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MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

$Cu(OAc)_2$–2,4-Lutidine–$ZnCl_2$ as an Effective Catalyst of Functionalization of Isobutylene Oligomers and 1,2-Polybutadiene with Methyl Diazoacetate

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Abstract—The possibility of [1+2]-cycloaddition of methoxycarbonylcarbene generated by catalytic decomposition of methyl diazoacetate in the presence of the $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ system to the carbon–carbon double bound in isobutylene oligomers and syndiotactic 1,2-polybutadiene was examined. A comparative analysis of physicochemical properties of the starting compounds and their functionalized products was performed.

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One of important lines in the development of macromolecular chemistry is chemical modification of polymers, allowing the physical and chemical properties of products to be varied in a wide range. Addition reactions as a functionalization route occupy a particular place in the chemistry of diene polymers because of high activity of the C=C bond in the macromolecule unit [1].

Syndiotactic 1,2-polybutadiene and isobutylene oligomers are convenient unsaturated substrates for chemical modification. The presence of reactive double bonds in pendant substituents in syndiotactic 1,2-polybutadiene and of terminal or trisubstituted C=C bonds in oligoisobutylene allows introduction of various chemical groups and preparation of products with new properties on the basis of these polymers. Substances of diverse classes, e.g., epoxides and aromatic amines, can be used as addition reagents [2].

Of particular interest are polymers containing along with unsaturated bonds cyclopropane rings. To such polymers belong polycyclopropane derivatives of fatty acids isolated form *Streptoverticillium fervens* and *Streptomyces* [3].

A cyclopropane fragment can be introduced into a macromolecule by cyclocopolyisomerization of 1,3-butadiene and ethylene [4]. This procedure, however, is very complex, and chemical modification of a macromolecular compound is preferable.

This paper deals with the reaction of syndiotactic 1,2-polybutadiene and of isobutylene oligomers with methyl diazoacetate in the presence of the catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ and with comparative analysis of the properties of the starting compounds (isobutylene oligomers and syndiotactic 1,2-polybutadiene) and their functionalized derivatives.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$, and the IR spectra, on a Shimadzu IR-Prestige-21 Fourier spectrometer, with samples prepared as liquid films. In our study we used $Cu(OAc)_2$ (Vekton), anhydrous $ZnCl_2$ (Reaktiv), isobutylene oligomers **I** ($n = 7$, $M_n \approx 504$, $n_D^{20} = 1.4671$) and **II** ($n = 10$, $M_n \approx 700$, $n_D^{20} = 1.4701$), and syndiotactic 1,2-polybutadiene (**III**) (Efremov Synthetic Rubber Plant, Joint-Stock Company; $M_n = 52600$, $M_w = 116600$, degree of crystallinity 18%, syndiotacticity 53%). The solvents used in this study (Et_2O, CH_2Cl_2, C_6H_{14}, $(CH_3)_2CO$, petroleum ether, EtOH, $CHCl_3$) and 2,4-lutidine were purified by standard procedures [5, 6].

Isobutylene oligomers **I** and **II** were purified by reprecipitation in the hexane–acetone system. The solvent was removed under reduced pressure. Oligomers **I** and **II** were analyzed by ^{13}C NMR and IR spectroscopy.

Syndiotactic 1,2-polybutadiene was purified to remove the stabilizer by reprecipitation from chloroform–ethanol. Then the polymer was washed twice with alcohol and vacuum-dried at 60°C to constant weight.

Syndiotactic 1,2-polybutadiene III, *n* = 974. Found, %: 88.52, 88.47; H 11.42, 11.45.Calculated, %: 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_C, ppm: 39.0 (CH), 41.4 (CH_2), 114.7 (CH_2=), 143.2 (CH=). IR spectrum, ν, cm^{-1}: 376, 669, 908, 993 (=CH); 1074, 1151, 1377, 1417 (=CH_2); 1456, 1639 (C=C); 2853, 2922, 2951.

The reaction of isobutylene oligomers with methyl diazoacetate in the presence of the catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ was performed by slow addition of 4 mmol of methyl diazoacetate in 7 ml of CH_2Cl_2 at 40°C to a stirred solution containing 0.005 mol 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** or **II** in 17 ml of CH_2Cl_2 until the gas evolution ceased. Then the solvent was removed under reduced pressure, petroleum ether was added to the residue, and the catalytic system was separated as a dark brown oil. The petroleum ether was removed under reduced pressure, and the residue was analyzed by ^{1}H and ^{13}C NMR and IR spectroscopy. The yields of **IV** and **V** were determined from the ^{1}H NMR spectra using benzene as internal reference.

