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Cu(OAc)₂-2,4-Lut-ZnCl₂ EFFICIENT CATALYST OF FUNCTIONALIZATION OF ISOBUTYLENE OLIGOMERS AND 1,2-POLYBUTADIENE WITH METHYLDIAZOACETATE

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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-ZnCl₂, 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 *Streptovorticillum fervens* and *Streptomyces* belong to antibiotics and inhibit the albuminous transfer of cholesteryl 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-ZnCl₂ catalytic system and analyze the properties of the starting compounds (isobutylene oligomers and syndiotactic 1,2-polybutadiene) vs. their functionalized derivatives.

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 Fourier-spectrophotometer Shimadzu IR-Prestige-21 in a liquid film. Cu(OAc)₂ ("Vekton") ZnCl₂ (anhydrous) ("Reaktiv"), oligomers of isobutylene (**I**) (*n* = 7, *M_n* = 504, *n_d²⁰* = 1.4671), (**II**) (*n* = 10, *M_n* = 700, *n_d²⁰* = 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 (Et₂O, CH₂Cl₂, C₆H₁₄, (CH₃)₂CO, petroleum ether (bp 313–343 K), EtOH, CHCl₃) 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. ^1H NMR -spectrum (d , ppm): 1.17 (m, 2H); 2.09 (m, 1H); 4.85; 4.95 (m, 2H, $\text{CH}_2=$); 5.34 (m, 1H, $\text{CH}=\text{}$). ^{13}C NMR spectrum, (d , ppm): 39.0 (CH); 41.4 (CH_2); 114.7 ($\text{CH}_2=$); 143.2 ($\text{CH}=\text{}$). IR spectrum, n/cm^{-1} : 376, 669, 908 and 993 ($=\text{CH}$), 1074, 1151, 1377, 1417($=\text{CH}_2$), 1456, 1639($\text{C}=\text{C}$), 2853, 2922, 2951.

Cyclopropanation of isobutylene oligomers with methyldiazoacetate in the presence of the $\text{Cu}(\text{OAc})_2$ -2,4-lutidine- ZnCl_2 catalytic system was carried out at 313 K by slow adding of 4 mmol of methyldiazoacetate in 7 ml of CH_2Cl_2 to a stirred solution containing 0.005 mmol of anhydrous ZnCl_2 , 0.03 mmol of 2,4-lutidine, 0.04 mmol of $\text{Cu}(\text{OAc})_2$ and 4 mmol of isobutylene oligomer (**I**, **II**) in 17 ml of CH_2Cl_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 removed at a reduced pressure; the residue was analyzed using ^1H NMR, ^{13}C NMR and IR spectroscopies. The yields of compounds (**IV**, **V**) were determined on the basis of ^1H NMR-spectra (benzene was used as an internal standard).

Functionalized isobutylene oligomer (**IV**) ($n = 7$; $n_d^{20} = 1.4583$). Yield is 32 %. Found (%): C 81.32, 81.36; H 13.14, 13.08; O 5.54, 5.56. $\text{C}_{39}\text{H}_{76}\text{O}_2$. 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). ^{13}C NMR 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 ($\text{C}=\text{O}$). IR spectrum, n/cm^{-1} : 546, 1095 and 1169($\text{C}-\text{O}$), 1242, 1278(OMe), 1364, 1375, 1433, 1454(CH of the cyclopropane ring), 1732($\text{C}=\text{O}$), 1748, 2868, 2954.

Functionalized isobutylene oligomer (**V**) ($n = 10$; $n_d^{20} = 1.4689$). Yield is 19 %. Found (%): C 82.78, 82.84; H 13.07, 12.98; O 4.15, 4.21. $\text{C}_{51}\text{H}_{100}\text{O}_2$. 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 ($\text{C}=\text{O}$). IR spectrum, n/cm^{-1} : 550, 1101 and 1177($\text{C}-\text{O}$), 1242, 1291(OMe), 1364, 1377, 1452 (CH in the cyclopropane ring), 1734($\text{C}=\text{O}$), 2868, 2930.

Cyclopropanation of syndiotactic 1,2-polybutadiene with the help of methyldiazoacetate in the presence of the $\text{Cu}(\text{OAc})_2$ -2,4-lutidine- ZnCl_2 catalytic system was carried out *via* slow adding of 37 mmol (calculating on one elementary link of the polymer chain) of methyldiazoacetate 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 $\text{Cu}(\text{OAc})_2$, 37 mol of syndiotactic 1,2-polybutadiene (**III**) in 50 ml of CH_2Cl_2 until the gassing end. The solvent was removed at the reduced pressure, petroleum ether was added to the residue, a catalytic system was separated 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. ^1H NMR spectrum (d , 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 (d , 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 ($\text{C}=\text{O}$). IR spectrum, n/cm^{-1} : 669, 758, 908 and 994 ($=\text{CH}$), 1084, 1168, 1263(OMe), 1342, 1417($=\text{CH}_2$), 1448(CH in the cyclopropane ring), 1639($\text{C}=\text{C}$), 1752($\text{C}=\text{O}$), 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 Ubellode 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 ($\eta_{rel} = \tau/\tau_0$) and specific ($\eta_{sp} = \eta_{rel} - 1$) viscosity were calculated. The characteristic viscosity was found by the method of

double extrapolation of the $\ln \eta_{rel}/s$ and η_{sp}/s values to the zero concentration.

