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Feature Article

New polymerization of dienes and related monomers catalyzed by late transition metal complexes

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ABSTRACT

This article reviews recent studies on the polymerization of 1,6-heptadienes and 2-aryl- and 2-alkoxy-1-methylenecyclopropanes catalyzed by Co, Fe, and Pd complexes. Co and Fe complexes with bis(imino)-pyridine ligands catalyze the cyclopolymerization of 1,6-heptadiene in the presence of MMAO to produce the polymer, which contains five-membered rings in the monomer units. The polymers with *cis*- or *trans*-five-membered rings are obtained selectively, depending on the complex used in the polymerization. The catalyst, prepared from the Co complex having a bis(imino)pyridine ligand and MMAO, promotes the polymerization of 2-aryl-1-methylenecyclopropanes without ring-opening. The reaction under ethylene atmosphere produces alternating copolymer of the two monomers to yield the polymers composed of the C4 repeating unit with a 1,1-cyclopropanediyl group. The alternating copolymer of ethylene and 7-methylenebicyclo[4.1.0]heptane undergoes thermal rearrangement to afford the polymer with C=C double bond in main chain. A radical pathway is proposed. Dinuclear π-allylpalladium complexes with bridging Cl ligands initiate living polymerization of 2-alkoxy-1-methylenecyclopropanes, which accompanies ring-opening of the monomer, to afford the polymers composed of the C_3 repeating units having alkoxy and vinylidene groups. A cyclic dinuclear π-allylpalladium complex reacts with 2-alkoxy-1-methylenecyclopropane in the presence of pyridine to produce the living polymer with macrocyclic structures. Block copolymerization of the two monomers that contain OR or $O(CH_2CH_2O)R$ as the substituents on the three-membered ring, results in the polymers with hydrophobic and hydrophilic segments.

1. Introduction

The metallocene catalysis for olefin polymerization has its origin in the study on soluble Ziegler catalysts, which had been initially intended to elucidate the mechanism of olefin polymerization using the heterogeneous Ziegler–Natta catalyst. Kaminsky catalyst, composed of the metallocenes and MAO co-catalyst, behaves as a single-site catalyst, and regulates molecular weights and polydispersity of the formed polyolefins. Proper introduction of the substituents to the cyclopentadienyl ligand of the catalyst changes stereoselectivity in the polymerization of α-olefins [1,2]. For example, the catalysts with C_2 symmetrical coordination around the metal centers (Ti, Zr) promote isotactic polymerization of propylene [3,4]. Syndiotactic poly(propylene), on the other hand, is obtained from the polymerization using the metallocene derivatives with a C_s symmetrical structure [5].

In these few decades, new classes of molecular catalysts were found for the olefin polymerization. Half-metallocenes [6–12] and non-metallocenes [13–15], using early transition metals, promote formation of polyolefins in high efficiency and unique selectivity. These complexes enabled smooth incorporation of α-olefins and cycloolefins to the copolymers with ethylene, and living polymerization of ethylene and α-olefins. The catalyst using late transition metals such as Ni, Fe, Co, and Pd attracted much less attention for a long period after the first discovery of Ziegler catalyst by *Nickel effect* in ethylene oligomerization. Cossee's mechanism, proposed for olefin polymerization by Ti catalyst [16,17], was evidenced by detailed studies on the reactions of olefins with organo-nickel and -iron complexes [18–21]. In 1995, Brookhart and his coworkers selected cationic Ni and Pd complexes with bulky diimine ligand as the new catalyst, and succeeded in high-mass polymerization of ethylene to produce low-density polyethylene [22]. The catalysis was then applied to polymerization of α-olefins, living polymerization of ethylene and α-olefins [23,24], isomerization polymerization of cycloolefins [25], copolymerization of ethylene with acrylic esters [26,27], emulsion polymerization of ethylene in water [28,29], and preparation of telechelic and end-tethered

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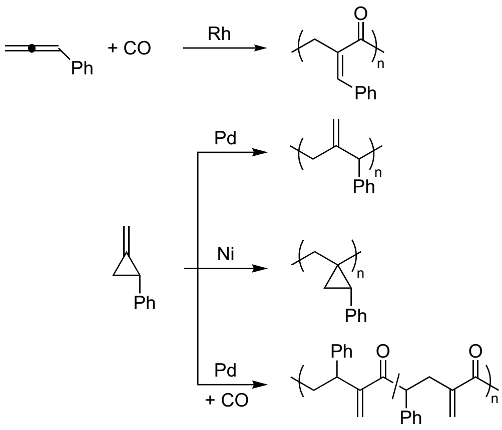
polyethylenes [30,31]. Brookhart, Gibson, and their respective co-workers, on the other hand, reported that Fe and Co complexes with tridentate nitrogen ligands also catalyzed smooth polymerization of olefins [32,33]. Many research groups investigated scope of the polymer synthesis using these late transition metal catalysts, structures and properties of the produced polyolefins, and the mechanism of the polymer growth [34–38]. Polymerization of the monomers other than simple olefins catalyzed by these complexes may provide new polymers and polymerization reactions, although the studies on this subject have been quite limited so far.

Polymerization of dienes and their isomers has also been of a significant interest because these doubly unsaturated compounds perform as a bifunctional monomer and often produce the polymers having unreacted C=C bond in the repeating units [39,40]. Not only the catalyst based on the early transition metals but also late transition metal catalyst promotes polymerization of the diene derivatives [41–49]. We reported Pd-, Ni-, and Rh-catalyzed polymerization of allenes and methylenecyclopropanes as well as alternating copolymerization of these monomers with CO, and prepared the polymers having new structures and properties, as summarized in Scheme 1 [50–63]. This article presents recent progress in the polymerization of non-conjugated dienes and methylenecyclopropane derivatives promoted by the late transition metal complexes that were known to catalyze olefin polymerization. Copolymerization of the above monomers with ethylene will be also described.

Chart 1 summarizes transition metal complexes used in this study. The Fe and Co complexes, **Fe-I**–**Fe-IV** and **Co-I**, promote olefin polymerization in the presence of MAO co-catalyst [32,33]. The Fe-catalyzed ethylene polymerization accompanies chain transfer via transmetalation of the polymer chain to organoaluminum co-catalyst and via β-hydrogen elimination, although the Co-catalyzed ethylene polymerization is free from the former chain transfer process [64]. The polymerization of ethylene using the Fe catalyst in the presence of $ZnEt_2$ causes rapid and reversible transfer of the growing polymer between Fe and Zn, and forms the polymer or oligomer with desired molecular weights [65]. Polymer growth catalyzed by these complexes is sensitive to steric hindrance of the monomers. The Co catalyst does not promote the polymerization of α-olefins due to slow insertion of the substituted olefins into the Co–C bond [66], while the Fe complexes polymerize propylene via 2,1-insertion of the monomer [67]. Complexes **Pd-I** and **Pd-II** contain a chelating diimine ligand whose aryl substituents on the coordinating *N*-atoms are sterically less bulkier than the complexes used as the catalysts for the olefin polymerization [34].



