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FUNCTIONALIZATION OF ISOBUTYLENE OLIGOMERS AND 1,2-POLYBUTADIENE WITH METHYLDIAZOACETATE IN THE PRESENCE OF Cu(OAc)₂-2,4-Lut-ZnCl₂ CATALYTIC SYSTEM

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Abstract. A catalytic method of the chemical modification of isobutylene oligomers and syndiotactic 1,2-polybutadiene on the C=C bond *via* the [1+2] cycloaddition of metoxycarbonylcarbene in the presence of Cu(OAc)₂-2,4-Lut-ZnCl₂ is proposed.

Keywords: chemical modification of polymers, methyl-diazoacetate, metal complex catalysis.

1. Introduction

The chemical modification of polymers, which allows to change widely their physical and chemical properties, is a significant direction of the chemistry of high molecular compounds. As a way of the functionalization the addition reactions rank a special place in the chemistry of diene polymers because of high reactivity of the C=C bond in the polymer link. Reaction reagents may be different class substances, for instance, epoxides, aromatic amines, and the like [1, 2].

The polyene structures containing conjugated cyclopropane cycles are of great interest. For example, polycyclopropane derivatives of fatty acids isolated from *Streptoverticillum fervens* and *Strepfomyces*, relate to antibiotics and are inhibitors of albuminous transfer of cholecteryl ether [3].

The purpose of the work is to investigate the catalytic [1+2] cycloaddition of metoxycarbonylcarbene generated from methyl-diazoacetate on C=C bonds of syndiotactic 1,2-polybutadiene and isobutylene oligomers in the cyclopropanation reaction in the presence of Cu(OAc)₂-2,4-Lut-ZnCl₂.

2. Experimental

The ¹H and ¹³C NMR spectra were registered on a spectrometer "Bruker AM-300" (300.13 and 75.47 MHz,

respectively) in CDCl₃. The IR spectra were recorded on a Forier-spectrophotometer Shimadzu IR-Prestige-21 in a liquid film. In the work Cu(OAc)₂ ("Vekton") ZnCl₂ (anhydrous) ("Reaktiv"), isobutylene oligomers **1** (*n* = 7, *M_n* = 504, *n_d²⁰* = 1.4671), **2** (*n* = 10, *M_n* = 700, *n_d²⁰* = 1.4701), and syndiotactic 1,2-polybutadiene **3** (JSC "Efremovski zavod SK", *M_n* = 52600, *m_w* = 116600, degree of crystallinity – 18 %, syndiotacticity – 53 %) were used.

Isobutylene oligomers were purified *via* the reprecipitation in the system hexane/acetone. The solvents were removed at the reduced pressure. Syndiotactic 1,2-polybutadiene was purified *via* the reprecipitation in the system chloroform/ethanol. Then, polymer was twice washed with alcohol. The polymer was dried in vacuum at 333 K up to a constant mass. The solvents used in the work (Et₂O, CH₂Cl₂, C₆H₁₄, (CH₃)₂CO, petroleum ether (boiling point is 313–343 K), EtOH, CHCl₃) and 2,4-lutidine were purified according to the standardized techniques [4, 5].

The cyclopropanation of isobutylene oligomers with methyl-diazoacetate in the presence of the catalytic system Cu(OAc)₂-2,4-lutidine-ZnCl₂ was carried out at 313 K by adding slowly of 4 mmol of methyl-diazoacetate in 7 ml of CH₂Cl₂ to a stirred solution containing 0.005 mmol of anhydrous ZnCl₂, 0.03 mmol of 2,4-lutidine, 0.04 mmol of Cu(OAc)₂ and 4 mmol of isobutylene oligomer **1,2** in 17 ml CH₂Cl₂ until gassing ends. A solvent was removed at the reduced pressure, petroleum ether was added to residuum, a catalytic system was isolated as a dark-brown oil. Petroleum ether was removed at a reduced pressure; the residue was analyzed using ¹H and ¹³C NMR and IR spectroscopy. The yields of compounds **4, 5** were determined on the basis of ¹H NMR spectrum (benzene – an internal standard).