Functionalized isobutylene oligomer IV, *n* = 7, n_D^{20} = 1.4583. Yield 32%. Found, %: C 81.32, 81.36, H 13.44, 13.08; O 5.54, 5.56. $C_{39}H_{76}O_2$. Calculated, %: C 81.25; H 13.19; O 5.56.^{1}H NMR spectrum, δ, ppm: 0.94, 0.96 both s (6H, 2Me); 1.11 m (1H, CH in cyclopropane ring); 1.34, 1.35 both s (6H, 2Me); 1.43 s (2H, CH_2); 1.52, 1.54 both s (6H, 2Me); 1.88 m (1H, C*H*CO_2Me, in cyclopropane ring); 3.68 s (3H, OMe). ^{13}C NMR spectrum, δ_C, 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, ν, cm^{-1}: 546, 1095 and 1169 (C–O); 1242, 1278 (OMe); 1364, 1375, 1433, 1454 (CH of cyclopropane ring); 1732 (C=O), 1748, 2868, 2954.

Functionalized isobutylene oligomer V, *n* = 10, n_D^{20} = 1.4689. Yield 19%. Found, %: C 82.78, 82.84, H 13.07, 12.98; O 4.15, 4.21. $C_{51}H_{100}O_2$. Calculated, %: C 82.26; H 13.44; O 4.30. ^{1}H NMR spectrum, δ, ppm: 0.94, 0.96 both s (6H, 2Me) 1.06 m (1H, CH in cyclopropane ring); 1.25, 1.32 both s (6H, 2Me); 1.41 s (2H, CH_2); 1.50, 1.52 both s (6H, 2Me); 1.87 m (1H, C*H*CO_2Me, in cyclopropane ring); 3.67 s (3H, OMe). ^{13}C NMR spectrum, δ_C, 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, ν, cm^{-1}: 550, 1101 and 1177 (C–O); 1242, 1291 (OMe), 1364, 1377, 1452 (CH in cyclopropane ring); 1734 (C=O); 2868, 2930.

The reaction of syndiotactic 1,2-polybutadiene with methyl diazoacetate in the presence of the catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ was performed by slow addition of 37 mmol (1 : 1, counting on monomeric unit of the 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 $Cu(OAc)_2$, and 37 mmol of syndiotactic 1,2-polybutadiene **III** in 50 ml of CH_2Cl_2 until the gas evolution ceased. Then the solvent was removed under reduced pressure, petroleum ether was added to the residue, and the catalytic system was separated in the form of a dark brown oil. The petroleum ether was evaporated under reduced pressure, and the product was purified by double reprecipitation in the chloroform–ethanol system, followed by vacuum drying at 60°C to constant weight.

Functionalized syndiotactic 1,2-polybutadiene VI. Yield 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 m (*Z* isomer, 1H, CH_2 in cyclopropane ring); 0.95 m (*Z* isomer), 1.02 m (*E* isomer) (1H, CH_2 in cyclopropane ring); 1.16 m (1H, CH); 1.57 m (1H, CH in cyclopropane ring); 3.65 s (3H, OMe). ^{13}C NMR spectrum, δ_C, 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, ν, cm^{-1}: 669, 758, 908, 994 (=CH); 1084, 1168, 1263 (OMe); 1342, 1417 (=CH_2); 1448 (CH in cyclopropane ring); 1639 (C=C); 1752 (S=O); 2843, 2916, 2970, 3072 (CH_2 in cyclopropane ring).

Thermal gravimetric analysis (TGA) of the initial and modified syndiotactic 1,2-polybutadiene was performed with a Q-1000 derivatograph (MOM, Hungary) in air at a heating rate of 5 deg min^{-1}. As the temperature of decomposition onset we took the temperature at which the sample undergoes 1 wt % weight loss.

The solution viscosities were measured at 25°C in an Ubbelohde-type suspended-level capillary viscometer. We measured the outflow time for polymer and oligomer solutions of various concentrations in chloroform. From the experimentally determined concentrations of the solvent and polymer solutions, we calculated the relative ($\eta_{rel} = \tau/\tau_0$) and specific ($\eta_{sp} = \eta_{rel} - 1$) viscosities. The intrinsic viscosity was found by double extrapolation of the ln η_{rel}/c and η_{sp}/c values to zero concentration.

The quantity $M_{s[\eta]}$ for the samples under consideration was found by the formula

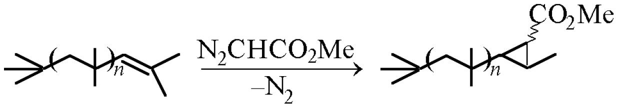
$$M_{s[\eta]} = \{S_0\eta_0[\eta]^{1/3}N_A/\Phi^{1/3}p^{-1}(1 - v\rho_0)\}^{3/2},$$

where S_0 is the sedimentation constant; η_0, solution viscosity (P); [η], intrinsic viscosity (dl g^{-1}); N_A, Avogadro number (6×10^{23} mol^{-1}); $\Phi^{1/3}p^{-1} = 2.5 \times 10^6$; $1 - v\rho_0$, Archimedean factor (buoyancy factor); v, specific partial volume; and ρ_0, solvent density.

