Cu(OAc)$_2$-2,4-Lut-ZnCl$_2$ EFFICIENT CATALYST OF FUNCTIONALIZATION OF ISOBUTYLENE OLGOMERS AND 1,2-POLYBUTADIENE WITH METHYLDIAZOACETATE

1Bashkir State University, 32 Zaki Validi str., 450005 Ufa, Russia
2Institute of Organic Chemistry of Ufa Centre of Sciences of the Russian Academy of Sciences, 71 Oktiabria ave., 71450054 Ufa, Russia; dokichev@anrb.ru
3Emmanuel Institute of Biochemical Physics of the Russian Academy of Sciences, 4 Kosygina str., 119334 Moscow, Russia; GEZaikov@yahoo.com

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Abstract: The possibility of [1+2] cycloaddition of metoxycarbonylcarbene generated by methyldiazoacetate decomposition in the presence of Cu(OAc)$_2$-2,4-Lut-ZnCl$_2$, to the C=C bond of isobutylene oligomers and syndiotactic 1,2-polybutadiene was studied. A comparative analysis of physical and chemical properties of the starting compounds and their functionalized products was made.

Keywords: chemical modification of polymers, methyldiazoacetate, [1+2] cycloaddition.

1. Introduction

Chemical modification of polymers allowing to change their physical and chemical properties within a wide range is one of the significant directions of macromolecular chemistry. Addition reactions as a way of functionalization hold a special place in chemistry of diene polymers due to the high reactivity of the C=C bond in a macromolecule link [1].

Syndiotactic 1,2-polybutadiene as well as isobutylene oligomers are convenient unsaturated substrates for chemical modification. Reactive double bonds in side substituents of 1,2-polybutadiene and terminal or trisubstituted C=C bonds in oligoisobutylene make it possible for various chemical groupings to be introduced in a polymer composition as the basis for synthesizing the products with new properties. Different classes of substances may serve as reaction reagents, for instance, epoxies, aromatic amines, etc. [2].

Polymers with structures containing cyclopropane rings together with unsaturated bonds are of particular interest. For example, polycyclopropane derivatives of fatty acids isolated from *Streptoverticillum fervens* and *Streptomyces* belong to antibiotics and inhibit the albuminous transfer of cholectery ether [3].

The cyclopropane fragment can be introduced into the macromolecule structure by polymerization as well, in particular, resulting from cyclocopolymerization of 1,3-butadiene and ethylene [4]. However, this technique being quite challenging to perform the chemical modification of high-molecular compounds is more preferable.

The purpose of the present study is to investigate the interaction of syndiotactic 1,2-polybutadiene and isobutylene oligomers with methyldiazoacetate in the presence of Cu(OAc)$_2$-2,4-Lut-ZnCl$_2$ catalytic system and analyze the properties of the starting compounds (isobutylene oligomers and syndiotactic 1,2-polybutadiene) vs. their functionalized derivatives.

2. Experimental

The $^1$H and $^{13}$C NMR spectra were registered on a spectrometer “Bruker AM-300” (300.13 and 75.47MHz, respectively) in CDCl$_3$. The IR spectra were recorded on a Forier-spectrophotometer Shimadzu IR-Prestige-21 in a liquid film. Cu(OAc)$_2$ (“Vekton”) ZnCl$_2$ (anhydro-)(“Reaktiv”), oligomers of isobutylene (I) ($n = 7, M_n = 504, n_k^{20} = 1.4671$), (II) ($n = 10, M_n = 700, n_k^{20} = 1.4701$), syndiotactic 1,2-polybutadiene (III) (JSC “Efremovski zavod SK”), $M_n = 52600, m_w = 116600$, degree of crystallinity is 18 %, syndiotacticity is 53 %) were used in our work. The solvents used (EtO, CH$_2$Cl$_2$, C$_6$H$_{14}$, (CH$_3$)$_2$CO, petroleum ether (bp 313–343 K), EtOH, CHCl$_3$) and 2,4-lutidine were purified according to standardized techniques [5, 6].
Isobutylene oligomers were purified via reprecipitation in the hexane/acetone system. The solvent was removed at the reduced pressure. Oligomers (I, II) were analyzed by $^{13}$C NMR and IR spectrometry.

