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Alternating Copolymerization of Ethylene with 7-Methylenebicyclo[4.1.0]heptane Promoted by the Cobalt Complex. Highly Regulated Structure and Thermal Rearrangement of the Obtained Copolymer

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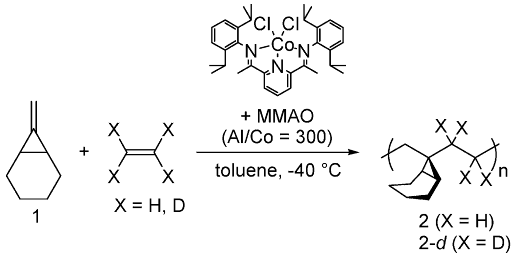
Alternating copolymerization of ethylene with substituted alkenes produces the polymer composed of C4 repeating units, which could hardly be obtained from a single monomer. Copolymerization of ethylene with α-olefin by metallocene catalyst forms an alternating copolymer,[1] while metallocenes and Ni and Pd complexes catalyze the copolymerization of ethylene with norbornene to afford hydrocarbon polymers that exhibit good optical transparency and high glass transition temperature.[2,3] Methylenecyclopropanes, which undergo the addition polymerization[4] or the ring-opening polymerization[5,6] depending on the catalyst employed, also function as the comonomer in the copolymerization with ethylene. Marks et al. reported the copolymerization of ethylene with 7-methylenebicyclo[4.1.0]heptane to afford polyethylene containing olefinic groups formed via insertion of the latter monomer into Zr−polymer bond and subsequent C−C bond cleavage of the three-membered ring.[7] Recently, we found that the alternating copolymerization of ethylene with 2-aryl-1-methylenecyclopropanes catalyzed by Co−bis(imino)pyridine complexes[8] forms polymers with cyclopropylidene groups.[9] In this paper, we report Co complex-catalyzed copolymerization of ethylene with 7-methylenebicyclo[4.1.0]heptane to afford the alternating copolymer with a highly regulated structure. Thermally induced ring-opening reaction of the copolymer, giving a new polymer with trisubstituted C═C bond in the main chain, is also described.

Scheme 1



Stirring a toluene solution of 7-methylenebicyclo[4.1.0]heptane (0.18 g), Co−bis(imino)pyridine complex (1.7 mM), and modified methylaluminoxane[10] (MMAO) ([Al]/[Co] = 300) for 1 h under ethylene atmosphere (1 atm) affords the alternating copolymer of the two monomers, **2**, at −40 °C (Scheme 1). The reaction using C_2D_4 as the comonomer produces the deuterated polymer **2-*d***. Poor solubility of the copolymer in THF and chloroform prevented determination of the molecular weight, although GPC analysis of the product of thermal isomerization of **2** shows the molecular weight of 5800 (vide infra). The $^{13}C\{^1H\}$ NMR spectrum was obtained by dissolving the polymer in $C_2D_2Cl_4$ at 130 °C, cooling the resulting solution, and measuring the spectrum at room temperature soon. The aliphatic carbon region of the spectrum (Figure 1A) contains seven sharp signals which are assigned to the carbons of the alternating copolymer unit based on comparison of the peak positions with those of 7,7-dibutylmethylenebicyclo[4.1.0]heptane.[11] No signals were found in the range δ 80−160, indicating that the product did not contain olefinic groups. The signals at δ 26.4 and 40.1 are attributed to the CH_2 carbons bonded to the three-membered ring of the polymer.[12] The former signal is assigned to the carbon on the same side of the cyclohexane-1,2-diyl group (carbon d in the formula of Figure 1A), while the latter is due to that on the opposite side (carbon b). Difference in the peak positions (14 ppm) is reasonable by taking difference of shielding effects of these carbons caused by the six-membered ring attached to the three-membered ring into consideration.[13] The $^{13}C\{^1H\}$ NMR spectrum of **2-*d*** shows five sharp signals at δ 19.1, 19.5, 22.7, 25.0, and 26.2, and two weak signals at δ 22.1 and 39.1 with broadening (Figure 1B). The positions of the latter signals are shifted from the corresponding signals of **2** (δ 23.0 and 40.1) with large isomer shifts (0.921 and 1.004 ppm, respectively). Thus, they are assigned to the CD_2 carbons derived from C_2D_4 monomer. All these results indicate that the copolymer of C_2D_4 and 7-methylenebicyclo[4.1.0]heptane, **2-*d***, contains partial structure i in Scheme 2 almost exclusively among four possible structures shown in Scheme 1.

