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COMMUNICATIONS

Published on Web 01/08/2002

Pd-Catalyzed Ring-Opening Copolymerization of 2-Aryl-1-methylenecyclopropanes with CO to Afford Polyketones via Alternating Insertion of the Two Monomers and C−C Bond Activation of the Three-Membered Ring

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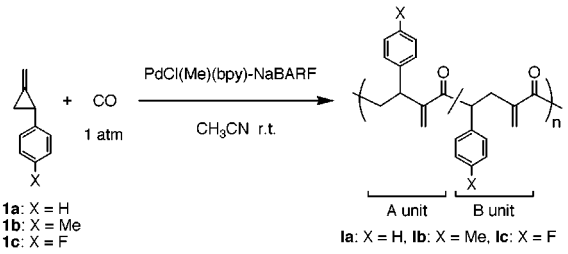
Received November 2, 2001; Revised Manuscript Received December 7, 2001

Palladium-complex-catalyzed copolymerization of alkene and CO forms various polyketones via alternating copolymerization of the two monomers.[1,2] The reactions of strained cyclic olefins with CO, which involve ring opening of the monomer, are thermodynamically favorable and are expected to produce the polymers with novel structures. Only a few reports of such polymerization, however, have appeared in the literature.[3] Copolymerization of methylenecyclopropane with CO catalyzed by a Pd−phosphine complex was recently shown to give the polyketone that contains a structural unit formed via ring-opening copolymerization as a minor component.[4] 2-Aryl-1-methylenecyclopropanes were found to undergo homopolymerization catalyzed by Pd−diimine complexes and form the structurally regulated hydrocarbon polymers.[5] In this contribution, we report ring-opening copolymerization of the cyclic monomer with CO, affording the polyketones exclusively composed of ring-opened structural units.



2-Phenyl-1-methylenecyclopropane (**1a**) reacts with CO (1 atm) in the presence of the catalyst, prepared in situ from PdCl(Me)(bpy) and NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$), to produce polyketone **Ia** (M_n = 19 000, M_w/M_n = 1.44 by GPC, polystyrene standards) in 84% yield at room temperature (eq 1). NMR spectroscopy including DEPT and $^{13}C-^{1}H$ COSY technique revealed the ring-opened structure of all the monomer units in the product. The polyketone contains the isomeric structural units **A** and **B**, both via ring-opening copolymerization, in 62:38 ratio. Figure 1(i) depicts the $^{13}C\{^{1}H\}$ NMR spectrum of **Ia**, showing the $=CH_2$ carbon signals at δ 123.5 and 124.9. The signals at δ 41.6−43.1 and 40.6−41.6 are assigned to the CH_2 and CHPh carbons of structural unit **A** in eq 1, respectively, on the basis of comparison of the positions with those of model compounds.[6] The peaks at δ 35.2−36.1 and 50.2−51.8 correspond to the structural unit **B**.

The structural unit of **Ia** contains a vinylidene group, which is similar to that of the homopolymer obtained by the Pd−diimine complex-catalyzed polymerization of the monomer at elevated temperature.[5] Isotope-labeled experiments, however, indicated a different insertion mode of the monomer and different end structure

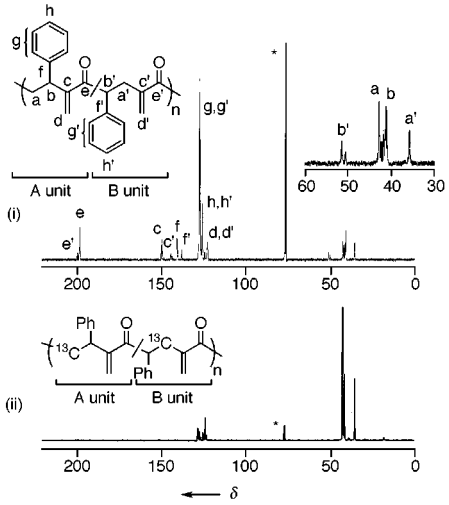


Figure 1. $^{13}C\{^{1}H\}$ NMR spectra of (i) **Ia** and (ii) **Ia-^{13}C** in $CDCl_3$ at 25 °C. The copolymerization of 2-phenyl-1-methylenecyclopropane (**1a**, **1a-^{13}C**) with CO was carried out in the presence of PdCl(Me)(bpy) ([Pd] = 25 mM, [**1a**]/[Pd] = 100) at 1 atm in CH_3CN at room temperature. The peaks with asterisks are due to the solvent.