Syndiotactic 1,2-polybutadiene was purified via reprecipitation in the chloroform/ethanol system. Then the polymer was twice washed with alcohol. The polymer was dried in vacuum at 333 K up to a constant mass.

Syndiotactic 1,2-polybutadiene (I) $n = 974$. Found (%): C 88.52, 88.47; H 11.42, 11.45. Calc. (%): C 88.87; H 11.13. $^1$H NMR -spectrum (δ, ppm): 1.17 (m, 2H); 2.09 (m, 1H); 4.85; 4.95 (m, 2H, CH$_2$=); 5.34 (m, 1H, CH=). $^{13}$C NMR spectrum, (δ, ppm): 39.0 (CH); 41.4 (CH$_2$); 114.7 (CH$_2$=); 143.2 (CH=). IR spectrum, v/cm$^{-1}$: 376, 669, 908 and 993 (s=CH), 1074, 1151, 1377, 1417(=CH$_3$), 1456, 1639(C=O), 2853, 2922, 2951.

Cyclopropanation of isobutylene oligomers with methylidiazocacetate in the presence of the Cu(OAc)$_2$-2,4-lutidine-ZnCl$_2$ catalytic system was carried out at 313 K by slow adding of 4 mmol of methylidiazocacetate in 7 ml of CH$_2$Cl$_2$ to a stirred solution containing 0.005 mmol of anhydrous ZnCl$_2$, 0.03 mmol of 2,4-lutidine, 0.04 mmol of Cu(OAc)$_2$, and 4 mmol of isobutylene oligomer (I, II) in 17 ml of CH$_2$Cl$_2$ till the gassing end. A solvent was removed at the reduced pressure, petroleum ether was added to the residuum, a catalytic system was isolated as dark-brown oil. Petroleum ether was evaporated at the reduced pressure. The product was purified twice via reprecipitation in the chloroform/ethanol system and dried in vacuum at 333 K up to a constant mass.

Functionalized syndiotactic 1,2-polybutadiene (VI). Yield is 20 %. Found (%): C 80.34, 80.32; H 10.36, 10.37; O 7.94, 7.98. $^1$H NMR spectrum (δ, ppm): 0.58 (E-isomer), 0.60 (Z-isomer) (m, 1H, CH$_2$ in the cyclopropane ring); 0.95 (Z-isomer) 1.02 (E-isomer) (m, 1H, CH$_2$ in the cyclopropane ring); 1.16 (m, 1H, CH); 1.57 (m, 1H, CH, in the cyclopropane ring); 3.65 (s, 3H, OMe). $^{13}$C NMR spectrum (δ, ppm): 14.1 (Z-isomer) 14.2 (E-isomer) (CH$_2$); 25.4 (Z-isomer) 25.5 (E-isomer) (CH); 27.6 (Z-isomer) 27.9 (E-isomer) (CH); 39.1 (CH$_2$); 41.7 (CH); 51.3 (OMe); 174.2 (C=O). IR spectrum, v/cm$^{-1}$: 3669, 758, 908 and 994 (=CH), 1084, 1168, 1263(OMe), 1342, 1417(=CH$_3$), 1448(CH in the cyclopropane ring), 1639(C=O), 1752(C=O), 2843, 2916, 2970, 3072 (CH$_2$ in the cyclopropane ring).

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

The viscosity of the solutions was determined at 298 K by Ubbelode capillary viscosimeter. The effluence time of solutions of oligomers and polymers in chloroform at different concentrations was measured. On the basis of obtained values for the solvent and polymers solutions the magnitudes of a relative ($\eta_r = \tau/\tau_0$) and specific (\eta_p = \eta_r\eta_v) viscosity were calculated. The characteristic viscosity was found by the method of
double extrapolation of the \( \ln \eta / c \) and \( \eta / c \) values to the zero concentration.

