Alternating Copolymerization

Cobalt-Complex-Catalyzed Copolymerization of Ethylene with 2-Aryl-1-methylenecyclopropanes

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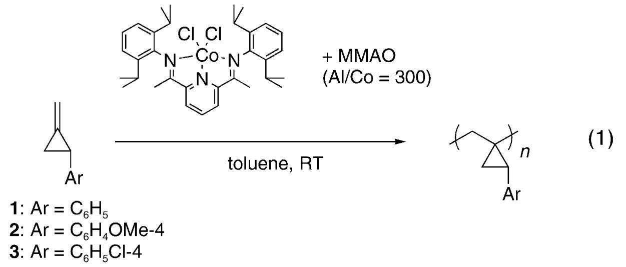
Copolymers of ethylene and monomers having polar functional groups, such as COOR and OR, have attracted attention because polymers with polar substituents exhibit properties that are not available to hydrocarbon polyolefins. Ni and Pd complexes with chelating N-ligands were reported to catalyze the random copolymerization of ethylene with acrylic esters[1] and with norbornene containing a COOR group,[2] while samarocenes initiate the block copolymerization of ethylene with acrylic esters to form AB type block copolymers.[3] Although the alternating copolymerization of ethylene with an α-olefin[4] and with norbornene[5] was promoted by Ti, Zr, Ni, and Pd complexes, there have been no reports on alternating copolymers of ethylene and vinyl monomers that have polar functional groups. Herein, we report the copolymerization of ethylene with 2-aryl-1-methylenecyclopropanes[6,7] that have OR or Cl groups promoted by a Co complex to afford new polymers comprising functionalized C_4 repeating units.

2-Aryl-1-methylenecyclopropanes (**1**–**3**) were smoothly polymerized in the presence of [$CoCl_2L$] (L = bis(imino)pyridine)[8,9] and MMAO (MMAO = modified methylaluminoxane) at room temperature to produce the polymer with a three-membered ring in each structural unit [Eq. (1)]. 2-Phenyl-1-methylenecyclopropane (**1**) underwent living polymerization and gave the polymer with molecular weights of $\bar{M}_n = 8500$ to 200000 ($\bar{M}_w/\bar{M}_n = 1.12$–1.19; $\bar{M}_n$ is the number-average molar mass, $\bar{M}_w$ is the weight-average molar mass) as shown in Figure 1.[10] Monomers **2** and **3**, with OMe and Cl groups on their respective phenyl rings, were also polymerized smoothly to form polymers with molecular weights of $\bar{M}_n = 3000$–43000, which varied depending on the initial monomer-to-catalyst ratio.



Copolymerization was conducted by adding MMAO to a toluene solution of the Co complex and 2-aryl-1-methylene-

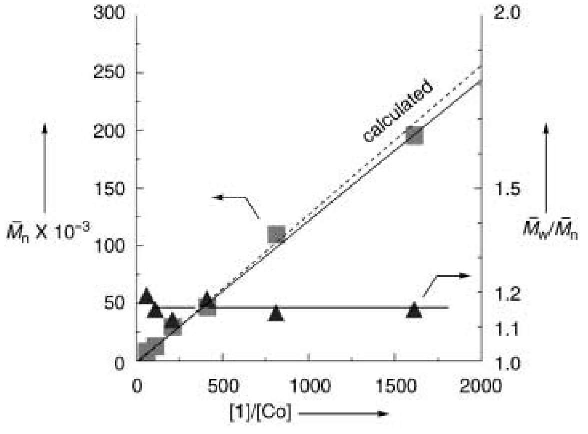


Figure 1. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymer of **1** plotted against initial monomer-to-Co molar ratio. Conditions: [Al]/[Co] = 300 in toluene at −40 °C. Dashed line shows the molecular weights calculated from $[\mathbf{1}]_0$/[Co].

