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Addition Polymerization of 3,3-Disubstituted Cyclopropenes in the Presence of a Palladium Complex Containing an Acyclic Diaminocarbene Ligand

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Abstract—Addition polymerization of 3-methyl-3-phenylcyclopropene and 3,3-di(*n*-propyl)cyclopropene in the presence of a palladium complex containing an acyclic diaminocarbene ligand was studied. When activated with the organoborate ($Na^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$), such complex catalyzes the addition polymerization of substituted cyclopropenes. The polymerization occurs selectively without opening of the cyclopropane ring. The copolymerization of 3,3-di(*n*-propyl)cyclopropene with a monomer of the norbornene series (5-ethylidene-2-norbornene) was monitored by a decrease in the intensity of the characteristic signals in the ^1H NMR spectra of the corresponding monomers. The substituted cyclopropenes were found to be more active monomers than norbornenes in the addition polymerization. The addition homopolymers of 3-methyl-3-phenylcyclopropene and 3,3-di(*n*-propyl)cyclopropene were characterized by differential scanning calorimetry, thermogravimetric analysis, and X-ray diffraction.

Keywords: addition polymerization, cyclopropene, 5-ethylidene-2-norbornene, palladium complexes, diaminocarbene ligand

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Addition polymers based on strained cycloolefins, as a rule, have high glass transition point, exhibit high heat and chemical resistance, and contain rigid backbones [1], which makes them promising as membrane materials for gas separation and pervaporation, as sorbents for gas transportation and storage, and as materials for micro- and optoelectronics. The key factors governing the choice of a cycloolefin derivative as a monomer are commercial availability and polymerization activity, which depends on the ring strain. Today, the majority of examples of addition polymerization are restricted to norbornene structures (see, e.g., [2–4]), whereas there are also other commercially available monomers with a strained ring. One of examples of such cycloolefins is cyclopropene. Only scarce data on addition polymerization of cyclopropenes are available [5–7]. Furthermore, the authors of the published papers have not found effective catalytic systems ensuring

preparation of polymer products with the molecular masses sufficient for further studying the mechanical and gas-transport properties of polycyclopropenes. Taking into account high reactivity of the cyclopropene ring in polymerization due to high ring strain, it is necessary to find catalytic systems that would not only effect polymerization of these monomers to obtain high-molecular-mass products but also catalyze specifically the selective reaction involving double bonds with the preservation of the cyclopropane ring.

As shown previously, catalytic systems based on palladium complexes with N-heterocyclic carbene ligands exhibit high activity in addition polymerization of cycloolefins, catalyze the polymerization of monomers with different functional bonds selectively via endocyclic double bond, and are insensitive to atmospheric oxygen and traces of water [3, 8–10]. The activity of these systems is determined by the structure

of the carbene ligand. We discovered previously [11] a new type of catalytic systems containing related acyclic diaminocarbene ligands for the addition polymerization of norbornenes. These Pd complexes, when activated with organoboron compounds, catalyze the addition polymerization of alkyl-substituted norbornenes to form high-molecular-mass soluble products. Therefore, it is topical, first, to further evaluate the catalytic potential of a new type of systems based on Pd complexes containing acyclic diaminocarbene ligands and, second, to prepare addition polymers from substituted cyclopropenes and to study their properties.

This study was aimed at establishing the possibility of performing the addition polymerization of substituted cyclopropenes in the presence of a catalytic system based on a palladium complex containing an acyclic diaminocarbene ligand, at evaluating the activity of this catalytic system in the reaction, and at characterizing the polymer products obtained.

EXPERIMENTAL

3-Methyl-3-phenylcyclopropene (M1) was prepared as described previously [12]. Methylene chloride [HPLC purity (>99.9%), Khimmed, Russia, T_b = 40–41°C] was refluxed over CaH_2 (96%, catalog no. UN 1404) in an argon flow (99.998%, Argon, Russia) for 5 h and distilled. Chloroform (chemically pure grade, Khimmed, T_b = 61–62°C) was refluxed over CaH_2 in an argon flow for 5 h and distilled. NaH (95%, Khimmed, catalog no. 22344-1), dimethyl sulfoxide (chemically pure grade, Komponent-Reaktiv, Russia, catalog no. 2-451-11), methyltriphenylphosphonium bromide (98%, Merck, catalog no. 130079), 4-heptanone (98%, Merck, catalog no. 101745), tetrahydrofuran [HPLC purity (>99.9%), Panreac, catalog no. 361736], $HgCl_2$ (98%, Merck, catalog no. 413445), NH_4Cl (analytically pure grade, REAKhIM, Russia, catalog no. 010316), cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide, >99%, Acros Organics, catalog no. 22716-0100), bromoform (pure grade, LenReaktiv, Russia, catalog no. 181245), NaCl (pure grade, Komponent-Reaktiv, catalog no. 2-245-10), $MgSO_4 \cdot 7H_2O$ (chemically pure grade, REAKhIM, catalog no. 120054), Mg (chemically pure grade, Komponent-Reaktiv, catalog no. 3-303-10), potassium tert-butylate (≥98.0%, Merck, catalog