Functionalized isobutylene oligomer (**4**) (*n* = 7), *n_d²⁰* 1.4583, yield 32 %. Found (%): C, 81.32; H, 13.14; O,

5.54. $C_{39}H_{76}O_2$. Calc. (%): C, 81.25; H, 13.19; O, 5.56. 1H NMR spectrum (*d*, ppm): 0.94, 0.96 (both are s, 6H, 2Me); 1.11 (m, 1H, CH, in the cyclopropane ring); 1.34, 1.35 (both are s, 6H, 2Me); 1.43 (s, 2H, CH_2); 1.52, 1.54 (both are s, 6H, 2Me); 1.88 (m, 1H, $CHCO_2Me$, in the cyclopropane ring); 3.68 (s, 3H, OMe). NMR ^{13}C -spectrum (*d*, ppm): 12.0, 17.4 (2CH); 27.3 (Me); 29.4 (Me); 29.7 (CH_2); 31.5 (CH); 33.0 (C), 51.3 (OMe); 167.1 (C=O). IR spectrum, n/cm^{-1} : 546, 1095 and 1169(C–O), 1242, 1278(OMe), 1364, 1375, 1433, 1454(CH of the cyclopropane ring), 1732(C=O), 1748, 2868, 2954.

Functionalized isobutylene oligomer (**5**) (*n* = 10), n_d^{20} 1.4689, yield 19 %. Found (%): C, 82.78; H, 13.07; O, 4.15. $C_{51}H_{100}O_2$. Calc. (%): C, 82.26; H, 13.44; O, 4.30. 1H NMR spectrum (*d*, ppm): 0.94, 0.96 (both are s, 6H, 2Me) 1.06 (m, 1H, CH, in the cyclopropane ring); 1.25, 1.32 (both are s, 6H, 2Me); 1.41 (s, 2H, CH_2); 1.50, 1.52 (both are s, 6H, 2Me); 1.87 (m, 1H, $CHCO_2Me$, in the cyclopropane ring); 3.67 (s, 3H, OMe). ^{13}C NMR spectrum (*d*, ppm): 12.2, 17.4 (2CH); 27.3 (Me); 29.4 (Me); 29.7 (CH_2); 31.4 (CH); 32.9 (C), 51.3 (OMe); 167.3 (C=O). IR spectrum, n/cm^{-1} : 550, 1101 and 1177(C–O), 1242, 1291(OMe), 1364, 1377, 1452 (CH of the cyclopropane ring), 1734(C=O), 2868, 2930.

The cyclopropanation of syndiotactic 1,2-polybutadiene with methyl diazoacetate in the presence of the catalytic system $Cu(OAc)_2$ -2,4-lutidine- $ZnCl_2$ was carried out via slowly adding of 37 mmol (calculating on one elementary link of polymer chain) of methyl diazoacetate in 10 ml of CH_2Cl_2 to a stirred solution containing 0.06 mmol of anhydrous $ZnCl_2$, 0.32 mmol of 2,4-lutidine, 0.037 mmol of $Cu(OAc)_2$, 37 mol of syndiotactic 1,2-polybutadiene **3** in 50 ml of CH_2Cl_2 until gassing ends. A solvent was removed at a reduced pressure, petroleum ether was added to a residue, a catalytic system was separated as a dark-brown oil. Petroleum ether was evaporated at a reduced pressure. The product was purified twice *via* reprecipitation in a system chloroform/ethanol and dried in vacuum at 333 K to a constant mass.

Functionalized syndiotactic 1,2-polybutadiene (**6**), yield 20 %. 1H NMR spectrum (*d*, ppm): 0.85 (m, 1H, CH, in the cyclopropane ring); 1.17 (m, 2H, CH_2); 2.09 (m, 1H, CH); 2.32 (m, 1H, CH, in the cyclopropane ring); 3.65 (s, 3H, OMe). ^{13}C NMR -spectrum (*d*, ppm): 15.4 (CH); 25.1 (CH_2); 28.2 (CH); 38.8 (CH); 41.3 (CH_2); 51.0 (OMe); 170.1 (C=O). IR spectrum, n/cm^{-1} : 669, 758, 908 and 994 (=CH), 1084, 1168, 1263(OMe), 1342, 1417(=CH $_2$), 1448 (CH of the cyclopropane ring), 1639(C=C), 1752(C=O), 2843, 2916, 2970, 3072 (CH_2 of the cyclopropane ring).