The \( M_{\eta(n)} \) value for investigated specimens was found by the equation:

\[
M_{\eta(n)} = \left( \frac{S_0 \cdot \eta_0 \cdot [\eta]^{1/3} \cdot N_A}{\Phi^{1/3} \cdot \rho^{-1} \cdot (1 - \rho \cdot \eta_0)} \right)^{3/2}
\]

where \( S_0 \) – sedimentation constant; \( \eta_0 \) – solvent viscosity, \( \Phi^{1/3} \) – characteristic viscosity, \( N_A \) – Avogadro constant (6.021 \times 10^{23} \text{ mol}^{-1}); \( \rho^{-1} \) – Archimedean factor (factor of floatability); \( v \) – partial specific volume; \( \rho_0 \) – solvent density.

The sedimentation coefficient \( S_e \) was determined by ultracentrifuge MOM-3180 at a rotor speed of 50000 rpm, 298 K and concentration range of polymer solution 0.1–0.5 g·dl⁻¹.

### 3. Results and Discussion

Earlier, we have developed a novel catalytic system \( \text{Cu(OAc)}_2 \cdot 2,4\text{-Lut-ZnCl}_2 \) to produce the products of cyclopropanation of low molecular unsaturated compounds with methyldiazoacetate in high yields [7].

Isobutylene oligomers 1,2-containing a three-substituted C≡C bound react with methyldiazoacetate in the presence of \( \text{Cu(OAc)}_2 \cdot 2,4\text{-Lut-ZnCl}_2 \) to give corresponding cyclopropancarboxylic acid methyl esters (IV, V) in yields of 32 and 19 %, respectively. Besides esters (IV) and (V), products of methoxycarbonylcarbene recombination – fumaric and maleic acids’ methyl esters were isolated from the reaction mass in the total yield of 20 %.

![Diagram](image)

It should be noticed that the \( \text{Cu(OAc)}_2 \cdot 2,4\text{-Lut-ZnCl}_2 \) catalytic system in this interaction shows an activity comparable with that in reactions of cyclopropanation of terminal monoolefins (hexane-1) and 1,3-dienes with methyldiazoacetate. Increasing of a carbon chain length leads to decreasing of target ethers yields [8].

The analysis of the \( ^{13}\text{C} \) NMR spectra confirms the presence of a cyclopropane fragment in compounds (IV) and (V). The characteristic signals of carbon atoms in a cyclopropane cycle appear in the region of \( \delta^{13}\text{C} = 12–17 \) ppm, a signal of quaternary carbon atom of the ester group resonates in the region of \( \delta^{13}\text{C} = 169–171 \) ppm. In comparison with initial oligomers the absorption band appears in IR spectra of ester (IV) and (V), which corresponds to oscillation of the C=O bond in the region of 1732–1747 cm⁻¹, the 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 OMe group. Further, identity of the structures (IV, V) was confirmed via determination of their molecular weights by measuring the condensation heat effects. It is registered that \( M_e \) values for products modified by methoxycarbonylcarbene and starting compounds differ by 72 units.

The starting isobutylene oligomers and functionalized products (IV, V) dissolve well in various organic solvents (benzene, hexane, diethyl ether). The characteristic viscosity values for oligomers (I, II) and compounds (IV, V) in chloroform have no principle differences ([\( \eta \]) = 0.0171 dl·g⁻¹ for the product (IV), [\( \eta \]) = 0.0165 dl·g⁻¹ for the starting isobutylene oligomer (I); [\( \eta \]) = 0.021 dl·g⁻¹ for the product (V), [\( \eta \]) = 0.019 dl·g⁻¹ for the starting isobutylene oligomer (II)). Calculated Huggins constants for parties of both processes have values > 10⁻²; it indicates a weak thermodynamic affinity of both starting oligomers and their products to chloroform. At the same time \( K_e \) values for compounds (IV) and (V) are less than corresponding values for oligomers (I) and (II).