no. 804918), isopropanol [HPLC purity (>99.9%), Panreac, catalog no. 361090], tert-butanol (≥99.5%, Merck, catalog no. 471712), Na_2SO_4 (chemically pure grade, LenReaktiv, catalog no. 130246), n-pentane (analytically pure grade, Komponent-Reaktiv, catalog no. 1-711-15), tricyclohexylphosphine (>98%, ABCR GmbH, catalog no. 264139), 4-heptanone (98%, Acros Organics, catalog no. 14655-5000), and n-hexane (chemically pure grade, Komponent-Reaktiv, catalog no. 2-008-06) were used without additional purification. The palladium complex containing the acyclic diaminocarbene ligand [Pd1 (I)] was synthesized as described previously [13]. tert-Butyl isocyanide (97%, Acros Organics, catalog no. 403600010) and $PdCl_2$ (59% Pd, Acros Organics, catalog no. 195200050) were used without additional purification. Diethylamine (≥99.0%, Alfa Aesar, catalog no. A11716.AE, T_b = 56–57°C) was refluxed over CaH_2 in an argon flow for 5 h and distilled. Acetonitrile [HPLC purity (>99.9%), Khimmed] was dehydrated on an SPS-7 solvent purification installation (MBraun).

The conversion of the monomers in addition polymerization was monitored by ^{1}H NMR spectroscopy.

The NMR spectra were recorded using $CDCl_3$ (99.96%, Sigma–Aldrich, catalog no. 212-742-4). The NMR spectra of the monomers and intermediates were recorded with a Fourier 300 HD NMR spectrometer (Bruker Corporation) at frequencies of 300.1 MHz for ^{1}H and 75.5 MHz for [13]C. The NMR spectra of the polymers were recorded with a Bruker AVANCE III HD NMR spectrometer operating at 400.1 MHz for ^{1}H and 100.6 MHz for [13]C. The chemical shifts were determined relative to the residual proton signal of chloroform (7.24 ppm, ^{1}H NMR) and chloroform carbon signal (77.00 ppm, ^{13}C NMR).

Analysis by gas chromatography–mass spectrometry was performed with a MAT 95 XL mass spectrometer (Finnigan) coupled with an HP 6890+ chromatograph (Agilent). The mass spectra were taken under the following conditions: electron ionization (ionization energy 70 eV), mass range 20–800 amu, resolution 1000, ion source temperature 200°C, scanning rate 1 s per decade. Chromatographing conditions: 30 m × 0.25 mm capillary column coated with DB-5 phase (polydimethylsiloxane containing 5% phenyl groups); carrier gas He (purity 99.995%, NII KM, Russia), flow split ratio 1 : 30; temperature schedule:

heating at a rate of 5 deg min^{-1} from 30 to 120°C, heating at a rate of 10 deg min^{-1} from 120 to 270°C, and keeping at 270°C for 10 min.

The IR spectra were recorded with an IFS-66-v/s Fourier spectrometer (Bruker) using the attenuated total reflection technique. The spectra were taken on a ZnSe crystal in the range from 4000 to 600 cm^{-1}, resolution 2 cm^{-1}, 15 absorption scans.

Calorimetric studies were performed with a TA-4000 differential scanning calorimeter (Mettler) with a DSC-30 cell at a heating rate of 20 deg min^{-1} under argon. Thermogravimetric analysis was performed with a Perkin–Elmer TGA-7 device at a heating rate of 10 deg min^{-1}.

X-ray diffraction patterns were taken with a DRON-3M diffractometer (Burevestnik, Russia) in the mode of recording the transmitted radiation (asymmetrical detector-focused quartz monochromator on the primary beam). Cu$_{K_\alpha}$ radiation (λ = 0.154 nm) was used. The diffraction patterns were taken point-by-point with an increment $\Delta 2\theta$ = 0.04° and accumulation time τ = 10 s.