The spectrophotometric studies of functionalized 1,2-polybutadiene were performed on a spectrophotometer Shimadzu 3100. The weight amounts of samples of the starting and modified syndiotactic 1,2-polybutadiene

(0.0100 ± 0.0001 g) were dissolved in diethyl ester and UV-spectra was registered. To carry out spectrophotometric measurements in diethyl ester standard solutions of anhydrous $Cu(OAc)_2$ and methyl diazoacetate (concentrations $C_m = 523 \cdot 10^{-4}$ mol/l and $C_m = 2.29 \cdot 10^{-4}$ mol/l, respectively) were prepared. For these solutions the values of extinction molar coefficients were determined: $\lambda_1 = 274$ nm, ($\epsilon_1 = 1690$) and $\lambda_3 = 224$ nm, ($\epsilon_3 = 2868$) for $Cu(OAc)_2$ solution and $\lambda_1 = 274$ nm, ($\epsilon_1 = 0$), and $\lambda_3 = 224$ nm, ($\epsilon_3 = 1838$) for $N_2CHCO_2CH_3$ solution.

A content of modified syndiotactic 1,2-polybutadiene **3** in a solution during the cyclopropanation with methyl diazoacetate was estimated using a UV-spectroscopy method on an intensive $n \rightarrow \pi^*$ absorption band in the region 220–225 nm, which corresponds to the transition of a C=O bond of carbonyl containing compounds [7]. For this purpose 10 ml of a reaction mass were taken in 15, 30, and 60, 120 min, separated from a catalyst, reprecipitated twice from a system chloroform/ethanol, dried in vacuum at 333 K up to a constant mass. UV-spectra of conversion samples were registered.

A dynamic thermogravimetric analysis of initial and modified syndiotactic 1,2-polybutadiene was performed in the air on a Derivatograph Q-1000 of system F. Paulic, I. Paulic, L. Ardey of a Hungarian company "MOM". The rate of the temperature growth was 5 grad/min. The sensitivity of balance was 100 mg/100 scale division. The temperature at which 1 % of the mass loss of the sample tested was observed was assumed as the temperature of the decomposition start.

3. Results and Discussion

Earlier, we have developed a novel catalytic system $Cu(OAc)_2$ -2,4-Lut- $ZnCl_2$ to produce the products of the cyclopropanation of low molecular unsaturated compounds with methyl diazoacetate in high yields [7].

Isobutylene oligomers **1,2** containing a three-substituted C=C bound react with methyl diazoacetate in the presence of $Cu(OAc)_2$ -2,4-Lut- $ZnCl_2$ to give corresponding cyclopropanecarboxylic acid methyl esters **4, 5** in yields 32 and 19 %, respectively. Besides esters **4** and **5**, from the reaction mass products of the recombination of methoxycarbonylcarbene – fumaric and maleic acids methyl esters, were isolated in the summary yield 20 %.

The results obtained confirm the data of the cyclopropanation of thermal olefins and dienes with methyl diazoacetate under similar conditions [8].

The analysis of the ^{13}C NMR spectra confirms the presence of a cyclopropane fragment in compounds **4** and **5**. The characteristic signals of carbon atoms in a cyclopropane cycle appear in the region $\delta^{13}C$ 12–17 ppm, a

signal of quaternary carbon atom of the ester group resonates in the region $\delta^{13}\text{C}$ 169–171 ppm. The results of the IR spectroscopy of compounds **4** and **5** testified to the presence of the cyclopropane ring and the ester group. In comparison with starting oligomers in IR spectra of ester **4** and **5** absorption bands appear, which correspond to the oscillation of the C=O bond at the region 1732–1747 cm^{-1} , C–O bond – at 1170–1177 cm^{-1} , as well as to the deformation oscillation of the C–H bond of the cyclopropane ring and methoxy group.

To modify syndiotactic 1,2-polybutadiene (SPB) **3** the cyclopropanation with methyl diazoacetate in the presence of a catalytic system $\text{Cu}(\text{OAc})_2$ -2,4-Lut-ZnCl₂ was carried out to produce functionalized polymer **6** containing *m*-links with a cyclopropane fragment in a yield 20 %.

The presence of cyclopropane characteristic signals of an ester group and cyclopropane ring in the ¹H, ¹³C NMR and IR spectra of compound **6** testified to the introduction of the cyclopropane fragments on the C=C bond into the macromolecule structure (Table 1).

