

π -Allylic Rhodium Complex Catalyzed Living Copolymerization of Aryllallenes with Carbon Monoxide To Give Structurally Regulated Polyketones

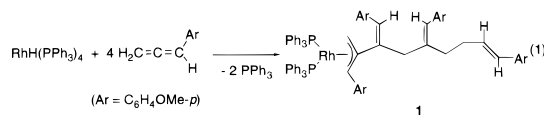
Kohtaro Osakada,* Jun-chul Choi, and Takakazu Yamamoto*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 226, Japan

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Palladium-catalyzed copolymerization of alkenes with carbon monoxide attracts considerable attention arising from the structure of the produced polymer with a high density of carbonyl functions and from potential utility as photodegradable materials.¹ This reaction has been recently extended to copolymerization of several dienes with carbon monoxide to give the corresponding polyketones shown in Chart 1.² A catalyst based on Pd compounds and chelating diamine has been reported to initiate copolymerization of 1,2-propadiene and CO to give the corresponding polyketone, $(\text{CH}_2\text{-C}(\text{=CH}_2))_n$.³ Control of structure and molecular weights in preparation of the polymers derived from 1,2-dienes and CO is of a significant interest since it has a unique enone structure in the repeating unit and can be converted into further functionalized derivatives. Here, we report the use of a new π -allylic rhodium complex for the first living copolymerization of 1,2-dienes with carbon monoxide to give new polyketones with a highly regulated structure.

The polymerization catalyst, $\text{Rh}[\eta^3\text{-CH}(\text{Ar})\text{C}\{\text{C}(\text{=CHAr})\text{-CH}_2\text{C}(\text{=CHAr})\text{CH}_2\text{CH}_2\text{CH}=\text{CHAr}\}\text{CH}_2](\text{PPh}_3)_2$ (**1**, $\text{Ar} = \text{C}_6\text{H}_4\text{-OMe-}p$), is obtained from reactions of $\text{RhH}(\text{PPh}_3)_4$ with (4-methoxyphenyl)allene in 1:4 and 1:5 molar ratios at room temperature. Complex **1** is isolated in high yields (>80%)



among many possible complexes that could result from the reaction of (4-methoxyphenyl)allene with $\text{RhH}(\text{PPh}_3)_4$.⁴ Figure 1 shows the molecular structure of **1** which possesses the π -allylic ligand formed through consecutive insertion of four (4-methoxyphenyl)allene molecules into the Rh–H bond of the

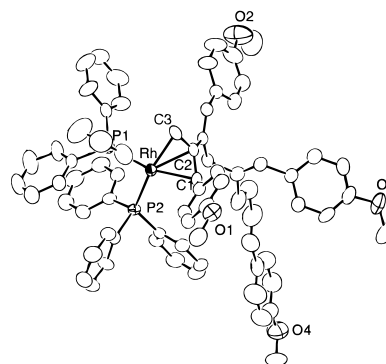
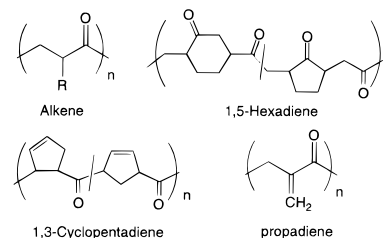


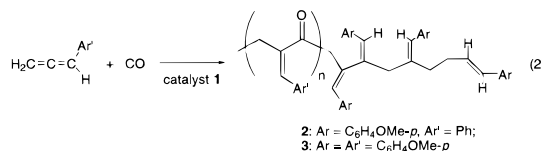
Figure 1. ORTEP drawing of $\text{Rh}[\eta^3\text{-CH}(\text{Ar})\text{C}\{\text{C}(\text{=CHAr})\text{-CH}_2\text{C}(\text{=CHAr})\text{CH}_2\text{CH}_2\text{CH}=\text{CHAr}\}\text{CH}_2](\text{PPh}_3)_2$ (**1**) with 30% thermal ellipsoidal levels. Hydrogens are omitted for simplicity.

Chart 1



starting complex.⁵ The NMR (¹H, ¹³C, ³¹P, ¹H–¹H COSY, and ¹H–¹³C COSY) spectra in solution are consistent with the crystallographic structure of the molecule.