The molecular masses were determined by gel permeation chromatography with a Waters high-pressure chromatograph equipped with a refractometric detector (Chromatopack Microgel-5, eluent chloroform, flow rate 1 mL min^{-1}, sample volume 200 μL, sample concentration 1 mg mL^{-1}) using a refractometric detector. The molecular masses were calculated by the standard procedure relative to monodisperse polystyrene standards (Agilent, catalog no. PL2010-0105).

Synthesis of 4-methyleneheptane. To 250 mL of dry dimethyl sulfoxide, we added under argon 10.5 g of a NaH dispersion (60% in mineral oil) and 86 g of methyltriphenylphosphonium bromide. The suspension was heated to 60°C and kept with stirring until the gas evolution ceased (~2 h). The mixture was cooled to room temperature, and 25 g of 4-heptanone was added dropwise (exothermic reaction). After 10 min, the mixture was again heated to 60°C and stirred for 3 h. Without stopping heating, the product was distilled off in a vacuum (14 mm Hg) into a trap cooled with liquid nitrogen. The product was obtained as a colorless liquid, 25 g, yield 100% (~12 mol % impurity of benzene from commercial phosphonium bromide).

^{1}H NMR (CDCl$_3$, δ, ppm): 4.70 s (2H), 2.05–1.98 m (4H), 1.53–1.34 m (4H), 0.90 t (^3J = 7.3 Hz, 6H).

^{13}C NMR (CDCl$_3$, δ, ppm): 150.0, 108.8, 38.4, 21.1, 14.0.

Synthesis of 1,1-dibromo-2,2-dipropylcyclopropane. To 66.8 ml of 10 M aqueous NaOH, we added at room temperature a mixture of 18.7 g of 4-methyleneheptane, 7.5 mL of methylene chloride, and 7.3 g of cetyltrimethylammonium bromide. To the resulting system, we added dropwise with vigorous stirring a mixture of 84.5 g of bromoform and 35 mL of methylene chloride. The mixture was vigorously stirred for 8 h at room temperature, after which the layers were separated. The aqueous layer was extracted with methylene chloride. All the organic layers were combined, washed with a saturated (~26%) NaCl solution, dried over MgSO$_4$, and evaporated on a rotary evaporator. The resulting semicrystalline mixture was dissolved in methylene chloride and evaporated with the addition of silica gel. Silica gel with the supported substance was placed in a Soxhlet extractor and washed with hexane for 3 h. The solution was cooled to room temperature and evaporated on a rotary evaporator. The product was distilled in a vacuum (65–70°C/6 mm Hg). The product was obtained as a colorless liquid, 31.8 g, yield 67%.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.72–1.30 m (8H), 1.37 s (2H), 0.94 t (^3J = 7.1 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 40.0, 37.0, 34.2, 32.9, 19.5, 14.1.

Synthesis of 2-bromo-1,1-di(n-propyl) cyclopropane. A four-necked flask equipped with a power-driven stirrer, two reflux condensers, and a dropping funnel was charged with 19 g of magnesium turnings and 30 mg of a 0.1% aqueous HgCl$_2$ solution 160 mL of dry tetrahydrofuran was added, and the mixture was heated to reflux and kept with stirring for 5 min for the magnesium activation. To the refluxing tetrahydrofuran, a mixture of 31.8 g of 1,1-dibromo-2,2-dipropylcyclopropane and 21 mL of methanol was added in one portion, after which the mixture was refluxed for an additional 30 min. Then, the system was cooled to room temperature and neutralized with water (35 mL). The system obtained was stirred for 10 min. The liquid fraction was transferred into a separating funnel and washed with a saturated (~28%) aqueous NH$_4$Cl solution. The aqueous layer was extracted with diethyl ether. All the organic fractions were combined, washed with a saturated (~26%) aqueous NaCl solution, dried over MgSO$_4$, and evaporated on a rotary evaporator. The product was distilled in a vacuum (68–70°C/14 mm Hg). The product was obtained as a colorless liquid, 21.1 g, yield 92%.

^{1}H NMR (CDCl$_3$, δ, ppm): 2.83 dd (J = 7.7, 4.3 Hz, 1H), 1.60–1.10 m (8H), 1.02–0.83 m (7H), 0.65–0.55 m (1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 37.5, 35.3, 30.1, 24.6, 21.9, 19.4, 19.2, 14.3, 14.2.