To modify syndiotactic 1,2-polybutadiene (SPB) (III) cyclopropanation with methyldiazoacetate in the presence of \( \text{Cu(OAc)}_2 \cdot 2,4\text{-Lut-ZnCl}_2 \) catalytic system was carried out to produce a functionalized polymer (VI) containing \( m \)-links with a cyclopropane fragment in the yield of 20 %.

![Diagram](image)

The presence of cyclopropane ester group and cyclopropane ring characteristic signals in the \( ^{1}H \) NMR, \( ^{13}\text{C} \) MR and IR spectra of compound (VI) testified to the introduction of the cyclopropane fragments on the C=C bond into the macromolecule structure. The NMR method also evidenced that cycloaddition of methoxycarbonylcarbene on the SPB C=C bond periodically takes place on one of ten vinyl C=C bonds at average; in \( ^{13}\text{C} \) NMR spectrum of the polymer (VI) the cyclopropane ring carbon atoms resonate in the area of 14, 25 and 28 ppm correspondingly. The moiety of cis- and trans-isomers of functionalized links of the compound (VI) is nearly equal.

Research of solubility of the starting 1,2-SPB and modified polymer (VI) showed that the product of cyclopropanation with methyldiazoacetate dissolves better in chloroform, hexane and toluene. Comparison of characteristic viscosity values for starting and functionalized polymers ([\( \eta \]) = 1.72 and 2.38 dl·g⁻¹ for compounds (III) and (VI), correspondingly) allowed to
determine Huggins constants (\( K_r \)) for both higher molecular compounds. The \( K_r \) value for functionalized 1,2-SPB (\( K_r = 0.43 \)) is less than for starting polybutadiene (\( K_r = 0.59 \)). The value < 0.5 indicates that chloroform is a good solvent for the cyclopropane product (VI) [9].

Apparent molecular weights (\( M_{\text{app}} \)) of the starting and functionalized syndiotactic 1,2-polybutadiene were determined by viscosity and sedimentation methods.

Sedimentation constants \( S_0 \) were determined by extrapolation of \( 1/S \), \( n \) to zero concentration. Results of determination of the apparent molecular weights \( M_{\text{app}} \) for starting and functionalized SPB are shown in the Table.

On the basis of \( M_{\text{app}} \) calculations the number of elementary links \( n \) and \( k \) were determined; for the product (VI) they are equal to 685 and 103 correspondingly.

<table>
<thead>
<tr>
<th>Compound</th>
<th>([\eta]_s)</th>
<th>(1-np_0)</th>
<th>(S_0 10^{13} \cdot s)</th>
<th>(M_{\text{app}})</th>
</tr>
</thead>
<tbody>
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<td>III</td>
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<td>1.19</td>
<td>8.4</td>
<td>37000</td>
</tr>
<tr>
<td>VI</td>
<td>2.3</td>
<td>1.30</td>
<td>10.1</td>
<td>50000</td>
</tr>
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</table>

According to the results of dynamic thermogravimetry analysis the temperature of the decomposition start of a modified 1,2-polybutadiene 60 was higher by 50% than that of initial polymer (VI). The destruction of both samples proceeds in two steps. The losses of the mass responsible for the first decomposition step (in the region of 523–673 K) is half in case of modified 1,2-polybutadiene than for the initial sample, but in the region of 673–773 K (the second decomposition step) burning of both samples proceeds approximately at the same rate (see Fig.).

### 3. Conclusions

1. It has been shown that Cu(OAc)$_2$-2,4-Lut-ZnCl$_2$ is an effective catalyst of cyclopropanation with methyl diazoacetate of \( C=\)C bonds of isobutylene oligomers as well as of syndiotactic 1,2-polybutadiene.

2. It has been determined that chloroform is a good solvent for functioning with methoxycarbonylcarbene syndiotactic 1,2-polybutadiene. Increasing of the characteristic viscosity of modified syndiotactic 1,2-polybutadiene is followed by decreasing of a viscometric Huggins constant.

3. As a result of functionalization by cyclopropane fragments syndiotactic 1,2-polybutadiene has been obtained with higher thermal stability compared to the starting polymer.

### References