Copolymerization of phenylallene and of (4-methoxyphenyl)allene with CO in the presence of a catalytic amount of **1** converts the monomers into polyketones $[\text{-CO-CH}_2\text{-C}(\text{=CHPh})\text{-}]_n$ (**2**) and $[\text{-CO-CH}_2\text{-C}(\text{=CHC}_6\text{H}_4\text{OMe-}p)\text{-}]_n$ (**3**), respectively.⁶ The ¹H NMR spectrum of **2** shows signals due to the repeating



unit formed through completely alternating insertion of phenylallene and carbon monoxide (Figure 2).⁷ Measurement using ROESY technique has revealed a *cis* orientation of the Ar and carbonyl groups in the repeating unit. The absence of structural unit from 1,2-polymerization and narrow peak width of the signals indicate highly regulated structure of the polymer chain. Small peaks at δ 3.6–3.8 are assigned to OMe hydrogens of the polymer end derived from **1**. The peak area relative to those of hydrogens in the repeating unit gives rise to M_n , which is

(5) X-ray data of **1**: triclinic, $P\bar{1}$ (No. 2), $a = 14.132(3)$ Å, $b = 18.519(7)$ Å, $c = 12.177(5)$ Å, $\alpha = 102.13(3)^\circ$, $\beta = 95.35(3)^\circ$, $\gamma = 95.60(2)^\circ$, $V = 3079$ Å³, $Z = 2$, $D_{\text{calc}} = 1.308$ g cm⁻³, $F(000) = 1268$, $\mu(\text{Mo K}\alpha) = 3.80$ cm⁻¹ for monochromated MoK α radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by full-matrix least-squares calculations. $R(R_w) = 0.062(0.044)$ for 7100 reflections with $I > 3\sigma(I)$ among 10709 unique reflections.

(6) The polymer products in this study have been treated with a large excess amount of MeOH before isolation and characterization in order to remove Rh and PPh₃ and are free from the metal and ligand.

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(2) (a) Drent, E. *Eur. Pat. Appl.* 504,985, 1992; *Chem. Abstr.* **1993**, *118*, 103023 (b) Borkowsky, S. L.; Waymouth, R. M. *Macromolecules* **1996**, *29*, 6377. (c) Nozaki, K.; Sato, N.; Nakamoto, K.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 659.

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(4) Insertion of four (4-methoxyphenyl)allene molecules into the Rh–H bond occurs rapidly at room temperature to give **1** selectively in the reactions of $\text{RhH}(\text{PPh}_3)_4$ and (4-methoxyphenyl)allene in 1:4 and 1:5 molar ratios. Once formed **1** does not react further with additional phenylallene or (4-methoxyphenyl)allene at this temperature. Formation of other complexes than **1** and $\text{RhH}(\text{PPh}_3)_4$ is not noted in the reaction mixture.

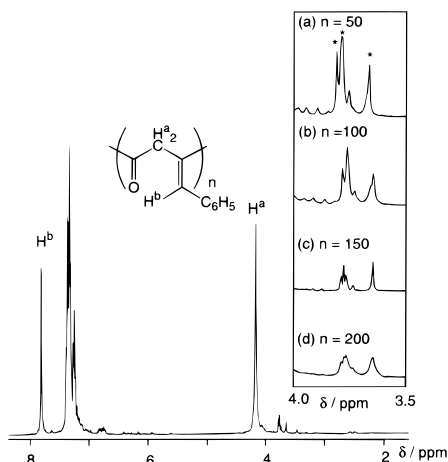


Figure 2. ^1H NMR spectrum of $(\text{CH}_2\text{-C(=CHPh)-CO})_n\text{-I}$ (**2**, $n = 50$) where I denotes the polymer end group derived from **1**. Decrease in the relative intensity of OCH_3 hydrogens of **1** caused by increase in the monomer/catalyst ratios is shown in inset.

Table 1. Results of Copolymerization of Phenylallene and CO Initiated by **1**

conditions ^a	product ^b		
$[\text{CH}_2=\text{C}=\text{CHPh}]_0/[\text{1}]$	$10^{-3}M_n$ (GPC) ^c	M_w/M_n ^c	$10^{-3}M_n$ (NMR) ^d
50	7.9	1.08	7.2 (7.8)
100	17.1	1.09	14.6 (15.0)
150	25.6	1.14	23.0 (22.2)
200	35.0	1.10	<i>e</i> (29.4)

^a Polymerization was carried out under CO (1 atm) in THF using 0.050 mmol of **1** at room temperature. ^b Polyketone **2** is obtained quantitatively in each reaction. ^c Determined by GPC using polystyrene standards. ^d Determined from ^1H NMR peak area ratio between the OCH_3 and CH_2 hydrogens, based on the molecular formula $\text{H-}[(\text{CH}_2\text{-C(=CHPh)-CO})_n\text{-CH}_2\text{C(=CH(Ar))}-\text{C(=CHAr)CH}_2\text{C(=CHAr)-CH}_2\text{CH}_2\text{CH=CHAr}]$ ($\text{Ar} = \text{C}_6\text{H}_4\text{OMe-}p$). Calculated molecular weights assuming quantitative efficiency of the initiator **1** are shown in parentheses. ^e Not determined due to small peak intensity of the OCH_3 hydrogens.