of the polymer between the copolymerization and homopolymerization. The copolymerization of 2-phenyl-1-methylenecyclopropane-3-^{13}C (**1a-^{13}C**) with CO produces **Ia-^{13}C** whose $^{13}C\{^{1}H\}$ NMR spectrum is shown in Figure 1(ii). The signals at δ 35.1−36.2 and 41.0−43.3 correspond to the ^{13}C-enriched CH_2 carbons in the polymer chain. In contrast, the homopolymerization of the same-labeled monomer introduces the enriched ^{13}C only at the vinylidene carbon of the polymer.

The above-mentioned labeled position of polyketone **Ia-^{13}C** indicates cleavage of a proximal C−C bond during the polymerization, as shown in Scheme 1. Insertion of CO into the Pd−alkyl bond of the growing polymer gives the acylpalladium intermediate. 1,2-Insertion of the methylenecyclopropane into the Pd−acyl bond forms a β-cyclopropylidenealkyl palladium intermediate that undergoes rapid β-alkyl elimination,[7] resulting in the formation of a Pd complex having an α- or β-phenyl alkyl ligand. Repetition of the above procedures accounts for the alternating copolymerization to produce the polyketone. The activation of $C-CH_2$ and C−CHPh bonds, promoted by Pd, forms the two repeating units **A** and **B**, respectively. The existence of units **A** and **B** in the polymer chain is consistent with 1,2-insertion of 2-phenyl-1-methylenecyclopropane. Copolymerization of α-olefins with CO also proceeds mostly via 1,2-insertion of the α-olefins into the Pd−acyl bond.[1,2c] It contrasts with the mechanism of the homopolymerization of 2-aryl-

10.1021/ja017460s CCC: $22.00

Scheme 1

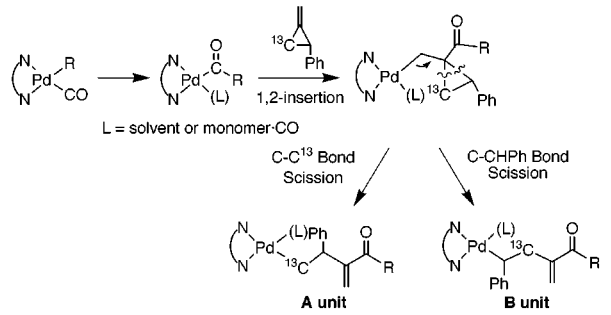


Table 1. Copolymerization of 2-Aryl-1-methylenecyclopropanes with CO Catalyzed by Pd Complexes[a]

runst	catalyst	time (h)	yield (%)	M_n (M_w/M_n)[b]
1[c]	PdCl(Me)(bpy) + NaBARF	3	84	19000 (1.44)
2[c]	PdCl(Me)(bpy) + $NaBF_4$	3	85	20000 (2.17)
3[c]	PdCl(Me)(bpy) + AgOTf	3	92	23000 (3.19)
4	PdCl(Me)(bpy)	66	60	17000 (1.72)
5	[(π-PhCHCHCH$_2$)Pd(bpy)]BF_4	15	37	450000 (2.40)
6[c,d]	PdCl(Me)(bpy) + AgOTf	3	87	28000 (4.57)
7[c,e]	PdCl(Me)(bpy) + AgOTf	3	77	34000 (3.65)

[a] The reaction conditions: [Pd] = 25 mM, [**1a**] = 2.5 M, CO pressure: 1 atm, at rt in CH_3CN unless otherwise stated. [b] Determined by GPC in THF vs polystyrene standards. [c] [Pd]:[Ag (or Na)] = 1:1.2. [d] Monomer **1b**. [Pd] = 12.5 mM, [**1b**] = 1.25 M, in THF. [e] Monomer **1c**. [Pd] = 12.5 mM, [**1c**] = 1.25 M, in THF.