Synthesis of 3,3-di(n-propyl)cyclopropene. A three-necked flask equipped with a dropping funnel and a long dephlegmator (~35 cm) with a tube connected to a trap that was cooled in a mixture of dry ice (Cold Circuit Technologies, Russia) and isopropanol (dry ice was added intermittently in an amount required to maintain the isopropanol temperature of –78.5°C, monitored with a thermometer) was charged under argon with 17.4 g of potassium tert-butylate and 90 mL of freshly distilled dry dimethyl sulfoxide. The suspension was heated to 50°C and kept at this temperature until the precipitate dissolved completely (5 min). The system was degassed at a pressure of 15–18 mm Hg, after which a mixture of 21.1 g of 2-bromo-1,1-dicyclopropylcyclopropane in 20 mL of dimethyl sulfoxide was slowly added through a dropping funnel. The product was formed immediately and was distilled into the receiver (boiling point of the product ~15°C). After the addition of the whole amount of the starting compound and cessation of the product distillation, the mixture was heated to 65°C and kept at this temperature until it ceased to boil. After that, the reaction mixture was allowed to cool to room temperature, and the system was filled with argon. The mixture from the trap containing, along with the product, also tert-butanol and dimethyl sulfoxide was transferred into a separating funnel, diluted with pentane, and washed with water. The aqueous layer was extracted with pentane. All the organic fractions were combined and dried over Na$_2$SO$_4$ in a refrigerator. Pentane was distilled off at atmospheric pressure. Then, the product was distilled in a vacuum (61–65°C/73 mm Hg). The product was obtained as a colorless liquid, 5.1 g, yield 40%.

^{1}H NMR (CDCl$_3$, δ, ppm): 7.28 s (2H), 1.47–1.35 m (4H), 1.18–1.00 m (4H), 0.83 t (^3J = 7.2 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 120.0, 41.1, 24.6, 20.3, 14.3. Mass spectrum (electron ionization): 124 (0.2%, M$^{+•}$), 136 (100%, C$_6$H$_9$).