Scheme 1. Polymerization and copolymerization of allenes and methylenecyclopropanes.

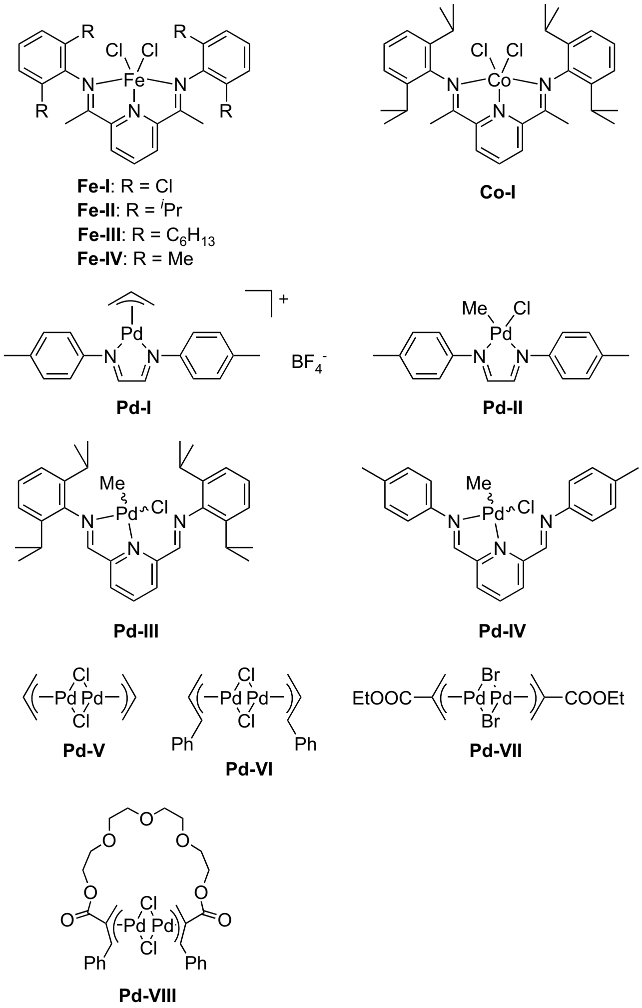


Chart 1. Fe, Co, and Pd complexes commonly used as the initiator or the catalyst of the polymerization.

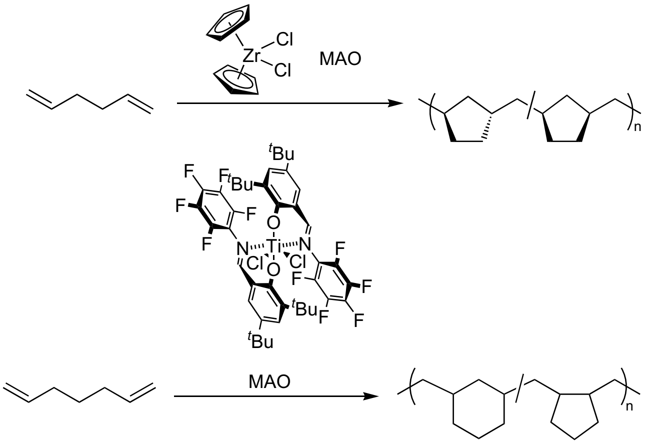
Macrocyclic complex **Pd-VIII** is newly prepared from the compound with two allyl groups connected with a long $(CH_2CH_2O)_n$ chain.

2. Cyclopolymerization of 1,6-heptadienes by Fe and Co complexes

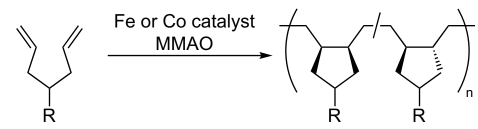
Polymers of norbornene and cycloolefins contain a cycloalkane group in every structural unit, which serves to improve their optical transparency and thermal stability. Polymerization of α,ω-dienes, which accompanies cyclization of the growing polymer end, may also produce the polymers having cyclic structures in the repeating units. This type of polymerization was known as the cyclopolymerization and was achieved by using early transition metal catalyst [68–85].

Most of the reactions reported so far involve insertion of the monomer without cyclization, in part, and leave unreacted vinyl pendants in the polymer molecule. Scheme 2 presents successful results of the cyclopolymerization with high efficiency in the cyclization [69,82]. The polymer molecule, however, contains *cis*- and *trans*-fused five-membered rings or five- and six-membered rings, and cyclization in the polymerization with high selectivity has not been achieved yet.

We conducted cyclopolymerization of 1,6-heptadiene using the Fe and Co complexes with the tridentate *N*-ligands [86].



Scheme 2. Cyclopolymerization of dienes by early transition metal complexes.



1a (R = H)
1b (R = OSiMe$_3$)

poly(**1a**)
poly(**1b**)

(1)

Catalysts prepared from the bis(imino)pyridine complexes of Fe and Co, **Fe-I**–**Fe-IV** and **Co-I**, and modified methylaluminoxane (MMAO) initiate the cyclopolymerization of 1,6-heptadiene (**1a**) in toluene at room temperature to produce –(CH_2–C_5H_8–CH_2)$_n$– (poly(**1a**)) (Eq. (1)). Table 1 summarizes results of the cyclopolymerization. Poly(**1a**) obtained by **Fe-I**/MMAO catalyst (run 1) has a regulated structure composed of the repeating units containing a *trans*-fused five-membered ring, and is free from six-membered ring or pendent 5-pentenyl group [87,88]. Minor ^{1}H NMR signals (δ_H 5.30–5.50) correspond to terminal 3- and 4-methylcyclohexenyl groups. Scheme 3 illustrates pathways for the polymer growth (i) and the chain transfer (ii).

The polymer growth involves initial 2,1-insertion of a vinyl group of the diene molecule and ensuing intramolecular 1,2-insertion of the remaining vinyl group, forming a five-membered ring (i). Intermolecular 1,2-insertion of the monomer would form the six-membered ring, similar to the cyclopolymerization of **1a** catalyzed by early transition metal complexes. The cyclohexylmethyl group attached to the metal center, thus formed, undergoes chain transfer via β-hydrogen elimination rather than further insertion of a new monomer into the M–polymer bond (ii). Molecular weight (M_n) of poly(**1a**) formed by **Fe-I** catalyst is estimated to be 14 000 on the basis of the relative intensity ratio of the ^{1}H NMR signals corresponding to the main chain and the terminal cyclohexenyl group. Thus, the five-membered ring is formed in high selectivity during the polymer growth, and formation of the six-membered ring results in chain transfer. The $^{13}C\{^1H\}$ NMR data of poly(**1a**) indicated the ratio of the *cis*- and *trans*-fused five-membered rings in the polymer molecule to be 95:5. Four CH carbon signals corresponding to triads of repeating units (δ 43–44) appear at almost equal intensities, suggesting an atactic sequence of the monomeric units. The catalysts prepared from **Fe-II** – **Fe-III** and MMAO form the polymer with lower molecular weight and *cis*–*trans* ratio (*cis* = 40–70%) (Table 1, runs 2, 3), while **Fe-IV**/MMAO exhibits high *cis* selectivity in the polymerization, similarly to **Fe-I**/MMAO (run 4).