The sedimentation coefficients S_c were determined with an MOM-3180 ultracentrifuge at a rotor rotation frequency of 50000 rpm, 25°C, in the interval of polymer solution concentrations of 0.1–0.5 g dl^{-1}.

Previously we developed a new effective catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ allowing products of reactions of low-molecular-weight unsaturated compounds with methyl diazoacetate to be prepared selectively in a high yield [7].

Isobutylene oligomers **I** and **II** containing trisubstituted C=C bond react with methyl diazoacetate in the presence of the $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ system to form the corresponding methyl esters of cyclopropanecarboxylic acid **IV** and **V** in 32 and 19% yield, respectively. Along with esters **IV** and **V**, we isolated from the reaction mixture dimethyl fumarate and dimethyl maleate formed by recombination of methoxycarbonyl carbene (total yield 20%):



I, $n = 7$
II, $n = 10$

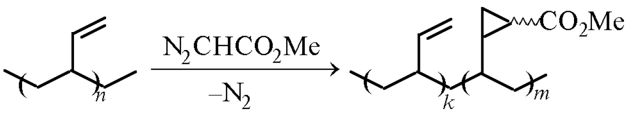
IV, $n = 7.32\%$
V, $n = 10.19\%$

It should be noted that the catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ shows the activity similar to that in the reaction of terminal monoolefins (1-hexene) and 1,3-dienes with methyl diazoacetate. With an increase in the length of the carbon chain, the yield of the target esters decreases [8].

The ^{13}C NMR spectra confirm the presence of a cyclopropane fragment in compounds **IV** and **V**. The characteristic signals of carbon atoms of the cyclopropane ring are manifested in the range of δ_C 12–17 ppm. The signal of the quaternary carbon atom of the ester group is observed at 169–171 ppm. In the IR spectra of products **IV** and **V**, as compared to those of the initial oligomers, the following bands appear (cm^{-1}): C=O stretching (1732–1747), C–O stretching (1170–1177), and C–H bending of the ring and OMe group. The authenticity of structures **IV** and **V** was confirmed by determining their molecular weights from the measured thermal effects of condensation (MTEC method). It was shown that the M_n values for the compounds modified with methoxycarbonylcarbene and starting compounds differ by 72 units.

The initial isobutylene oligomers and functionalized products **IV** and **V** are readily soluble in many organic solvents (benzene, hexane, chloroform, diethyl ether). The intrinsic viscosities of oligomers **I** and **II** and of compounds **IV** and **V** in chloroform (dl g^{-1}) differ insignificantly ([η] = 0.0171 for **IV**, [η] = 0.0165 for starting isobutylene oligomer **I**; [η] = 0.021 for product **V**, [η] = 0.019 for starting oligomer **II**). The calculated Huggins constants for the participants of both processes exceed 10^3, suggesting weak thermodynamic affinity of both the starting oligomers and their reaction products for chloroform. The K_h values for **IV** and **V** are lower than those for oligomers **I** and **II**.

With the aim of chemical modification of syndiotactic 1,2-polybutadiene (SPB) **III**, we performed its reaction with methyl diazoacetate in the presence of the catalytic system $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$. The macromolecular compound **VI** functionalized with cyclopropane fragments is formed in 20% yield:



III $k = m = n$ **IV**, 20%

Average molecular weights of **III** and **VI**

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

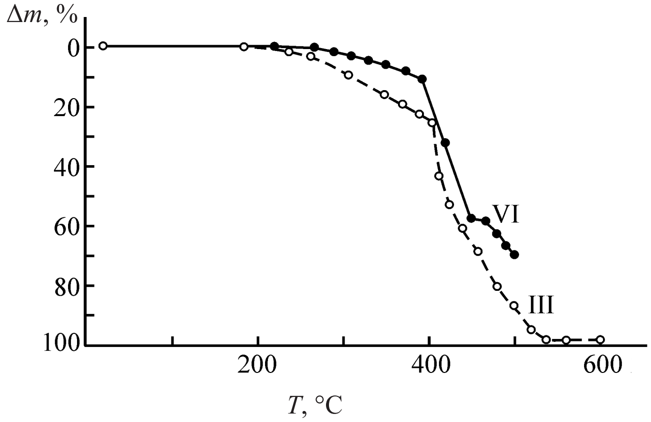
The presence of characteristic signals of the ester group and cyclopropane ring in the ^{1}H and ^{13}C NMR spectra and of the corresponding bands in the IR spectrum of **VI** confirms incorporation of cyclopropane fragments by carbene addition to the C=C bond. The NMR spectrum also proves that cycloaddition of methoxycarbonylcarbene to the C=C bond of SPB occurs periodically, to one of ten vinyl C=C bonds on the average. The carbon atoms of the cyclopropane ring give signals at 13, 25, and 28 ppm in the ^{13}C NMR spectrum of polymer **VI**. The fractions of *cis* and *trans* isomers of functionalized units of **VI** are approximately equal.