Addition polymerization of 3-methyl-3-phenylcyclopropene on the binary catalytic system. We prepared a 0.05 M solution of Pd1 complex (I) by dissolving 10.0 mg of Pd1 (I) in 0.48 mL of methylene chloride and separately a 0.04 M solution of the cocatalyst by dissolving 20 mg of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) in 0.56 mL of methylene chloride. All the components were mixed in amounts corresponding to the molar ratio of the components in the catalytic system Pd1/NaBARF = 1 : 3; i.e., 0.15 mL of a 0.05 M Pd1 solution was mixed with 0.56 mL of a 0.04 M NaBARF solution. The resulting mixture was kept in an ultrasonic bath for 20 min and then was filtered through a Teflon filter with the pore size of 0.2 μm. A glass vial was charged with 0.1 g of 3-methyl-3-phenylcyclopropene. The monomer was heated to 45°C. After that, 0.37 mL of the solution of the catalytic mixture in methylene chloride was added; the molar ratio of the components in the reaction mixture was M1/Pd1/NaBARF = 200/1/3. The mixture was vigorously stirred for 10 s and allowed to stand at 45°C for 45 h. Then, the mixture was poured into a beaker filled with methanol. The polymer was separated and vacuum-dried for 3 h to constant weight. Then, the polymer was reprecipitated from a chloroform solution with methanol and again dried in a vacuum; the procedure was repeated twice. The isolated polymer [poly(M1)] was a white solid powder. Yield 6%.
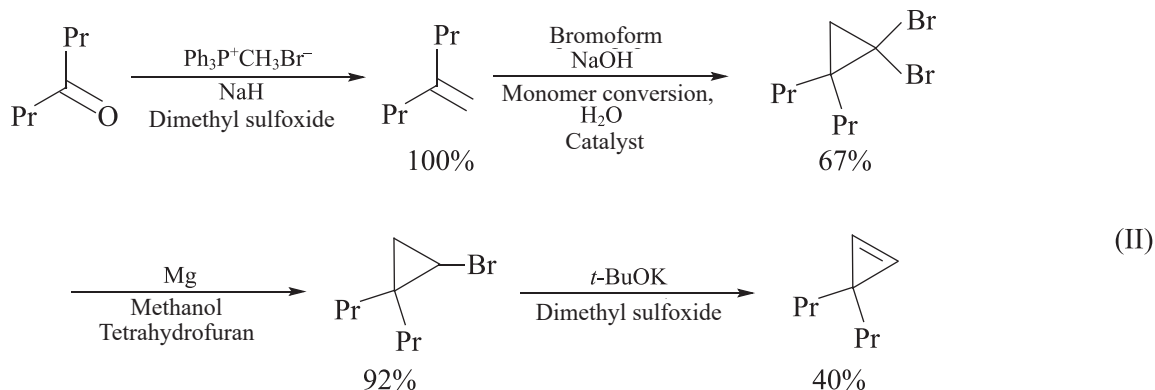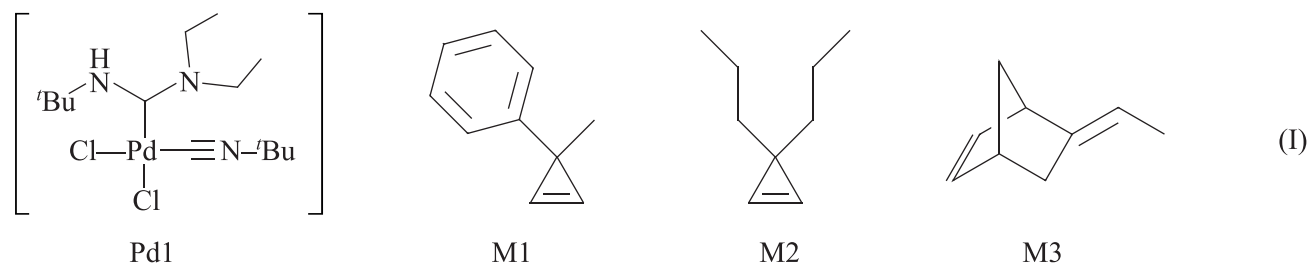
Addition polymerization of 3-methyl-3-phenylcycloprop-1-ene on the ternary catalytic system. We prepared a 0.05 M solution of the palladium complex by dissolving 20 mg of Pd1 in 0.96 mL of methylene chloride, separately a 0.04 M solution of the cocatalyst NaBARF by dissolving 80 mg of NaBARF in 2.26 mL of methylene chloride, and a 0.05 M solution of the phosphine by dissolving 25 mg of tricyclohexylphosphine (PCy$_3$) in 1.79 mL of methylene chloride. The components were mixed in amounts corresponding to the molar ratio of the components in the catalytic system Pd1/NaBARF/PCy$_3$ = 1/3/2; i.e., 0.60 mL of a 0.05 M Pd1 solution was mixed with 2.26 mL of a 0.04 M NaBARF solution and 1.20 mL of a 0.05 M tricyclohexylphosphine solution. The resulting mixture was kept in an ultrasonic bath for 20 min and then was filtered through a Teflon filter with the pore diameter of 0.2 μM. A glass vial was charged with 0.6 g of 3-methyl-3-phenylcyclopropene. The monomer was heated to 45°C. Then, 3.11 mL of a solution of the catalytic mixture in methylene chloride was added; the molar ratio of the components in the reaction mixture was M1/Pd1/NaBARF/PCy$_3$ = 200/1/3/2. The mixture was vigorously stirred for 10 s and then was kept at 45°C for 45 h. After that, the mixture was poured into a

beaker filled with methanol. The polymer was separated and vacuum-dried for 3 h to constant weight. Then, the polymer was reprecipitated from the chloroform solution with methanol and again vacuum-dried; the procedure was repeated twice. The isolated polymer [poly (M1)] was a white solid powder. Yield 34%, $M_n = 3.5 \times 10^3$, $M_w/M_n = 1.6$. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.80–6.30 m (5H), 2.25–0.50 m (5H). ^{13}C NMR (CDCl$_3$, δ, ppm): 146.2–140.0 m, 137.5–122.5 m, 37.5–22.0 m, 18.5–15.0 m. IR (ATR, cm^{-1}): 3054, 3022, 2951, 1027, 762.

Addition 3,3-di(n-propyl)cyclopropene polymer. ^{1}H NMR (CDCl$_3$, δ, ppm): 2.45–1.65 m (2H), 1.60–0.60 m (14H).

RESULTS AND DISCUSSION

This work is a pilot study of the polymerization of substituted cyclopropenes in the presence of Pd complexes containing acyclic diaminocarbene ligands. Therefore, in this step of the study we chose cyclopropenes with inert hydrocarbon groups: 3-methyl-3-phenylcyclopropene (M1) and 3,3-di(n-propyl) cyclopropene (M2). Monomer M2 was synthesized from di(n-propyl) ketone in 40% yield (II). The structure and purity of the monomers were confirmed by ^{1}H and ^{13}C NMR spectroscopy and by gas–liquid chromatography.