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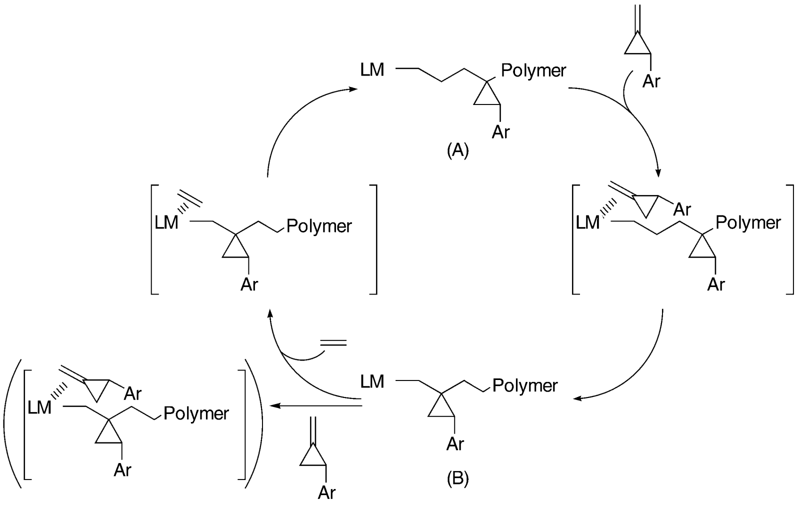
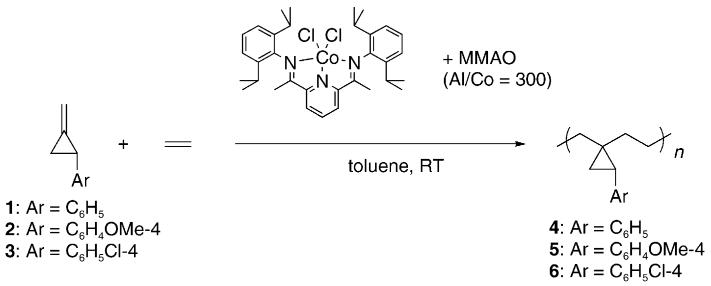
cyclopropane under ethylene (1 atm). The ^{1}H and ^{13}C{^{1}H} NMR spectra and GPC elution pattern of the copolymer from ethylene and **2** indicate a structure composed of two alternating monomer units as shown in Equation (2). Figure 2 shows the ^{13}C{^{1}H} NMR spectrum of the copolymer, which exhibits six sharp signals due to the aliphatic carbons at $\delta = 18$–40 ppm. The spectrum does not contain signals that arise from a homopolymer of the monomers or random copolymer units. A comparison of the spectrum with that of a model compound (1,1-dibutyl-2-phenylcyclopropane) and results from DEPT NMR spectroscopy also support the proposed structure.



Scheme 1. Mechanism of alternating copolymerization of ethylene with monomers **1**–**3**. ML denotes Co bonded to the bis(imino)pyridine ligand. See reference [8c,d] for the active species of the catalyst proposed for ethylene polymerization.



(2)

Scheme 1 depicts the mechanism proposed for the alternating copolymerization. The growing polymer with the Co–CH$_2$–CH$_2$ chain (A) undergoes coordination of **2** and 1,2-insertion of its C=C bond into the Co–C bond.[11,12] The formed intermediate (B) undergoes preferential ethylene insertion to regenerate A. The monomer reactivity ratios r_2 and r_{ethylene}[13] are determined to be 1.1 and 0.05, respectively, from the Fineman–Ross plots. The strong coordination of **2** to A suppresses the double insertion of ethylene to make the r_{ethylene} value small because the addition of 2-methyl-2-phenyl-1-methylenecyclopropane, which does not polymerize under these conditions, inhibits the ethylene polymerization catalyzed by the Co complex. All these results are in contrast with the alternating copolymerization of ethylene with norbornene catalyzed by Zr and Ti complexes, in which the double insertion of ethylene is much easier than that of the cyclic monomer ($r_{\text{ethylene}} > 1$, $r_{\text{norbornene}} = 0.36$–0.03).

