2-Amino-7-(3-thienyl)-3,4-dihydropyrido[3′,2′:4,5]thieno[3,2-*b*]pyrimidin-4-one (9). A moderate stream of HCl was passed for 5 min through a suspension of compound **8** (0.5 g) in ethanol (15 mL). The resulting solution was kept for 24 h at 5 °C. The solution was then alkalized with 10 mL of 10% Na_2CO_3, and the precipitate that formed was filtered off and washed with water, ethanol, and hexane. Yield 52%. M.p. >300 °C. IR, ν/cm^{-1}: 1625, 1638 (CONH) 3086, 3156, 3248 (NH, NH_2). ^{1}H NMR, δ: 6.95 (d, 1 H, C(4)H-thiophene); 7.28 (s, 1 H, C(2)H-thiophene); 7.29 (br.s, 2 H, NH_2), 7.48 (d, 1 H, C(8)H-pyridine, ^3J = 8.2 Hz); 7.53 (d, 1 H, C(5)H-thiophene); 8.32 (d, C(9)H-pyridine, ^3J = 8.2 Hz); 9.04 (br.s, 1 H, NH).

4-Hydroxy-7-(2-thienyl)pyrido[3′,2′:4,5]thieno[3,2-*b*]pyridin-2(1H)-one (11). Compounds **3a** (0.01 mol) and **10** (0.01 mol) were added in succession with stirring to a solution of EtONa obtained from 0.46 g (0.01 mol) of sodium and 30 mL of ethanol. The reaction mixture was stirred for 1 h at 20 °C and then refluxed for 2 h. After cooling, the reaction mixture was acidified with 2 mL of 10% HCl, and the precipitate was separated and washed with water, ethanol, and hexane. Yield 82%. M.p. >300 °C. IR, ν/cm^{-1}: 1624, 1638 (CONH), 3104 (NH). ^{1}H NMR, δ: 6.37 (d, 1 H, C(3)H); 7.25 (t, 1 H, C(4)H-thiophene); 7.80 (d,1 H, C(3)H-thiophene); 7.87 (d, 1 H, C(8)H, ^3J = 8.1 Hz); 8.15 (s, 1 H, C(5)-thiophene); 8.16 (d, 1H, C(9)H, ^3J = 8.1 Hz); 10.45 (br.s, 1 H, OH); 11.68 (br.s, 1 H, NH).

3-Bromo-6-(5-bromothienyl-2)-isothiazolo[5,4-*b*]pyridine (12). A mixture of compound **3a** (5 mmol) and bromine (15 mmol) in chloroform (25 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from nitromethane. Yield 67%. M.p. 248—251 °C. IR, ν/cm^{-1}: 1590, 1604 (C=N). ^{1}H NMR, δ: 7.41 (d, 1 H, C(3)H-thiophene); 7.42 (d, 1 H, C(4)H-thiophene); 8.12 (d, C(5)H, ^3J = 8.2 Hz); 8.28 (d, 1 H, C(4)H, ^3J = 8.2 Hz).

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Synthesis of Pd catalysts based on a nonbornene—CO copolymer and their properties in the carbomethoxylation of propylene

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It was found that carboxylation of norbornene (*nbn*) in the presence of the $PdCl_2$—PPh_3—HCl catalytic system is accompanied by alternating copolymerization of *nbn* with carbon monoxide to form norbornanecarboxylic acid (yield ~20%) and a *nbn*-CO copolymer (yield ~80%, M_w = 1600, M_w/M_n = 1.6). The Pd^{II} salt of poly(norbornaneketone)carboxylic acid is a highly active catalyst for the carbomethoxylation of propylene.

Key words: copolymerization, norbornene, carbon monoxide, palladium catalyst, propylene carbomethoxylation.

Metal-containing polymers with controlled distribution of metal atoms in the chain are of considerable interest as catalyst precursors. It is believed that such catalytic systems can possess a number of advantages: enhanced activity and stability, easy regeneration, *etc.*[1] Polymerization of unsaturated compounds catalyzed by

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metal complexes with inclusion of a metal atom in the polymer structure may prove to be an efficient method for synthesizing catalysts of this type.

In the present work we studied the carboxylation of norbornene in the presence of the catalytic system $PdCl_2$—PPh_3—HCl that gives an alternating copolymer of norbornene with carbon monoxide. The difference of this reaction from the previously reported reactions of this type is that a palladium-containing copolymer of norbornene and CO terminated by a COOH group is formed in addition to norbornanecarboxylic acid. The palladium salt of the polyketonenorbornanecarboxylic acid resulting from this reaction displays high catalytic activity in the carbomethoxylation of propylene.

The products of alternating copolymerization of CO with olefins, polyketones $[C(O)CH(R)CH_2]_n$ that are of interest as photo- and biodegradable materials and can readily be modified by chemical methods due to the presence of the CO group,[2,3] can be obtained from CO and a series of olefins, such as propylene, butenes, hex-1-ene, styrene, norbornene, *etc.*, in the presence of palladium complexes.[2—7] However, the possibility of inclusion of a metal in the composition of such polyketones has not been previously reported.

Experimental

The reaction of norbornene (0.53 mol), water (1.39 mol), and CO (60 atm) in dioxane (50 mL) was carried out in a stainless steel autoclave (250 mL) equipped with a stirrer.