(I)

(II)

Pr: *n*-propyl; *t*-Bu: *tert*-butyl; Ph: phenyl.

The addition polymerization of the synthesized cyclopropenes M1 and M2 was performed in the presence of the Pd complex Pd1 (I) containing an acyclic diaminocarbene ligand (III).

(III)
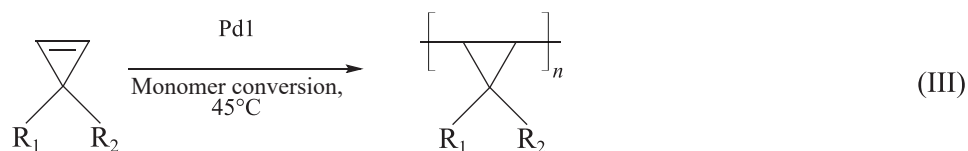
M1: R$_1$ = methyl, R$_2$ = phenyl; M2: R$_1$ = R$_2$ = *n*-propyl.

Table 1. Conditions and results of the polymerization of 3-methyl-3-phenylcyclopropene and 3,3-di(*n*-propyl)cyclopropene in the presence of the Pd complex with the acyclic diaminocarbene ligand

Monomer (M)	PCy$_3$/Pd1 molar ratio	M/Pd1 molar ratio	c(M), M	Yield, %	M_n	M_w/M_n
3-Methyl-3-phenylcyclopropene	0/1	200	1.65	6	–	–
3-Methyl-3-phenylcyclopropene	2/1	200	1.24	34	3500	1.6
3-Methyl-3-phenylcyclopropene	2/1	100	1.0	39	3300	1.7
3,3-Di(n-propyl)cyclopropene	2/1	100	1.5	20[a]	8600	2.7

Reaction conditions: precatalyst: Pd complex with acyclic diaminocarbene ligand Pd1 (I); cocatalyst: sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF); PCy$_3$, tricyclohexylphosphine; molar ratio [Pd]/[NaBARF] = 1/3; solvent: methylene chloride: polymerization time 45 h; temperature 45°C; (–) not determined.
[a] Polymerization time 22 h, 60°C.

Table 2. Structural characteristics of addition polymers

Polymer	$(2\theta)_1$, deg	d_1, Å	$(2\theta)_2$, deg	d_2, Å	$(2\theta)_3$, deg	d_3, Å	$(2\theta)_4$, deg	d_4, Å	References
Poly(3-methyl-3-phenylcyclopropene)	8.07	10.9	9.7	9.1	15.0	5.9	20.2	4.4	This work
Poly(5-ethylidene-2-norbornene)	8.5	10.4	17.4	5.1	–	–	–	–	[14]
Polynorbornene	10.0	8.8	18.5	4.7	–	–	–	–	[15]

The spacings were calculated by the Bragg equation $d = \lambda/2\sin\theta$, where d is the interplanar spacing, θ is the glancing angle, $\lambda = 1.54$ Å; (–) no corresponding peaks in the diffraction pattern.

Complex Pd1 without cocatalyst, organoborate NaBARF, did not catalyze the polymerization of M1 and M2. The activation of this complex with NaBARF in an amount of 3 equiv relative to Pd enhanced the catalyst activity: All the monomers studied were involved in the polymerization on the Pd1/NaBARF catalytic systems. However, the yields of the corresponding polymers were low (Table 1), which is associated most probably with the low stability of the catalytic system, because in 1 h Pd^0 particles appeared in the reaction mixture. Introduction of an additional ligand, tricyclohexylphosphine, into this system considerably enhanced its catalytic activity and the yields of the polymers formed (Table 1). The synthesized addition homopolymers based on M1 and M2 are readily soluble in chloroform, tetrahydrofuran, and methylene chloride. Analysis of the molecular-mass characteristics of the polymerization products shows that, with the Pd1/NaBARF/PCy$_3$ catalytic system, it is possible to prepare polymers of cyclopropene derivatives with the molecular masses somewhat lower than the theoretical values and with unimodal molecular-mass distribution (Table 1). This fact suggests the occurrence of addition polymerization of the monomers on catalytic sites of the same type and the occurrence

of the chain termination to form active catalytic species initiating the formation of new polymer chains. The broader molecular-mass distribution of the polymer based on M2 is associated most probably with hindered diffusion of the monomer molecules to active catalytic sites, which is caused by the fact that the polymerization is performed at higher monomer concentration in the reaction mixture. The structure and purity of the addition homopolymers of M1 and M2 were confirmed by ^{1}H and ^{13}C NMR spectroscopy and by IR spectroscopy. The ^{1}H and ^{13}C NMR data show that the polymerization of the cyclopropenes occurs selectively and the strained three-membered ring is not opened in the course of the polymerization.