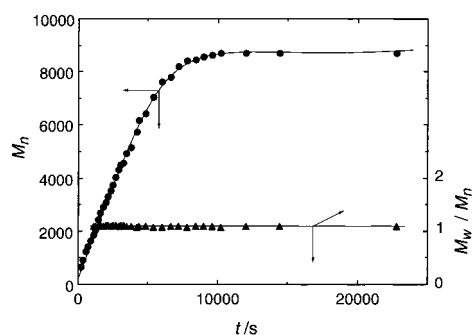


Figure 3. Change in M_n and M_w/M_n of growing polymer during polymerization of phenylallene (55 mol/l) and CO initiated by **1**. A small portion of the solution obtained by a syringe is quenched by MeOH and analyzed by GPC (polystyrene standards) for each plot. The final molecular weight of the product is consistent with the initial molar ratio of phenylallene and **1**.

close to that from GPC using polystyrene standards. Molecular weights of **1** increase with increase in the monomer/catalyst ratio without significant change of polydispersity ($M_w/M_n = 1.08\text{--}1.14$) as summarized in Table 1. Figure 3 depicts change in molecular weight of the growing polymer during the reaction. Molecular weight of the polymer increases with narrow molecular weight distribution ($M_w/M_n < 1.11$) until consumption of phenylallene. The above results imply that the copolymerization proceeds without any chain transfer reaction.

Copolymerization of phenylallene with carbon monoxide catalyzed by **1** and ensuing addition of (4-methoxyphenyl)allene

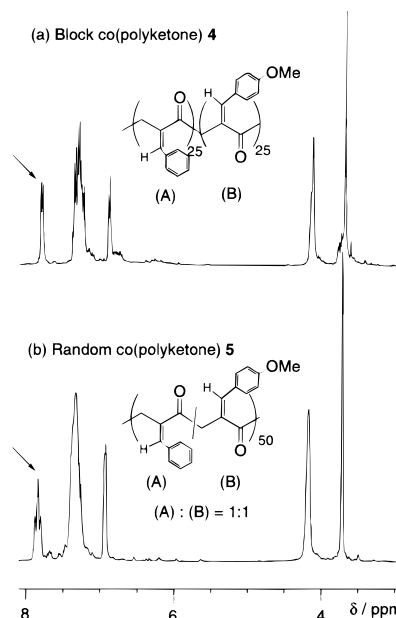
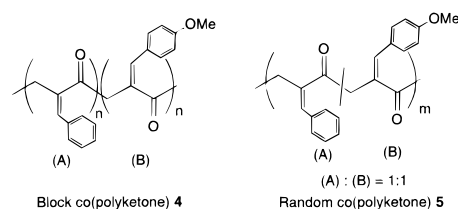


Figure 4. ^1H NMR spectra of block copolyketone **4** and random copolyketone **5**. Positions of the vinylic hydrogen signals are shown with arrows.

Chart 2



to the resulting mixture afford block copolyketone **4**, whose structure is shown in Chart 2.⁸ An equimolar mixture of phenylallene and (4-methoxyphenyl)allene reacts with carbon monoxide to give **5** containing units A and B randomly. Figure 4 compares the ^1H NMR spectra of **4** and **5**. Copolymer **4** shows two sharp peaks due to vinyl hydrogens of the blocks $\text{AAA}\cdots\text{A}$ (δ 7.82) and $\text{BBB}\cdots\text{B}$ (δ 7.80). The corresponding vinylic hydrogen of **5** appears at δ 7.7–7.9 as three peaks, which are resulted from random sequence of the structural units A and B.⁹

All of the above results, including narrow molecular weight distribution of **2** during the polymerization reaction and formation of the block copolymer **4**, indicate that **1** catalyzes living copolymerization of the arylallenes with carbon monoxide to afford new polyketones under mild conditions.

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Supporting Information Available: Full experimental details, crystallographic data of complex **1**, and NMR, GPC, and DSC data of the polymers (30 pages). See any current masthead page for ordering and Internet access instructions.

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(8) GPC analyses of the reaction mixture in preparation of the block copolyketone show unimodal patterns with narrow molecular weights distribution ($M_w/M_n = 1.09\text{--}1.10$) before addition of the second monomer ((4-methoxyphenyl)allene) and after consumption of both monomers.

(9) The three ^1H NMR peaks of **5** at δ 7.7–7.9 in a 1:2:1 area ratio can be assigned to the triads ABA (and BAB), ABB (AAB, BAA, and BBA), and AAA (and BBB), respectively. ABB and BBA as well as AAB and BAA are equal to each other.