The catalyst composed of **Co-I** and MMAO is also effective for the cyclopolymerization of **1a** (run 5). The molecular weight determined from the ^{1}H NMR spectrum ($M_n = 10\,000$) agrees well with that determined from GPC using an RI detector and a polystyrene standard ($M_n = 10\,700$, $M_w/M_n = 1.95$). The $^{13}C\{^1H\}$ NMR spectrum of the obtained polymer suggests the presence of *trans*-1,2-cyclopentanediyl rings exclusively. Relative peak area ratio of the two CH carbon peaks (δ 46.2 and 46.8) indicates a moderate degree of control in tacticity of the *trans*-five-membered rings (50% of the major triad), although the major microstructure is not determined unambiguously.

These results are in contrast to the cyclopolymerization of 1,6-heptadiene by early transition metal complexes, where the polymer having six-membered rings are obtained selectively [68–85]. The polymerization proceeds via successive 1,2-insertion of the two vinyl group of the diene monomer. Recently, Coates reported that titanium complexes with phenoxyimine ligands bring about cyclopolymerization of 1,6-heptadiene to afford the polymer containing both five and six-membered ring, which is accounted for by the occurrence of 2,1- as well as 1,2-insertion of the vinyl group of the diene during the polymerization [82].

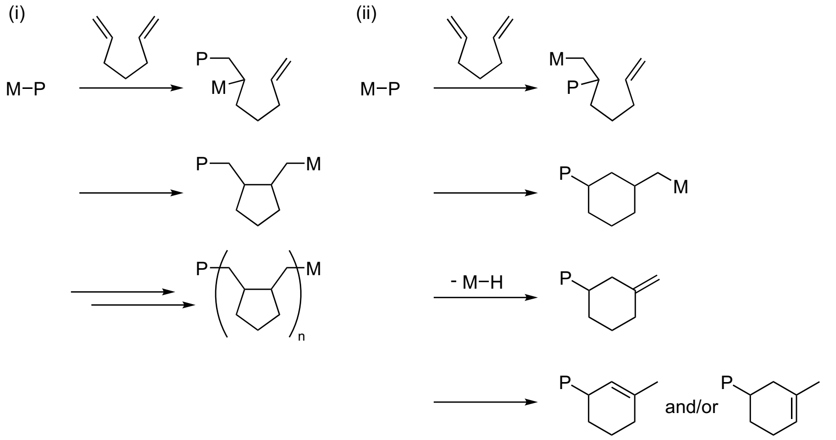
Both the Fe and Co complexes catalyze the cyclopolymerization efficiently, although stereochemical structure of the produced poly(**1a**) differs clearly depending on the catalyst. The *cis*- and *trans*-five-membered rings of the polymers are formed under kinetic and thermodynamic control, respectively, as shown in Scheme 4.

The Fe complex was reported to promote propylene polymerization via 2,1-insertion of the monomer, while the Co complex is not active in polymerization of α-olefins. The above cyclopolymerization catalyzed by these complexes involves intermolecular 2,1-insertion of the monomer. Chelating coordination of the 1,6-diene to the metal probably occurs prior to insertion of a vinyl group into the Co–C bond, and renders 2,1-insertion sterically favorable even in the Co-catalyzed reactions. Fe complexes of π-coordinated 1,6-heptadiene and the alkyl titanium complex with the coordinated pendent vinyl group were reported to prefer a chair type conformation of the chelate ring [89]. Thus, initial 2,1-insertion of the C=C bond of the coordinated diene to the

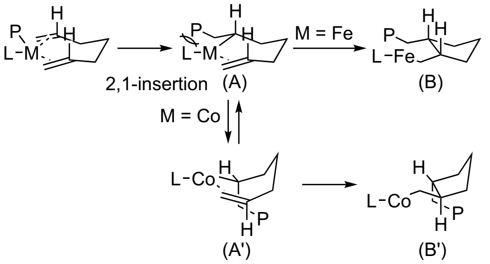
Table 1
Cyclopolymerization of 1,6-heptadienes by Fe and Co complexes[a]

Run	Monomer	Catalyst	[Al]/[M]	Yield (%)	M_n	M_w/M_n	*cis*/*trans*[b]
1	**1a**	**Fe-I**	50	98	14 000[c]	2.4[d]	95:5
2	**1a**	**Fe-II**	50	62	3000[c]		70:30
3	**1a**	**Fe-III**	50	78	4300[c]		40:60
4	**1a**	**Fe-IV**	50	78	6000[c]		95:5
5	**1a**	**Co-I**	212	89	10 000[c] 10 700[e]	2.0[e]	<1:>99
6[f]	**1b**	**Fe-I**	50	98	2700[d]	3.5[d]	>99:<1
7	**1b**	**Co-I**	212	86	43 300[e]	1.6[e]	<1:>99

[a] Reaction conditions: Fe or Co complex = 12 μmol, [monomer]/[Fe or Co] = 100, solvent = toluene (1.2 mL), reaction time = 5 h, at room temperature.
[b] Determined by $^{13}C\{^1H\}$ NMR.
[c] Determined by ^{1}H NMR.
[d] Determined by GPC detected by FTIR (based on polystyrene standard).
[e] Determined by GPC detected by RI (based on polystyrene standard).
[f] Solvent = toluene (0.6 mL).



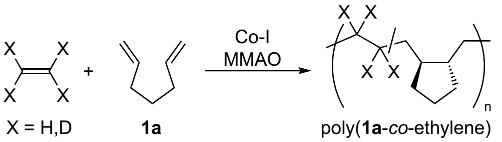
Scheme 3. Pathways for (i) polymer growth and (ii) chain transfer in cyclopolymerization of 1,6-heptadiene.



Scheme 4. Mechanism of cyclopolymerization of **1a** by Fe and Co complexes.

metal–polymer bond takes place smoothly keeping the chair conformation, forming the intermediate (**A**) with a 5-pentenyl ligand. In the cyclopolymerization catalyzed by **Fe-I**-MMAO, direct 1,2-insertion of the remaining C=C bond into the metal–carbon bond produces (**B**) with a *cis*-five-membered ring. The intermediate (**A**) in the polymerization catalyzed by **Co-I**-MMAO, however, changes the structure prior to the cyclization; decoordination and recoordination of HC=CH$_2$ group and accompanying change of the ring conformation leads to intermediate (**A′**). Further insertion of the vinyl group affords the intermediate (**B′**) having thermodynamically favored *trans*-five-membered ring. Kinetic results of the polymerization indicate that the Co complex-promoted cyclopolymerization involves the cyclization as the rate-determining step, which allows isomerization of the structure of the intermediate via repeated decoordination and recoordination of the vinyl group before the cyclization.