The $M_{s[\eta]}$ value for investigated specimens was found by the equation:

$$M_{s[h]} = \left(\frac{S_0 \cdot h_0 \cdot [h]^{1/3} \cdot N_A}{\Phi^{1/3} \cdot p^{-1} \cdot (1 - \nu r_0)} \right)^{3/2}$$

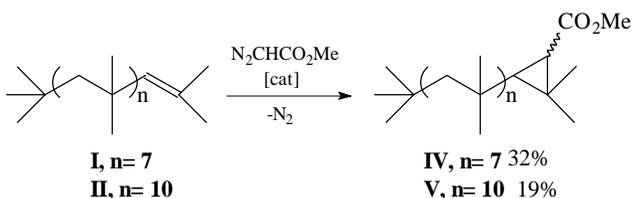
where S_0 – sedimentation constant; η_0 – solvent viscosity, Pz; $[\eta]$ – characteristic viscosity, dl·g⁻¹; N_A – Avogadro constant (6·10²³ mol⁻¹); $\Phi^{1/3} p^{-1} = 2.5 \cdot 10^6$; $1 - \nu r_0$ – Archimedean factor (factor of floatability); ν – partial specific volume; ρ_0 – solvent density.

The sedimentation coefficient S_c 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 Cu(OAc)₂-2,4-Lut-ZnCl₂ 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 bond react with methyldiazoacetate in the presence of Cu(OAc)₂-2,4-Lut-ZnCl₂ to give corresponding cyclopropanecarboxylic 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 %.



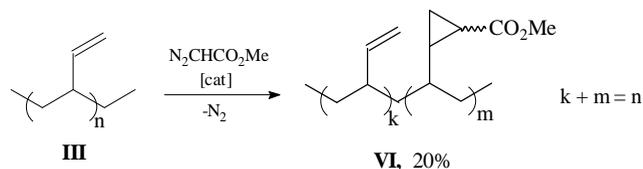
It should be noticed that the Cu(OAc)₂-2,4-Lut-ZnCl₂ catalytic system in this interaction shows an activity comparable with that in reactions of cyclopropanation of terminal monoolefins (hexane-1) and 1,3-dienes with methyldiazoacetate. Increasing of a carbon chain length leads to decreasing of target ethers yields [8].

The analysis of the ¹³C 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 quarternary 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 1732–1747cm⁻¹, the C–O bond – at 1170–1177cm⁻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_n 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 dissolvents (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 > 10³; it indicates a weak thermodynamic affinity of both starting oligomers and their products to chloroform. At the same time K_x 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 Cu(OAc)₂-2,4-Lut-ZnCl₂ catalytic system was carried out to produce a functionalized polymer (**VI**) containing *m*-links with a cyclopropane fragment in the yield of 20 %.



The presence of cyclopropane ester group and cyclopropane ring characteristic signals in the ¹H NMR, ¹³C 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 ¹³C 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_x) for both higher molecular compounds. The K_x value for functionalized 1,2-SPB ($K_x = 0.43$) is less than for starting polybutadiene ($K_x = 0.59$). The value < 0.5 indicates that chloroform is a good solvent for the cyclopropane product (VI) [9].

Apparent molecular weights ($M_{s[\eta]}$) 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 $1/S_c$ values to zero concentration. Results of determination of the apparent molecular weights $M_{s[\eta]}$ for starting and functionalized SPB are shown in the Table.

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

Table

Apparent molecular weights of the compounds (III) and (VI)

Compound	$[\eta]$, dl·g ⁻¹	$1-\nu\rho_0$	$S_0 \cdot 10^{13}$, s	$M_{s[\eta]}$
III	1.7	1.19	8.4	37000
VI	2.3	1.30	10.1	50000

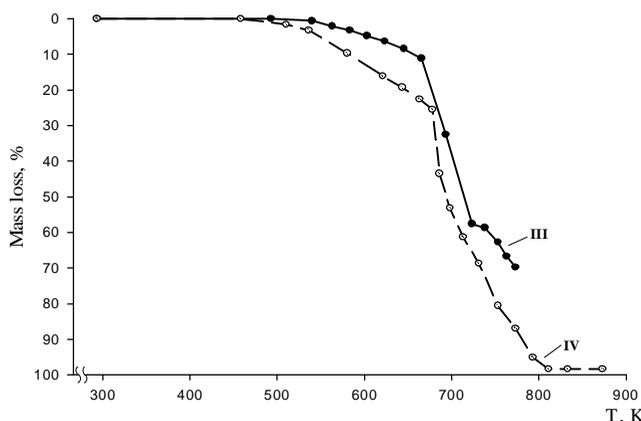


Fig. 1. Thermogravimetry analysis of the starting (III) and functionalized 1,2-polybutadiene (VI) in the air

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 $\text{Cu}(\text{OAc})_2\text{-}2,4\text{-Lut-ZnCl}_2$ is an effective catalyst of cyclopropanation with methyldiazoacetate 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.

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Cu(OAc)₂-2,4-Lut-ZnCl₂ – ЕФЕКТИВНИЙ КАТАЛІЗАТОР ФУНКЦІОНАЛІЗАЦІЇ ІЗОБУТИЛЕНОВИХ ОЛІГОМЕРІВ ТА 1,2-ПОЛІБУТАДІЕНІВ МЕТИЛДІАЗОАЦЕТАТОМ

Анотація. Вивчено можливість [1+2] циклоприсднання метоксикарбонілкарбену, одержаного розкладом метилдіазоацетату в присутності $\text{Cu}(\text{OAc})_2\text{-}2,4\text{-Lut-ZnCl}_2$, до C=C зв'язків ізобутиленових олігомерів та синдіотактичного 1,2-полібутадієну. Проведено порівняльний аналіз фізичних і хімічних властивостей вихідних і функціональних продуктів.

Ключові слова: хімічна модифікація полімерів, метилдіазоацетат, [1+2] циклоприсднання.