It is not always correct to judge the reactivity of cyclopropene and related cycloolefin monomers, norbornene derivatives, from the results of addition polymerization because of the possible effect of microimpurities present in the monomers on the polymerization process. Therefore, we studied the copolymerization of a cyclopropene derivative, monomer M2, with a model monomer of the norbornene series, 5-ethylidene-2-norbornene (M3).
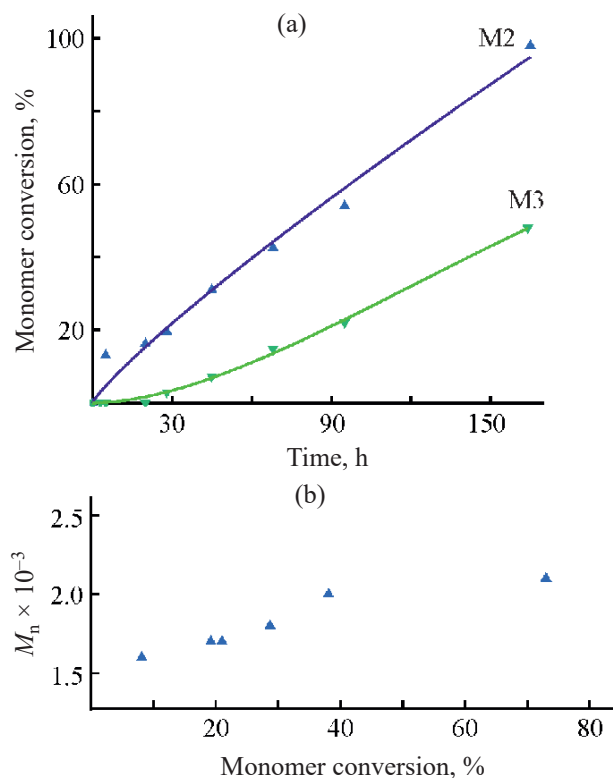
Fig. 1. (a) Monomer conversion as a function of polymerization time and (b) copolymer molecular mass (M_n) as a function of the monomer conversion. (M2) 3,3-di(*n*-propyl)cyclopropene and (M3) 5-ethylidene-2-norbornene; precatalyst: Pd complex with acyclic diaminocarbene ligand Pd1 (I); cocatalyst: sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF); molar ratio [Pd]/[NaBARF]/[PCy$_3$] = 1/3/2 (PCy$_3$ is tricyclohexylphosphine), initial molar ratio of the monomers 50/50, [M2] = [M3] = 0.75 M, [M3]/[Pd] = [M2]/[Pd] =100/1, dichloromethane, 45°C.
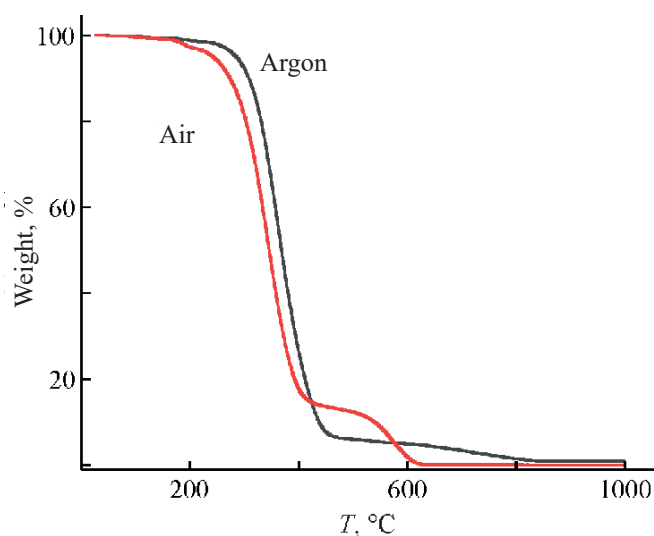

Fig. 2. Thermogravimetric analysis curves for addition poly(3-methyl-3-phenylcyclopropene).