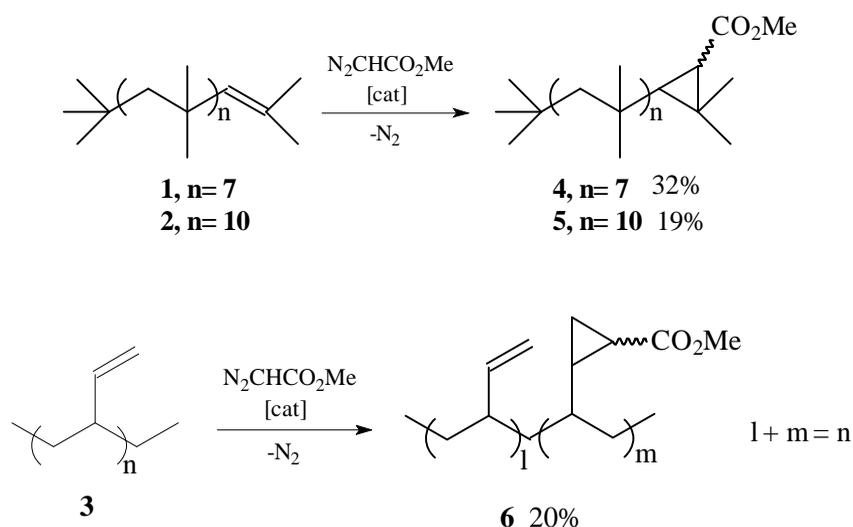


Table 1

Spectral characteristics of the compounds

Compound	UV spectrum, λ/nm	IR spectrum, ν/cm^{-1}	NMR ¹³ C spectrum, δ/ppm
N ₂ CHCO ₂ CH ₃	224 (C=O)	1669 ($\nu(\text{C}=\text{O})$)	45.9 (CHN ₂) 51.7 (OCH ₃) 167 (C=O)
 3	-	908 and 993 ($\nu(=\text{CH})$); 1417($\nu(=\text{CH}_2)$), 1456, 1639($\nu(\text{C}=\text{C})$)	39.0 (CH); 41.4 (CH ₂); 114.7 (CH ₂ =); 143.2 (CH=)
 6	223.8 (C=O)	1752 ($\nu(\text{C}=\text{O})$)	51.0 (OMe) 170.1 (C=O)

The UV-spectrum of polymer **6** differs from that of starting polybutadiene **3** that testified the presence of several chromophor groups in its macromolecule. The differential absorption spectrum of the polymer solutions reduced to the same concentration $[3] = [6] = 0.417 \text{ g/l}$ (Fig. 1, curve 3 obtained *via* the subtraction of curve 1 from curve 2) shows three absorption maxima: $\lambda_1 = 274 \text{ nm}$, $\lambda_2 = 257 \text{ nm}$ and $\lambda_3 = 223.8 \text{ nm}$.

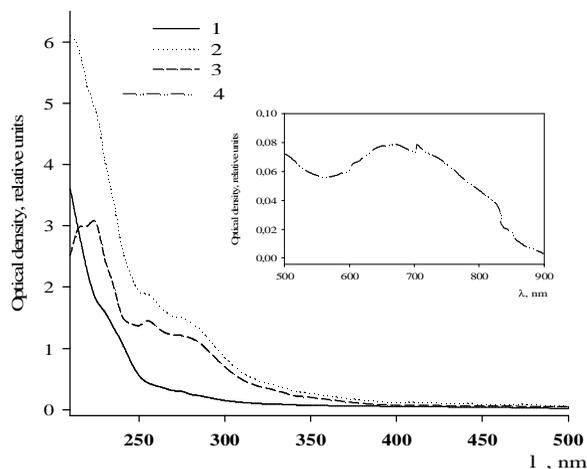


Fig. 1. Electron absorption spectra of solutions ($[3] = [6] = 0.417 \text{ g/l}$): solution of polymer **3** in Et_2O (1); solution of functionalized polymer **6** in Et_2O (2); the differential spectrum of curves 2 and 1 (3) and solution of $\text{Cu}(\text{OAc})_2$ in Et_2O (4)

The position of absorption maximum observed on the differential spectrum at $\lambda = 223.8 \text{ nm}$ (Fig. 1, curve 3) coincides with $\lambda = 224 \text{ nm}$ ($\epsilon = 18381/\text{mol}\cdot\text{cm}$) characteristic for the $n \rightarrow \pi^*$ transition of a C=O bond in an ester group of methyldiazoacetate. That indicates that functionalized polymer **6** contains the same chromophor group as diazoacetic acid methyl ester.