Scheme 3 depicts the mechanism proposed for the polymer growth. The growing polymer with the $Co{-}CH_2{-}CH_2{-}$ bond (**A**) undergoes 1,2-insertion of 7-methylenebicyclo[4.1.0]heptane into the Co−C bond.[14] Precoordination of the C═C double bond of the bicyclic monomer occurs at the opposite side of the six-

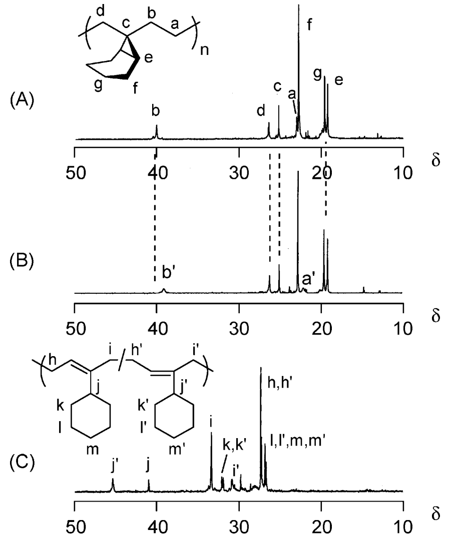


Figure 1. $^{13}C\{^1H\}$ NMR spectra of (A) **2**, (B) **2-*d***, and (C) **3** in $C_2D_2Cl_4$ at room temperature. The samples of **2** and **2-*d*** were prepared by dissolving the polymers at 130 °C for a short period (ca. 1 min) in the solvent and cooling the solution rapidly in order to avoid thermal isomerization of the polymer.

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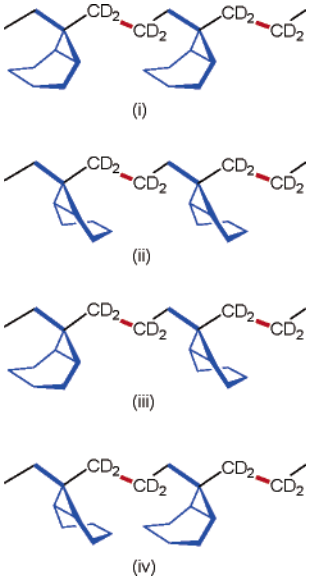
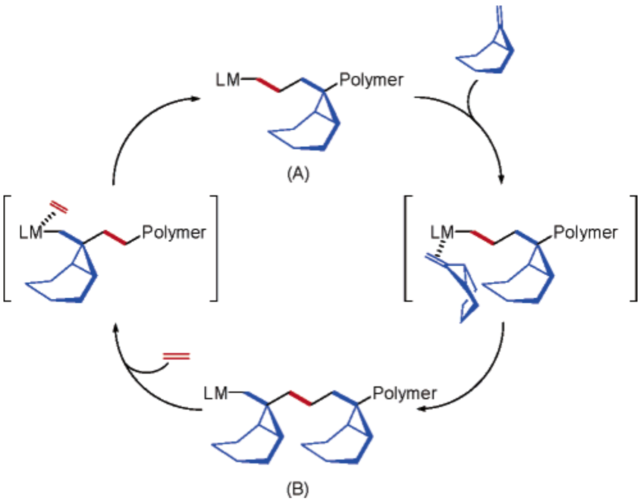
Scheme 2