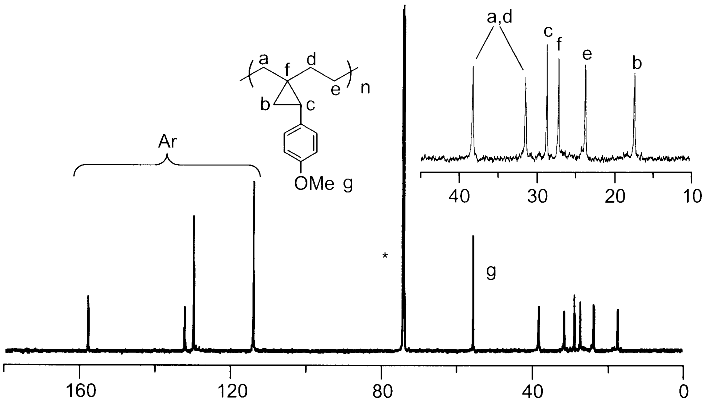
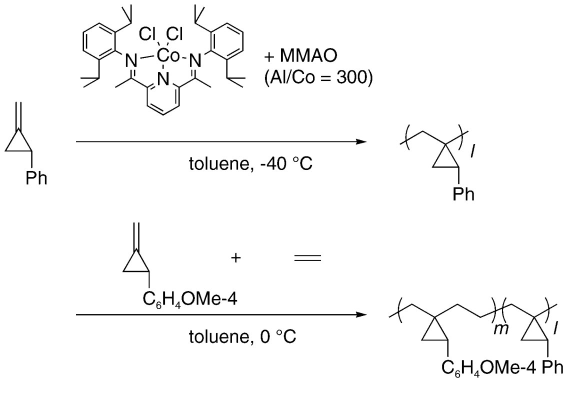


Figure 2. ^{13}C{^{1}H} NMR spectrum of poly(2-(4-methoxyphenyl)-1-methylenecyclopropane-*alt*-ethyene). Conditions: 1 atm of ethylene in toluene −40 °C ([**2**]$_0$ = 28 mM, [ethylene]$_0$ = 135 mM). The signal with the asterisk is due to the solvent (C$_2$D$_2$Cl$_4$).

The alternating copolymerization, which is initiated by the living polymer of 2-phenyl-1-methylenecyclopropane ($\bar{M}_n = 9300$, $\bar{M}_w/\bar{M}_n = 1.14$), affords an AB block copolymer, $\text{-}(CH_2\text{-}\overline{CCH_2C}HPh)_l\text{-}(CH_2\text{-}CH_2\text{-}CH_2\text{-}\overline{CCH_2C}H(C_6H_4OMe\text{-}4))_m\text{-}$ ($l{:}m = 29{:}71$, $\bar{M}_n = 28\,000$, $\bar{M}_w/\bar{M}_n = 1.77$) [Eq. (3)]. The produced polymer molecules contain the segment composed of C$_4$ units that have an OMe group, which is probably softer than the other segment composed of C$_2$ units with phenylcyclopropylidene group.[6c]



(3)

In summary, we have found that the Co complex promotes the living addition polymerization of 2-phenyl-1-methyhlencyclopropane and the alternating copolymerization of ethylene with 2-aryl-1-methylenecyclopropanes. The resulting copolymers have a regulated structure composed of C$_4$

repeating units with a three-membered ring. The polymerization is tolerant of functional groups such as methoxy and chloro groups. We are continuing to investigate the copolymerization of ethylene with other functionalized monomers.

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[10] Re-addition of **1** to the reaction mixture after consumption of the initially charged monomer ($\bar{M}_n = 8300$, $\bar{M}_w/\bar{M}_n = 1.16$) induces the polymerization to afford a product with an increased molecular weight and a narrow molecular weight distribution ($\bar{M}_n = 26000$, $\bar{M}_w/\bar{M}_n = 1.14$); this result also indicates that the living polymerization is efficient. A slightly lower efficiency of the initiation than the ideal living polymerization is ascribed to slow or insufficient activation of the Co complex by MMAO. See also: P. Mehrkhodavandi, R. R. Schrock, L. L. Pryor, *Organometallics* **2003**, *22*, 4569–4583.

[11] Polymerization of methylenecyclopropane catalyzed by Zr and Ni complexes is proposed to involve the 1,2-insertion of the monomer into the M−C σ bond (See refs [6b] and [7]). The 1,2-insertion of monomer is also supported by an end functionalization experiment.

[12] Recent papers on ethylene polymerization by Co catalyst (Ref [8c,d]) suggested that the Co^{III} complex is most likely the active species in the reaction.

[13] $r_{\mathbf{2}} = k_{\mathbf{2},\mathbf{2}}/k_{\mathbf{2},\mathrm{ethylene}}$ and $r_{\mathrm{ethylene}} = k_{\mathrm{ethylene,ethylene}}/k_{\mathrm{ethylene},\mathbf{2}}$, in which $k_{\mathbf{2},\mathbf{2}}$ and $k_{\mathbf{2},\mathrm{ethylene}}$ denote the rate constants for the insertion reactions of **2** and ethylene into the Co−C bond of $Co{-}CH_2{-}\overline{CCH_2C}H(C_6H_4OMe\text{-}4)$, respectively.