The study of conversion samples of polybutadiene **3** cyclopropanation using an UV spectroscopy method showed that the increase of the absorption at $\lambda = 224 \text{ nm}$ is accompanied by the change of color from colorless up to light green (Table 2).

Table 2

Change of color of the solution and content of functionalized 1,2-polybutadiene **6**

Time, min	Absorption at $\lambda = 224 \text{ nm}$	Color of the polymer solution in Et_2O	Molar part of the polymer 6
0	1.451	Colorless	0
15	1.810	Daffodil	0.044
30	3.084	Yellow	0.047
60	2.010	Light-green	0.057
120	2.390	Light-green	0.085
240	4.115	Light-green	0.118

Dry residues of conversion samples differ considerably by the intensity of the coloration (from yellow to green), which is caused by the presence of a catalyst, coordinated with a polymer macromolecule. The results are testified by the dynamic thermogravimetric analysis data: after polymer burning an insignificant amount of black powder (CuO) is remained.

A summary content of functionalized links in syndiotactic 1,2-polybutadiene owing to the addition of metoxycarbonylcarbene on a C=C bond estimated using an UV spectrometry is 12–13 mol %.

According to the results of dynamic thermogravimetric analysis the temperature of the decomposition start of modified 1,2-polybutadiene **6** was higher by 50 K than that of initial polymer **6**. The destruction of both samples proceeds in two steps. The losses of the mass responsible for the first decomposition step (at the region 523–673 K) is half in case of modified 1,2-polybutadiene as compared with the initial sample, but at the region 673–773 K (the second decomposition step) burning of both samples proceeds approximately at the same rate (Fig. 2).

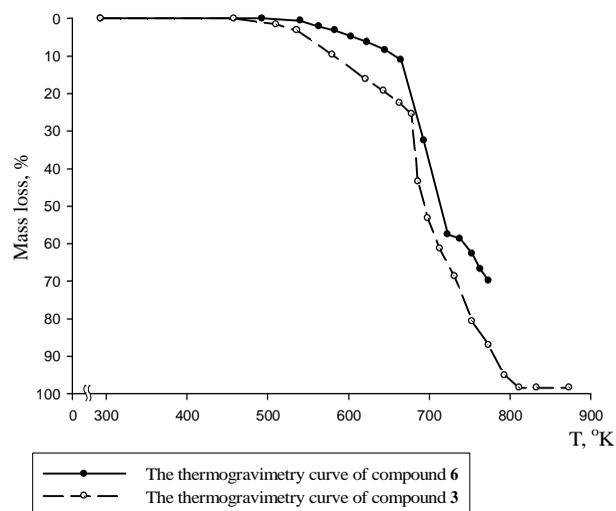


Fig. 2. The thermogravimetric analysis of the starting **3** and functionalized 1,2-polybutadiene **6** on air

4. Conclusions

Thus, a novel simple and effective catalyst $\text{Cu}(\text{OAc})_2\text{-2,4-Lut-ZnCl}_2$ of cyclopropanation of C=C bonds of both isobutylene oligomers and syndiotactic 1,2-polybutadiene with methyldiazoacetate was proposed. Syndiotactic 1,2-polybutadiene functionalized with cyclopropane fragments possesses higher thermostability in comparison with the initial polymer.

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ФУНКЦІОНАЛІЗАЦІЯ ІЗОБУТИЛЕНОВИХ ОЛІГОМЕРІВ ТА 1,2-ПОЛІБУТАДІЕНІВ МЕТИЛДІАЗОАЦЕТАТОМ У ПРИСУТНОСТІ КАТАЛІТИЧНОЇ СИСТЕМИ $\text{Cu}(\text{OAc})_2\text{-}2,4\text{-Lut-ZnCl}_2$

Анотація. Запропоновано каталітичний метод хімічної модифікації ізобутиленових олігомерів і синдіотактичного 1,2-полібутадієну по $\text{C}=\text{C}$ зв'язкам внаслідок реакції 1,2-циклоприсєднання метоксикарбонілкарбену у присутності $\text{Cu}(\text{OAc})_2\text{-}2,4\text{-Lut-ZnCl}_2$.

Ключові слова: хімічна модифікація полімерів, метилдіазаацетат, металокомплексний каталіз.