Catalyst composed of **Co-I** and MMAO copolymerizes 1,6-heptadiene (**1a**) with ethylene (1 atm) in toluene to produce the polymer with five-membered rings (Eq. (2)).

 (2)

Poly(**1a**-*co*-ethylene) is insoluble in THF and CHCl$_3$ at room temperature, but dissolves in 1,1,2,2-tetrachloroethane at 130 °C. ^{1}H NMR spectrum of the polymer indicates incorporation of the diene unit to the copolymer in 3%. By varying ethylene pressure and concentration of **1a** in the reaction, content of the diene unit in the copolymer can be increased up to 50%. ^{13}C{^{1}H} NMR spectrum contains signals at δ 30.2 and 28.8, which are assigned to CH$_2$ carbons of the ethylene unit adjacent to the monomer unit derived from **1a**. Small broad ^{1}H NMR signals due to the terminal CH=CH$_2$ group are observed at δ 4.9 and 5.9, but the copolymer obtained from **1a** and C$_2$D$_4$ does not show ^{1}H NMR signals at the positions, indicating that the growing polymer undergoes chain transfer via β-hydrogen elimination of the –CH$_2$–CH$_2$–Co (or –CD$_2$–CD$_2$–Co) end group.

Fig. 1 summarizes DSC results of the copolymers. Polyethylene obtained by **Co-I**/MMAO shows the endothermic peak due to T_m at 131 °C. Poly(**1a**-*co*-ethylene) with low contents of the monomer unit from **1a** (5% and 35%) also shows T_m at lower temperature (116 °C and 109 °C, respectively). The latter polymer exhibits glass transition at −25 °C, which is lower than T_g of poly(**1a**) obtained by the same Co catalyst. Melting point becomes negligible in the polymer containing 50% of the repeating unit from **1a**. Thus, thermal properties of the polymers vary depending on the content or the diene monomer unit.

The cyclopolymerization involves insertion of a C=C bond of the monomer and subsequent isomerization of the polymer end via the cyclization, and can be classified into isomerization polymerization. The classical isomerization polymerization using cationic initiator tends to form the polymer with thermodynamically favored structure. The Fe complex-catalyzed cyclopolymerization formed the polymers with a kinetically favored structure, while the Co catalyst with the same *N*-ligand produced the thermodynamically controlled product.

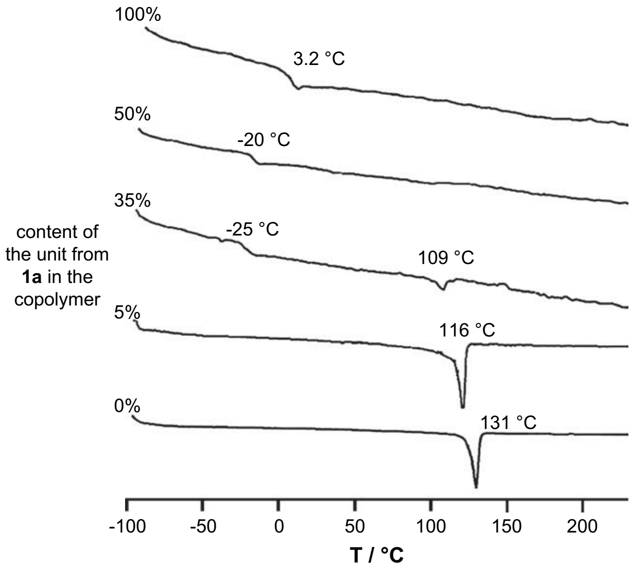


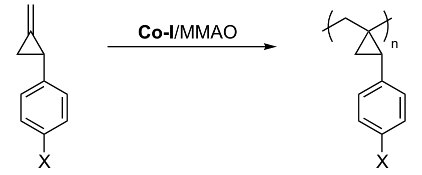
Fig. 1. DSC profiles of poly(**1a**-*co*-ethylene).

It has been reported that the copolymerization of 1,6-heptadiene with ethylene by Fe complexes with bis(imino)pyridine ligands also forms the polymers containing five-membered rings [90]. Catalyst composed of **Fe-II** and MMAO actually afford a polymer by the reaction of 1,6-heptadiene (**1a**) with ethylene (1 atm) in toluene. However, the obtained polymer was revealed to be a mixture of poly(**1a**) and polyethylene. It has been reported that the polyethylene obtained by the Fe complex shows bimodal molecular weight distribution [64]. The heterogeneity of the active species in the polymerization may account for the formation of the homopolymers in this reaction.

Copolymerization of 5,7-dimethyl-1,6-octadiene has been examined by using Fe complex and MAO. In this case, however, homopolyethylene without incorporation of the diene monomer was obtained [91].

3. Polymerization of methylenecyclopropanes catalyzed by Co complex

Methylenecyclopropane is a cyclized isomer of dienes, and tends to undergo ring-opening on addition of cation and radical species. Metallocene complexes of early transition metal complexes, such as zirconium and lutetium, have been reported to promote selective ring-opening polymerization of methylenecyclopropanes and methylenecyclobutanes [92–97]. We reported ring-opening polymerization of 2-aryl-1-methylenecyclorpanes promoted by π-allylic Pd complexes [55]. The reaction promoted by **Co-I**/MMAO catalyst, however, produces the polymers having the three-membered rings, as shown in Eq. (3) [98,99]. The Co catalyst, which is inactive for polymerization of α-olefins, polymerizes the disubstituted olefins smoothly. A primary driving force of the polymer growth is release of ring strain of the methylenecyclopropane caused by insertion of the C=C double bond into the M–polymer bond.