A study of the solubility of the initial 1,2-SPB **III** and modified polymer **VI** showed that the product of cyclopropanation with methyl diazoacetate dissolves better in chloroform, hexane, and toluene. Comparison of the intrinsic viscosities of the starting and functionalized polymers ([η] = 1.72 and 2.38 dl g^{-1}, respectively) allowed determination of the Huggins constant K_h for both macromolecular compounds. The K_h value for functionalized 1,2-SPB **VI** ($K_h = 0.43$) is lower than that for the starting polybutadiene ($K_h = 0.59$). The value lower than 0.5 indicates that chloroform is a good solvent for cyclopropanated product **VI** [9].

The average molecular weights $M_{s[\eta]}$ of the initial and functionalized syndiotactic 1,2-polybutadiene were determined using viscometric and sedimentation methods. The sedimentation constants S_0 were determined by extrapolation of $1/S_c$ to zero concentration. The results of determining the average molecular weights $M_{s[\eta]}$ of the initial and functionalized SPB are given in the table.

From the results of calculating $M_{s[\eta]}$, we determined the numbers of elementary units *n* and *k*, which for product *VI* were equal to 685 and 103, respectively.

According to TGA data, the temperature at which modified 1,2-polybutadiene **VI** starts to degrade is 50°C higher as compared to **III**. Degradation of both samples occurs in two steps. The weight loss corresponding to the first step of the degradation (in the range 250–400°C) in the case of the modified 1,2-polybutadiene is two times lower as compared to the initial samples, and in the range 400–500°C (second step of degradation) the burn-out of both polymers occurs at an approximately equal rate (see figure).



TGA data for the starting (**III**) and functionalized (**VI**) 1,2-polybutadiene in air. (Δ*m*) Weight loss and (*T*) temperature.

CONCLUSIONS

(1) The $Cu(OAc)_2$–2,4-lutidine–$ZnCl_2$ system efficiently catalyzes modification with methyl diazoacetate of the C=C bonds both in isobutylene oligomers and in syndiotactic 1,2-polybutadiene.

(2) Chloroform is a good solvent for syndiotactic 1,2-polybutadiene functionalized with methoxycarbonylcarbene. An increase in the intrinsic viscosity of the modified syndiotactic 1,2-polybutadiene is accompanied by a decrease in the viscometric Huggins constant.

(3) Functionalization of syndiotactic 1,2-polybutadiene with cyclopropane fragments enhances its heat resistance.

REFERENCES

1. Kayumova, M.A., Kukovinets, O.S., Sigaeva, N.N., et al., *Vysokomol. Soedin.*, *Ser. B*, 2008, vol. 50, no. 8, pp. 1546–1552.

2. Gainullina, T.V., Kayumova, M.A., Kukovinets, O.S., et al., *Vysokomol. Soedin., Ser. A,* 2005, vol. 47, no. 9, pp. 1739–1741.

3. Barrett, A., Kasdorf, K., and Williams, D., *J. Chem. Soc., Chem. Commun.*, 1994, pp. 1781–1782.

4. Pragliola, S., Milano, G., Guerra, G., and Longo, P., *J. Am. Chem. Soc.*, 2002, vol. 124, no. 14, pp. 3502–3503.
5. *Organikum. Organisch-chemische Grundpraktikum*, Becker, G. et al., Eds., Berlin: Wissenschaften, 1976.
6. *Reagents for Organic Synthesis*, Fieser, L.F. and Fieser, M., Eds., New York: Wiley–Interscience, 1967–1979, vol. 5.
7. Gareev, V.F., Yangirov, T.A., Bakeeva, A.D., et al., *Vestn. Bashkirsk. Gos. Univ.*, 2008, vol. 13, no. 4, pp. 886–890.
8. Gareev, V.F., Sultanova, R.M., Biglova, R.Z., et al., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2008, no. 8, pp. 1750–1752.
9. Rafikov, S.R., Budtov, V.P., and Monakov, Yu.B., *Vvedenie v fiziko-khimiyu rastvorov polimerov* (Introduction to Physical Chemistry of Polymer Solutions), Moscow: Nauka, 1978.