1-methylenecyclopropanes containing selective 2,1-insertion of C=C double bond of the monomer into the π-allyl−Pd bond.[5a] Homopolymerization of methylenecyclopropanes catalyzed by metallocene compounds and by Ni complex takes place via 1,2-insertion, similarly to the copolymerization in this study.[5b,8]

Expansion of the three-membered ring during the polymerization renders insertion of 2-phenyl-1-methylenecyclopropane followed by rearrangement of the growing polymer thermodynamically favorable. To examine the effect of the monomer structure on the reaction rate, we conducted kinetic measurement of the polymerization. The reaction obeys first-order kinetics with respect to the concentration of 2-phenyl-1-methylenecyclopropane at −30 to 0 °C. The observed rate constant at 0 °C in THF-d_8 is 5.4×10^{-4} s^{-1} with catalyst concentration of 12.5 mM (k_{obsd}/[catalyst] = 4.4×10^{-5} s^{-1}(cat mmol)$^{-1}$). The first-order kinetics indicates that the rate-determining step of the polymer growth is the insertion of methylenecyclopropane into the Pd−C bond rather than CO insertion, similarly to most alkene−CO copolymerization reported thus far.[9] It is contrasted with the Rh-catalyzed copolymerization of arylallenes with CO although both allene and methylenecyclopropane have a more reactive C=C double bond than alkene.[10]

Table 1 summarizes the results of the polymerization. AgOTf and $NaBF_4$ are also effective as the cocatalyst for the copolymerization (runs 2, 3), suggesting that the cationic Pd complexes act as the efficient catalysts for the ring-opening copolymerization. PdCl(Me)(bpy) catalyzes the polymerization in the absence of the additives, but in a much lower rate (run 4). π-Allyl−Pd complex also promoted the copolymerization to give the copolymer with a high molecular weight (M_n = 450 000) in a lower yield (run 5). It is attributed to a much slower insertion of CO into the Pd−π-allyl bond than that into the Pd−Me bond.[11] 2-Phenyl-1-methylenecyclopropanes having Me or F substituents on the phenyl ring also undergo copolymerization to give the corresponding polyketones (runs 6, 7).

In summary, we found the Pd-complex-catalyzed ring-opening copolymerization of 2-aryl-1-methylenecyclopropanes with CO to afford the new polymers. The polymer growth, including alternating insertion of the monomers and C−C bond activation of the three-membered ring of the polymer, is well-regulated by the Pd complex.

Acknowledgment. The present work was partly supported by Sumitomo Foundation.

Supporting Information Available: Experimental procedures for polymerization and IR and NMR data of the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Selected $^{13}C\{^1H\}$ NMR data of **Ia** and the structurally analogous compounds indicated the polymer structure unambiguously. **Ia**: δ 35.7, 41.8, 42.2, 42.7 (CH_2), 41.1, 41.4, 50.3, 51.3 (CH), 123.5, 124.9 (=CH_2), 126.3, 126.9 (*p*-Ph), 127.8, 127.9, 128.0, 128.2, 128.6 (*o*-, *m*-Ph), 138.6, 141.5 (*ipso*-Ph), 144.8, 145.2, 150.1, 150.4, 150.9 (C=), and 198.6, 198.8, 199.9, 200.1, 200.7 (C=O). CH_2=CHCHPhCH$_2$C(=O)CH_3: δ 30.4 (CH_3), 44.3 (CH), 48.7 (CH_2), 114.4 (CH_2=), 140.4 (=CH), 126.4 (*p*-Ph), 127.4−128.2 (*o*-, *m*-Ph), 142.6 (*ipso*-Ph), and 206.7 (C=O). CH_2=CHCH$_2$-CHPhC(=O)CH_3: δ 28.99 (CH_2Me), 36.1 (CH_2), 59.4 (CH), 116.6 (CH_2=), 135.8 (=CH), 127.3 (*p*-Ph), 128.3−128.9 (*o*-, *m*-Ph), 138.4 (*ipso*-Ph), and 207.6 (C=O). As for the last compound, see: Molander, G. A.; Cameron, K. O. *J. Am. Chem. Soc.* **1993**, *115*, 3339.

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JA017460S