The results of studying the copolymerization kinetics (Fig. 1a) show that the cyclopropene derivative exhibits higher polymerization activity: The M2 conversion in the polymerization was considerably higher than that of 5-ethylidene-2-norbornene. With time, virtually quantitative conversion of the cyclopropene derivative was reached, whereas the conversion of 5-ethylidene-2-norbornene by the moment of complete exhaustion of M2 was below 50%. Thus, the cyclopropene derivative is more active than the norbornene derivative in the addition polymerization. Taking into account the presence of bulkier substituents in M2 and their close location to the double bond undergoing polymerization, the observed higher polymerization activity of cyclopropene derivatives compared to that of 5-ethylidene-2-norbornene is most probably due to higher ring strain energy. With an increase in the conversion of the monomers, the molecular masses of the copolymers formed gradually increase (Fig. 1b).

The degradation temperature of these polymers (5% weight loss) exceeded 200°C (Fig. 2); i.e., the polymers exhibit high heat resistance, despite the presence of strained cyclopropane rings in the backbone.

Differential scanning calorimetry shows that the polymers prepared are glassy. The glass transition points of poly(M1) and poly(M2) are higher than their degradation temperatures. The differential scanning calorimetry curves contain no melting peaks, which indicates that the polymers are amorphous.

The X-ray diffraction analysis of the synthesized homopolymer based on M1 shows that it is amorphous (Fig. 3). There are four broad peaks in the diffraction pattern of poly(M1) (Fig. 3). On the contrary, in the diffraction patterns of addition polymers based on 5-ethylidene-2-norbornene and unsubstituted norbornene (Table 2) there are only two broad peaks. The peaks in the diffraction pattern of poly(M1) at 2θ from 8° to 12° characterize the spacings between the chains and backbone segments, and the peaks at 2θ from 15° to 23° characterize the spacings between the structural fragments within one chain and suggest agglomeration of pendant substituents with the probable formation of the corresponding nanosized phases.

CONCLUSIONS

Addition polymerization of two cyclopropenes with hydrocarbon substituents in the presence of a Pd
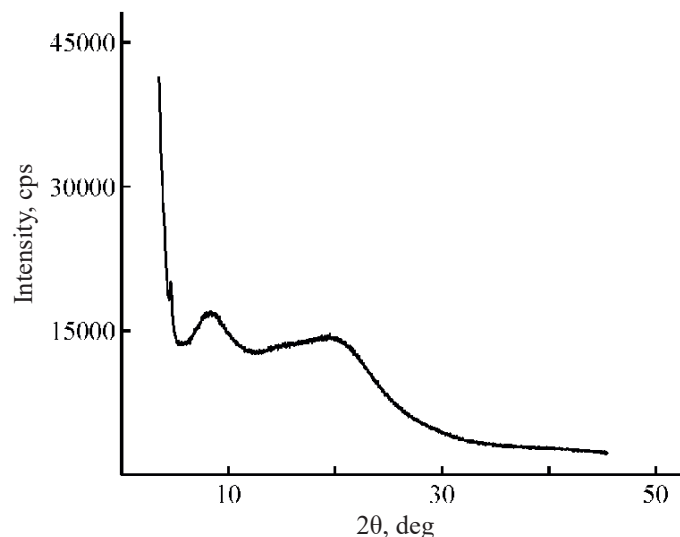
Fig. 3. Diffraction pattern of addition poly(3-methyl-3-phenylcyclopropene).

complex containing an acyclic diaminocarbene ligand was studied. The binary catalytic system based on this complex activated with an organoboron cocatalyst allows substituted cyclopropenes to be involved in polymerization, but the yield of the polymer products in this process is low. Introduction of phosphine into this catalytic system considerably enhanced its activity and allowed preparation of the target polymers in considerably higher yields. Cyclopropenes are considerably more active monomers than norbornene derivatives. The synthesized polymers based on the cyclopropenes studied are amorphous and glassy. They have the required heat resistance, which opens prospects for the development of new functional polymer materials based on these polymers. Therefore, further studies aimed at revealing the structure–property relationships for these polymers are topical.

ADDITIONAL INFORMATION

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AUTHOR CONTRIBUTION

E.I. Medentseva: synthesis of the polymers; A.P. Khrychikova: synthesis of the polymers; E.V. Bermesheva: synthesis of the polymers, data processing, manuscript preparation, description of the physicochemical properties of the polymers; K.V. Potapov: synthesis of 3-methyl-3-phenylcyclopropene and 3,3-di(*n*-propyl)cyclopropene; M.V. Bermeshev: manuscript preparation, interpretation of the research results.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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