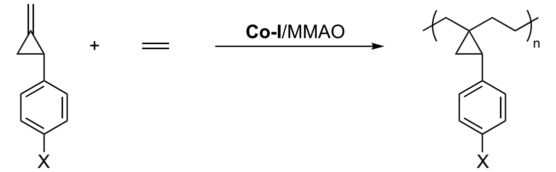


2a: X = H
2b: X = OMe
2c: X = Cl

poly(**2a**): X = H
poly(**2b**): X = OMe
poly(**2c**): X = Cl

(3)

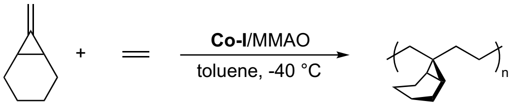
Poly(**2a**)–poly(**2c**) show the ^{1}H and ^{13}C{^{1}H} NMR signals due to the cyclopropane ring at δ −0.5 to 2.6 (^{1}H) and δ 10–50 (^{13}C{^{1}H}) and no signals which can be assigned to olefinic carbons and hydrogens, indicating no occurrence of ring opening during the polymerization. The NMR data indicate that the polymers have a completely regulated head-to-tail linkage of the monomer units. Polymer of **2a** obtained from the reaction below 0 °C has the molecular weight almost the same as those calculated from the ratio of the initially charged monomer to the Co catalyst (50:1 to 1600:1, $M_n = 8500$–200 000). Addition of new monomer to the reaction mixture after the first-stage polymerization ([monomer]/[Co] = 50, $M_n = 8300$, $M_w/M_n = 1.16$) results in the second-stage polymerization to afford the polymer with a higher molecular weight and narrow molecular weight distribution ([monomer]/[Co] = 100, $M_n = 26\,000$, $M_w/M_n = 1.14$). Thus, the living polymerization takes place, and the polymer end is stable at room temperature. It is probably because the polymer growth via 1,2-insertion of the monomer forms the cyclopropylmethylcobalt complex having no β-hydrogen. Ethylene polymerization using the same Co catalyst, on the other hand, accompanies severe chain transfer due to β-hydrogen elimination of the CH_2CH_2Co group, giving the polymer with a broad molecular weight distribution ($M_w/M_n > 2.3$). Analogous Fe complexes do not catalyze the polymerization of the 2-substituted-1-methylenecyclopropanes in spite of high catalytic activity of the complexes for ethylene and propylene polymerization. Brookhart et al. established selective 2,1-insertion of the propylene in the polymerization [67], and 2-aryl-1-methylenecyclopropanes with 1,1-disubstituted olefinic group are sterically congested, and do not undergo 2,1-insertion.



2a: X = H
2b: X = OMe
2c: X = Cl

poly(**2a**-*alt*-ethylene): X = H
poly(**2b**-*alt*-ethylene): X = OMe
poly(**2c**-*alt*-ethylene): X = Cl

(4)



3

poly(**3**-*alt*-ethylene)

(5)

The Co-complex-catalyzed polymerization of the methylenecyclopropanes **2a**–**2c** under ethylene atmosphere affords the copolymer containing the two monomer units in alternating sequences (Eq. (4)). 7-Methylenebicyclo[4.1.0]heptane (**3**) also copolymerizes with ethylene to afford the alternating copolymer (Eq. (5)), although the Co complex does not catalyze homopolymerization of the bulky monomer.

The polymerization of **2a** and ethylene is actually initiated by addition of MMAO to the toluene solution of the **Co-I** and **2a** ([**2a**]/[Co]/[Al] = 200/1/300, [**2a**] = 0.027 M) under ethylene atmosphere (1 atm). GPC analysis of the produced polymer shows unimodal elution pattern observed by RI and UV (254 nm) detectors ($M_n = 58\,000$, $M_w/M_n = 2.84$ (RI)). The copolymerization of **2b** or **2c** with ethylene also proceeds to give the corresponding copolymers. Thus, the growing species is tolerant with MeO and Cl groups. Film of the alternating copolymer of **2a** and ethylene shows higher transparency compared to polyethylene and isotactic polypropylene as shown in Fig. 2. The latter two polymers contain microcrystalline domains which tend to scatter visible light, while the copolymer molecules hardly form such crystalline domains less easily due to the small membered rings. The ^{1}H NMR results of the copolymers confirm the 1:1 ratio of the monomer units from the methylenecyclopropanes and from ethylene.

Scheme 5 depicts four kinds of monomer insertion in the copolymerization. Repetition of cross-propagation reactions, (ii) and (iii), in high selectivity produces the alternating copolymer, similar to the conventional alternating copolymerization. The copolymerization with high ethylene monomer fraction ([ethylene]$_0$/([ethylene]$_0$ + [**2c**]$_0$) > 0.6) leads to formation of the alternating copolymer, while the reaction with lower ethylene concentration ([ethylene]$_0$/([ethylene]$_0$ + [**2c**]$_0$) < 0.6) yields the polymer containing methylenecyclopropane unit in main. Thus, the growing polymer having an ethylene terminal unit undergoes insertion of **2c** selectively (ii). On the other hand, the growing polymer having methylenecyclopropane terminal may undergo both insertion of ethylene (iii) and of methylenecyclopropane (iv), and relative rate for the insertion reactions varies depending on the concentration of the two monomers. At the high ethylene to methylenecyclopropane ratio, insertion of ethylene to the methylenecyclopropane terminal becomes favorable and occurs predominantly, giving the

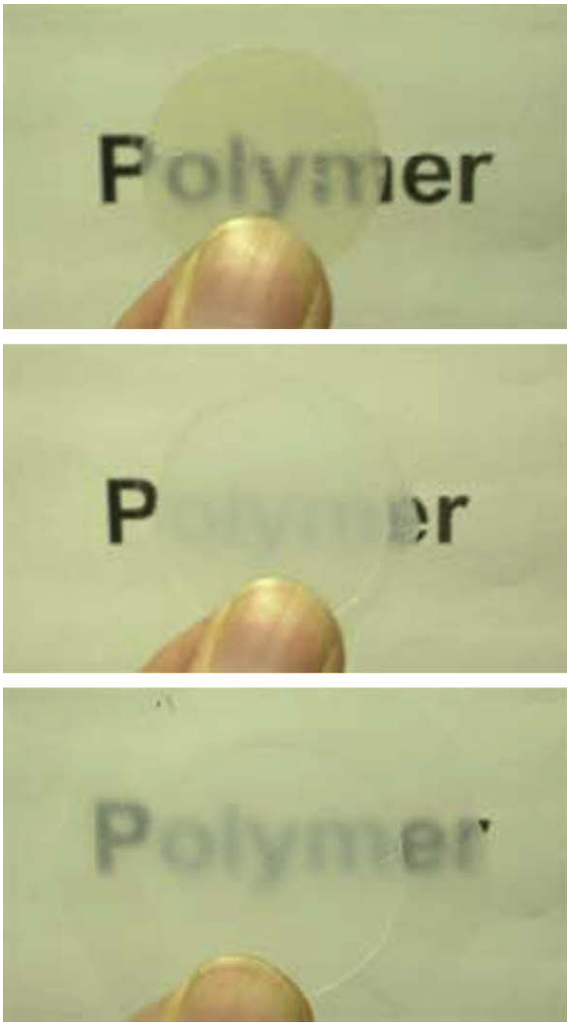
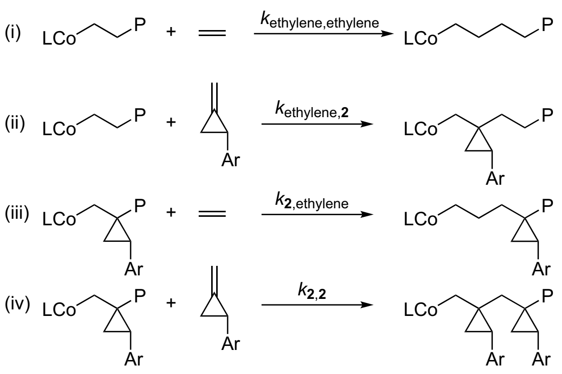