A catalyst containing $PdCl_2$ (5.7 mmol), PPh_3 (37.6 mmol), and HCl (55 mmol) was used in the reaction. The synthesis was performed at 100 °C. After 4 h, a product was obtained that contained norbornanecarboxylic acid and a solid polymeric material in 20 and 75% yields, respectively. The latter product was washed with dioxane, water, an acid, and an alkali to give a dark-grey powder insoluble in dioxane, water, $CHCl_3$, and MeOH and soluble in benzene, toluene, and CCl_4.

Tests of the catalysts in the carbomethoxylation of propylene were performed in a steel autoclave (250 mL) equipped with a stirrer and containing *p*-xylene, T = 100 °C, p_{CO} = 3.0 MPa. The concentrations in the starting mixture were as follows (mol L^{-1}): $6.0 \cdot 10^{-3}$ of Pd, 6.2 of MeOH, 3.1 of C_3H_6. The PPh_3/Pd molar ratio was 6. The amount of HCl added was 0.5 mL. The reaction rate was monitored by the consumption of CO from a calibrated high-pressure vessel, from which carbon monoxide was fed into the reactor as it was consumed in the reaction.

The reaction products were analyzed by GLC using the OV-225 liquid phase.

Results and Discussion

The solid polymeric material resulting from the carbonylation of norbornene was studied by several physicochemical methods.

The IR spectrum of the material (in KBr pellets) displays intense absorption bands with maxima at 1708 and 1576 cm^{-1}, the former of which can be attributed to ν(CO) in the polyketone structure.[2]

These results are also confirmed by ^{13}C NMR spectra, in which the carbonyl group is displayed as a signal with δ 210.635. The spectrum also contains signals with δ 53.350 and 40.688 attributed to the norbornane structure.[2]

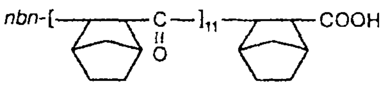
Thermogravimetric analysis with heating at the rate of 10 °C min^{-1} in nitrogen showed that the material starts to decompose at 350 °C (the maximum decomposition corresponds to 419.7 °C).

The characteristics determined for the material are very similar to those reported for a polymer, the product of alternating copolymerization of norbornene with CO obtained by carbonylation in the presence of the catalytic system $Pd(CH_3COO)_2$—2,2′-bypyridine—*p*-toluenesulfonic acid—nitrobenzene in THF environment.[2]

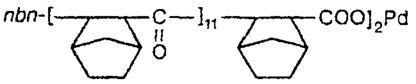
On the other hand, there are significant differences that suggest that the material obtained in this work is of a different nature. In particular, these differences include the relatively low molecular mass that characterizes the material as an oligomer, as well as its narrow molecular mass distribution. For example, the molecular mass determined by gel-penetrating chromatography in toluene relative to a polystyrene standard is M_w = 1600, and the ratio M_w/M_n is 1.6. It should be noted for comparison that in the case of the copolymer reported previously,[2] M_w = 6100.

It was also unexpectedly found that the material under study contains strongly bonded Pd. The atomic surface concentrations of elements determined by XPS were found to be (at.%): 85.1 C1*s*, 12.5 O1*s*, 0.05 Pd3*d*, while the value E_{max} = 336.5 eV suggests the presence of Pd^{II} in the material.[8] The latter probably forms a salt with the terminal COO groups of the chain, as evidenced by the presence of an absorption band at 1576 cm^{-1} in the IR spectrum.

In our opinion, the above results of analyses (the formation of a copolymer under carboxylation conditions, the presence of norbornane moieties in its structure, the presence of a Pd salt) agree most adequately with the following composition of the copolymer:



(80%),



(20%),

where *nbn* indicates norbornane.

The atomic concentrations of the elements calculated for this composition are (at.%): 11.8 O1*s*, 88.1 C1*s*, 0.04 Pd, in satisfactory agreement with the XPS results for the concentrations of these elements. It was found that the palladium-containing polymer (Pd^{II}-*nbn*(CO)-polymer) obtained in this work has a high catalytic activity for carbonylation. For example, in carbo-

Table 1. Carbomethoxylation of propylene using various precursors of Pd^{II}-catalysts

Catalyst precursor	Turnover $/h^{-1}$	Composition of products (mol.%)	
		Methyl butyrate	Methyl isobutyrate
Pd^{II}-*nbn*(CO)-polymer	5000	62	38
$PdCl_2(PPh_3)_2$	500	62	38
$Pd(OAc)_2$	380	50	50
$PdCl_2$	360	49	51

Note. Conditions of the synthesis: [Pd] = 6 mmol L^{-1}, PPh_3/Pd = 6 (mol.), HCl = 0.5 mL, [MeOH] = 6.2 mol L^{-1}, *p*-xylene (15 mL) as the solvent, $[C_3H_6]$ = 3.1 mol L^{-1}, T = 100 °C, p_{CO} = 3.0 MPa.

methoxylation of propylene (see Table 1) in the presence of triphenylphosphine, the polymer-containing catalyst catalyzes the reaction with a turnover of 5000 h^{-1}, whereas the use of other precursors of Pd^{II}-catalysts only makes it possible to perform the reaction, at best (*e.g.*, when $PdCl_2(PPh_3)_2$ is used), with an activity that is an order of magnitude lower. The selectivity and isomeric distribution of reaction products are almost the same.

The enhanced catalytic activity of the palladium-polymeric system should probably be explained by involvement in the catalysis of a greater amount of active centers formed under the action of components of the reaction medium.

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