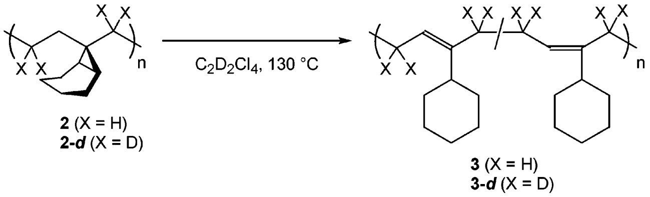


Scheme 3

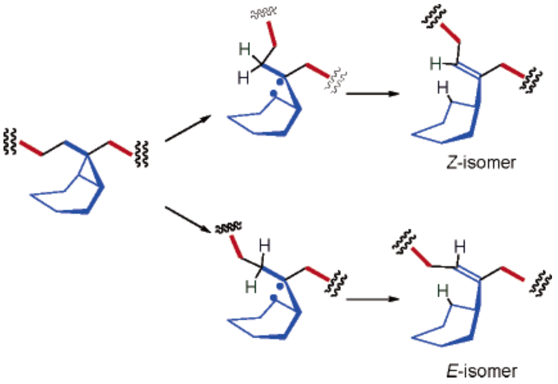


membered ring in order to avoid steric repulsion between the ring of the coordinated monomer and that of the polymer end. The formed intermediate **B** undergoes insertion of ethylene preferentially to regenerate **A**. Strong coordination of 7-methylenebicyclo[4.1.0]heptane to the Co center of **A** prevents double insertion of ethylene, similar to the copolymerization of ethylene with 2-phenyl-1-methylenecyclopropane.[9] Double insertion of 7-methylenebicyclo[4.1.0]heptane is also inhibited due to steric bulkiness of the monomer. In fact, homopolymerization of 7-methylenebicyclo[4.1.0]heptane promoted by the Co complex is quite slow,[15] although the zirconocenes catalyze the smooth polymerization of the same monomer without ring opening.[7] It contrasts with the results that the copolymerization of ethylene (1 atm) with 2-phenyl-1-methylenecyclopropane (>150 mM) accompanies double insertion of the cyclic monomer to produce the polymer having oligo(methylenecyclopropane) units.

Scheme 4



Scheme 5



Heating a $C_2D_2Cl_4$ solution of **2** at 130 °C for 12 h changes the $^{13}C\{^1H\}$ NMR spectrum, as shown in Figure 1C. The signals of **2** at δ 18−24 are not observed after heating, while signals at δ 123 and 145 are newly generated and assigned to olefinic carbons of the product of the thermal reaction. The DEPT spectrum of the polymer after heating showed a pair of the CH carbons at δ 41.0 and 45.4. Comparison of the spectrum with those of 2-cyclohexyl-2-butene[16] and poly(isoprene)[17] indicates that the product of thermolysis is polymer **3**, having a structure of poly(2-cyclohexyl-1,3-butadiene) (Scheme 4). The appearance of a pair of signals for each carbon of the cyclohexyl ring suggests the presence of trans and cis C=C bond in the polymer chain. GPC analysis of **3**, which is soluble in THF, showed that M_n and M_w/M_n of the polymer are 5800 and 1.69. **2-*d*** also undergoes the thermal isomerization to afford the corresponding deuterated polymer **2-*d***. ^2H NMR spectrum of **3-*d*** showed broad large signals at δ 1.15 and 1.93 (CD_2) and a much smaller signal at δ 5.05 (=CD).

This type of thermal rearrangement of the fused rings takes place also in organic molecules. 2-Methyl-1-phenylcyclopropane was reported to undergo photoisomerization into 4-phenyl-1-butene.[18] We conducted thermal reactions of 7,7-dimethylbicyclo[4.1.0]heptane and 7,7-dibutylbicyclo[4.1.0]heptane in $C_2D_2Cl_4$ at 130 °C for 12 h and observed clean formation of 1-isopropylcyclohexene and (*E*)-5-cyclohexyl-4-nonene, respectively.[19] These isomerization reactions are considered to proceed via formation of biradical species followed by 1,4-migration of a hydrogen atom. Thus, the thermal isomerization reaction of **2** and **2-*d*** also causes homolytic cleavage of the C−C bond of three-membered ring to form biradical species, shown in Scheme 5. Abstraction of a hydrogen from the CH_2 group in the polymer chain by the radical within the six-membered ring forms the C=C double bond in the main chain. The cyclohexyl radical of **2-*d*** abstracts mainly the hydrogen from the CH_2 group on the same side of the cyclohexane-1,2-diyl group with respect to the cyclopropane plane. Thus, the repeating unit containing a −HC= group is contained in much more amount than that with a −DC= group. Formation of *Z*- and *E*-olefinic group indicates that both hydrogens of the CH_2 group undergoes the 1,4-migration.

The first DSC scan of **2** shows an endothermic peak at 100 °C on heating, corresponding to the thermal isomerization of the copolymer, and no exothermic peak on cooling. The second scan exhibits transition due to

T_g at 52 °C. The results suggest that the isomerization of **2** occurs also in the solid state.

In summary, the Co catalyst does not cause homopolymerization of 7-methylenebicyclo[4.1.0]heptane but promotes alternating copolymerization of ethylene with it smoothly and stereoselectively at -40 °C to afford the polymer with a unique structure. The polymer has entirely different structure from the product of the copolymerization of the same monomers catalyzed by zirconocenes. Strained partial structure of the alternating copolymer facilitates its clean thermal conversion.

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

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