Fig. 2. Clarity of the hydrocarbon films (a) poly(**2a**-*alt*-ethylene) (haze 0.28), (b) polyethylene (haze 0.77), and (c) isotactic polypropylene (haze 0.58).

alternating copolymer. The reactivity ratios defined from the rate constants of the reactions, $r_{(\mathbf{2b})}$ ($k_{\mathbf{2b},\mathbf{2b}}/k_{\mathbf{2b},\mathrm{ethylene}}$) and $r_{(\mathrm{ethylene})}$ ($k_{\mathrm{ethylene,ethylene}}/k_{\mathrm{ethylene},\mathbf{2b}}$), are determined to be 1.1 and 0.05, respectively, based on Fineman–Ross plots of the copolymerization [100,101]. Double insertion of ethylene is strictly inhibited because of preferential coordination of the methylenecyclopropane with severe ring strain around the C=C bond. 2-Methyl-2-phenyl-1-methylenecyclopropane did not undergo the copolymerization with ethylene. The reactivity ratios of the other monomers, ($r_{\mathbf{2a}}$, r_{ethylene}) and ($r_{\mathbf{2c}}$, r_{ethylene}), were obtained similarly to be (0.3, 0.01) and (0.18, 0.03), respectively.



Scheme 5. Four possible insertion reactions in copolymerization of 2-aryl-1-methylenecycloropanes (**2a**–**2c**) with ethylene.

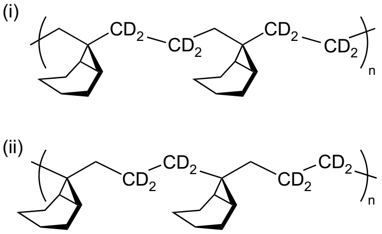
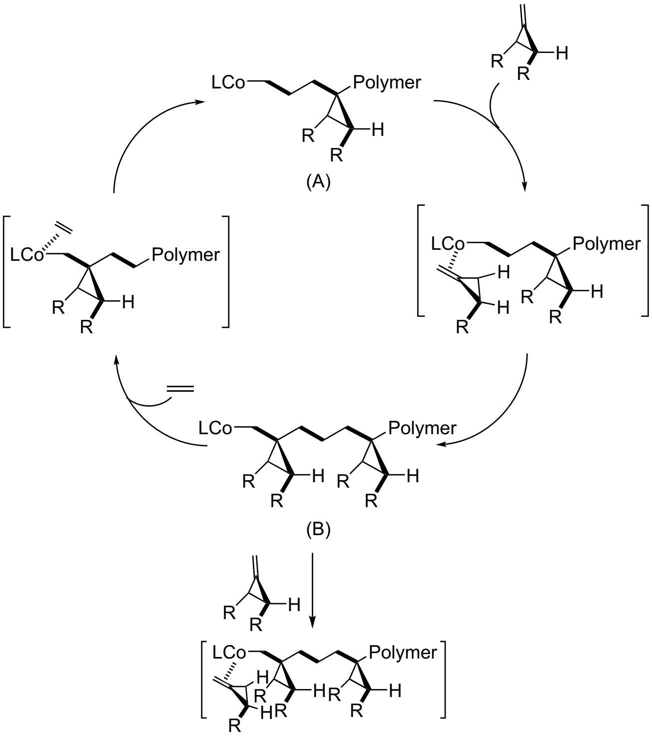


Chart 2. Structure of poly(3-*alt*-ethylene-d_4).

The reaction of **3** (0.18 g) with ethylene (1 atm) in the presence of **Co-I** and MMAO ([Co] = 1.7 mM, [Co]/[**3**]/[Al] = 1/200/300) gave the corresponding copolymer in 0.18 g (67% based on **3**) after 1 h (Eq. (5)) [102]. The obtained polymer is sparingly soluble in THF and $CHCl_3$ at room temperature, which prevented determination of the molecular weight by GPC. $^{13}C\{^1H\}$ NMR spectrum in $C_2H_2Cl_4$ (130 °C) showed the structure formed by alternating copolymerization. The reaction using C_2D_4 as the comonomer produces the deuterated polymer poly(**3**-*alt*-ethylene-d_4), which was revealed to be composed of the structure shown in Chart 2(i) rather than that in Chart 2(ii) exclusively.

Scheme 6 depicts the mechanism proposed for the alternating copolymerization. The growing polymer with the Co–CH_2–CH_2–bond (**A**) undergoes smooth coordination of methylenecyclopropane and 1,2-insertion of its C=C bond into the Co–C bond to form intermediate **B**. Pre-coordination of the C=C bond of methylenecyclopropane monomer occurs at the opposite side to the substituents on the cyclopropane ring in order to avoid steric repulsion between the coordinated monomer and the polymer end. The formed intermediate **B** undergoes preferential insertion of ethylene into the Co–C bond. Strong coordination of C=C bond of

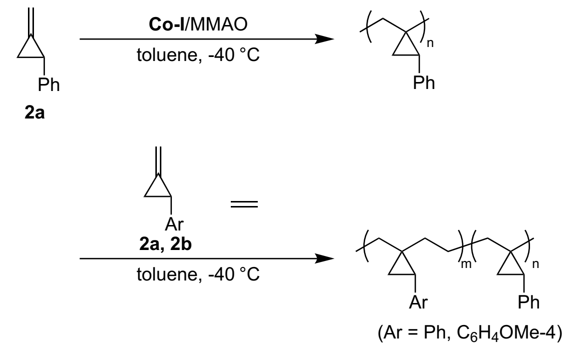


Scheme 6. Mechanism of alternating copolymerization of ethylene with methylenecyclopropane. LCo denotes Co bonded to the bis(imino)pyridine ligand.

the methylenecyclopropane to the Co center prevents double insertion of ethylene. At higher concentration of methylenecyclopropane, double insertion of methylenecyclopropane may take place to some degree. Small $r_{ethylene}$ values (0.01–0.05) calculated from the Fineman–Ross plots suggest selective insertion of methylenecyclopropanes into the Co–CH$_2$–CH$_2$– bond. This is in contrast with the alternating copolymerization of ethylene with norbornene catalyzed by the Zr and Ti complexes, in which double insertion of ethylene is much easier than that of the cyclic monomer ($r_{ethylene} > 1$). Both the coordination and insertion of the methylenecyclopropanes to transition metal are thermodynamically favored process owing to release of ring strain of the molecule caused by change of the sp^2 carbon to the sp^3 carbon with a small bond angle in the three-membered ring. Copolymer of ethylene with **2b** has a lower content of ethylene monomer unit than that obtained from copolymerization of ethylene with **2a** and **2c**, which is consistent with larger r_{2b} (1.1) than r_{2a} (0.30) and r_{2c} (0.18). The alternating copolymerization of **3** with ethylene occurs even at high concentration of the bicyclic monomer because double insertion of **3** is prohibited due to the sterically bulky structure of the monomer.

