

3. Sidorov O.I., Dubkov K.A., Semikolenov S.V., et al., Polym. Sci., Ser. D, 11(2018) 215-224.
4. Sidorov O.I., Evseev N.E., Dubkov K.A., et al., Polym. Sci., Ser. D, 13(2020) 85-88.