The alternating copolymerization, which is initiated by the living polymer of **2a** ([**2a**]/[Co] = 60, $M_n = 12\,000$, $M_w/M_n = 1.09$), affords an AB block copolymer, $\text{-}(CH_2\text{-}CCH_2CHPh\text{-}CH_2\text{-}CH_2)_m\text{-}(CH_2\text{-}CCH_2CHPh)_n\text{-}$ ($M_n = 75\,000$, $M_w/M_n = 1.76$). GPC of the block copolymer showed a single elution, indicating complete consumption of the prepolymer. In a similar manner, addition of **2b** and ethylene to the living polymer of **2a** ([**2a**]/[Co] = 50, $M_n = 9300$, $M_w/M_n = 1.14$) forms the block copolymer $\text{-}(CH_2\text{-}CCH_2CH(C_6H_4OMe\text{-}4)\text{-}CH_2\text{-}CH_2)_m\text{-}(CH_2\text{-}CCH_2CHPh)_n\text{-}$ ($M_n = 28\,000$, $M_w/M_n = 1.77$). The two segments, $\text{-}(CH_2\text{-}CCH_2CHPh)\text{-}$ and $\text{-}(CH_2\text{-}CCH_2CH(C_6H_4OMe\text{-}4)\text{-}CH_2\text{-}CH_2)\text{-}$, are observed by NMR spectroscopy, and TLC (silica gel) of the copolymer (eluent: CHCl$_3$) resulted in a single spot at $R_f = 0.16$, which differs from that of poly(**2a**) ($R_f = 1.0$) and poly(**2b**-*alt*-ethylene) ($R_f = 0.12$). All these results indicate that the obtained polymer is not a blend of poly(**2a**) and poly(**2b**-*alt*-ethylene), but the block copolymer shown in Scheme 7.

Results of DSC measurement of the obtained polymers and block copolymers of the methylenecyclopropanes are summarized in Table 2. Poly(**2a**) –poly(**2c**) show relatively high glass transition temperature ranging 146–181 °C, which is ascribed to the rigid polymer structure having the cyclopropylidene group and the aryl substituents [57,58]. Alternating copolymers, in contrast, show their T_g at 71–108 °C, due to incorporation of flexible ethylene repeating unit in the main chain. T_g of the copolymers increases with increase of the monomer unit from the methylenecyclopropanes. The DSC of the above block copolymers showed glass transition both at 70–83 °C and at 160 °C with weak intensity.

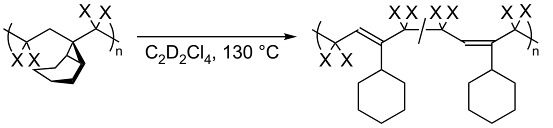


Scheme 7. Synthesis of poly{**2a**-*b*-(**2a**-*alt*-ethylene)} and poly{**2a**-*b*-(**2b**-*alt*-ethylene)}.

Table 2
DSC results of polymers and copolymers

Polymers and copolymers	T_g/°C
poly(**2a**)	178
poly(**2b**)	146
poly(**2c**)	181
poly(**2a**-*alt*-ethylene)	71
poly(**2b**-*alt*-ethylene)	71
poly(**2c**-*alt*-ethylene)	108
poly{**2a**-*block*-(**2a**-*alt*-ethylene)}	83
poly{**2a**-*block*-(**2b**-*alt*-ethylene)}	70,160

Heating poly(**3**-*alt*-ethylene) at 130 °C in 1,1,2,2-tetrachloroethane for 12 h changed the polymer structure. The produced polymer is soluble in THF and CHCl$_3$ at room temperature, although the starting polymer does not dissolve in these solvents. The NMR spectra indicate the signals (δ_H 5.09 and 5.13, δ_C 123 and 145), assigned to the olefinic hydrogen and carbon nuclei. DEPT spectrum and comparison of the ^{13}C{^{1}H} NMR spectrum with those of 2-cyclohexyl-2-butene and poly(isoprene) indicate that the produced polymer has the structure of



(6)

poly(**3**-*alt*-ethylene) (X = H)
poly(**3**-*alt*-ethylene) (X = D)

4 (X = H)
4-*d* (X = D)

poly(2-cyclohexyl-1,3-butadiene), **4**, as shown in Eq. (6). A pair of the signals for each carbon of the cyclohexyl ring is assigned to the *trans* and *cis* C=C groups in the polymer chain. GPC analysis of **4** shows $M_n = 5800$ and $M_w/M_n = 1.69$. poly(**3**-*alt*-ethylene-d_4) also undergoes the thermal isomerization to afford the corresponding deuterated polymer **4-*d***. Fig. 3 shows change in DSC results at the first and second heating. The first DSC scan of poly(**3**-*alt*-ethylene) shows an endothermic peak at 100 °C on heating and no exothermic peak on cooling. The second scan exhibits transition at 52 °C (T_g) and no other peaks up to 180 °C. The results suggest that the ring-opening isomerization of **4** occurs in the solid state. Organic compounds with similar structures also undergo the ring-opening isomerization. Heating of 7,7-dimethylbicylco[4.1.0]-heptane and 7,7-dibutylbicylco[4.1.0]- heptane in C$_2$D$_2$Cl$_4$ at 130 °C

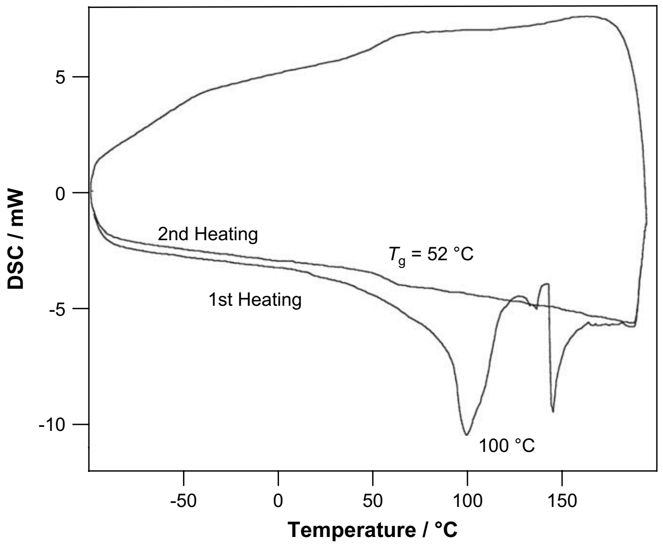
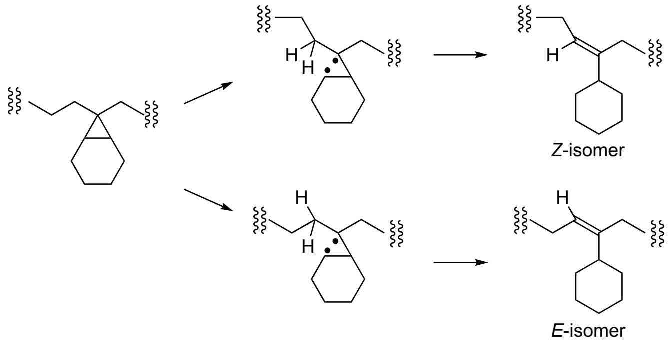


Fig. 3. DSC curve of poly(**3**-*alt*-ethylene).



Scheme 8. Mechanism of thermal isomerization.

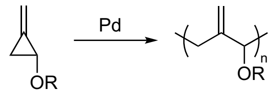
for 12 h gave 1-(2-propyl)-cyclohexene and 5-cyclohexyl-4(*E*)-nonene, respectively.

The isomerization reactions proceed via biradical species which undergo 1,4-migration of a hydrogen atom. The thermal isomerization reactions of poly(**3**-*alt*-ethylene) and poly(**3**-*alt*-ethylene-d_4) also involve homolytic cleavage of C–C bond of the three-membered ring to form the biradical species, as shown in Scheme 8. Abstraction of $H^\bullet$ from the CH_2 group of the main chain by the cyclohexyl radical forms the C=C double bond in the main chain. Results of the thermal reaction of poly(**3**-*alt*-ethylene-d_4) indicates that the hydrogen is abstracted stereoselectively from the CH_2 group on the same side of the cyclohexane-1,2-diyl group with respect to the cyclopropane ring. 1,4-Migration of a hydrogen of the CH_2 group results in formation of *Z* and *E*-olefinic groups in **4** and **4-*d***.

4. Polymerization of 2-alkoxy-1-methylenecyclopropanes by Pd catalysts

The Pd complexes with chelating dinitrogen ligands, such as **Pd-I**, catalyze the ring-opening polymerization of 2-aryl-1-methylenecyclopropanes as well as the copolymerization with CO, to produce the polymers with vinylidene groups, as shown in Scheme 1 [56–63].

2-Alkoxy-1-methylenecyclopropanes (**2d**–**2k**) also polymerize in the presence of the Pd catalysts to give the polymers with the vinylidene and alkoxy groups in the structural unit (Eq. (7)) [103].



2d: R = Bu poly(**2d**): R = Bu
2e: R = ^{t}Bu poly(**2e**): R = ^{t}Bu
2f: R = Me poly(**2f**): R = Me
2g: R = Cy poly(**2g**): R = Cy
2h: R = CH_2OMe poly(**2h**): R = CH_2OMe
2i: R = CH_2CH_2OMe poly(**2i**): R = CH_2CH_2OMe
2j: R = $(CH_2CH_2O)_2Me$ poly(**2j**): R = $(CH_2CH_2O)_2Me$
2k: R = $(CH_2CH_2O)_3Me$ poly(**2k**): R = $(CH_2CH_2O)_3Me$ (7)

Although the structure of the polymers is common to those of 2-aryl-1-methylenecyclopropanes, the Pd complexes suited as the catalysts differs clearly among the monomers. Cationic Brookhart-type Pd complexes with a chelating diimine ligand, **Pd-I** and **Pd-II**/NaBARF (BARF = $B\{C_6H_3(CF_3)_2\}_4^-$), are effective for the ring-opening polymerization of 2-aryl-1-methylenecyclopropanes, whereas the reaction of 2-butoxy-1-methylenecyclopropane (**2d**) using the same catalyst yields the polymer with low molecular weights ($M_n = 1500$ and 1300). Complexes with a tridentate *N*-ligand (**Pd-III**, **Pd-IV**) polymerize to yield the polymer **2d** with $M_n = 12\,000$–$15\,000$ ($M_w/M_n = 1.11$–1.26), but the *N*-ligands bonded to Pd is decoordinated from the metal center during the polymerization. Actual structure of the growing polymer in these reactions is similar to the reaction promoted by $[(\pi\text{-}C_3H_5)PdCl]_2$ (**Pd-V**) and $[(\pi\text{-}PhC_3H_4)PdCl]_2$ (**Pd-VI**). Scheme 9 shows the structure of the growing polymer (**A**) formed by insertion of C=C double bond of the monomer at both Pd centers of the molecule and ensuing isomerization of growing end. Polymer **A** has the dinuclear structure with a $Pd(\mu\text{-}Cl)_2Pd$ core and a molecular weight higher than the calculated from the monomer to Pd ratio. Addition of PPh_3 to the polymer changes the end group to allylPdCl(PPh_3) and/or allylPdCl$(PPh_3)_2$ structure, and the molecular weight by GPC should become close to the calculated value from the monomer/Pd ratio [104]. In fact, GPC measurement of the polymer, after completion of the polymerization ([**2d**]/[Pd] = 50) without quenching, showed a unimodal elution pattern with the molecular weight ($M_n = 9000$, $M_w/M_n = 1.08$) that is significantly higher than the value calculated from the monomer-to-Pd ratio ($M_{n,calc} = 6300$). The polymer after quenching with PPh_3 has the molecular weight close to the calculated value, $M_n = 5900$ ($M_w/M_n = 1.05$). The polymerization by **Pd-VI** displays the first-order kinetics with respect to the monomer, and has an activation energy E_a of 67.0 kJ mol^{-1}, which is close to that of 2-phenyl-1-methylenecyclopropane (67.6 kJ mol^{-1}).

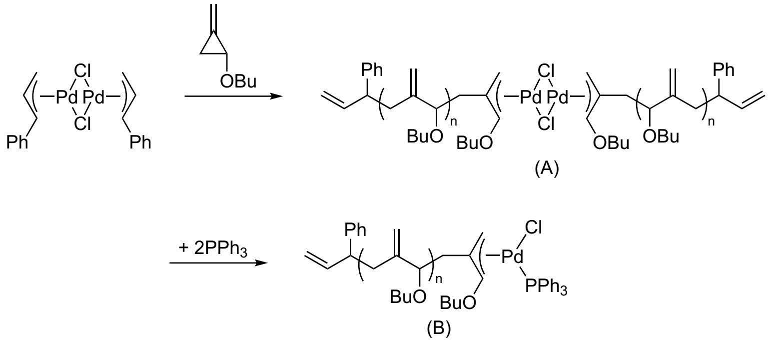
$^{13}C\{^1H\}$ NMR spectra of the mixtures of **Pd-V** or **Pd-VI** and 2-butoxy-1-methylenecyclopropane ([monomer]/[Pd] = 0.1 and 10) showed the signals which indicate the structure similar to **A** in Scheme 9. The signals at δ 54.3, 110.2, and 110.5 are assignable to CH_2, CH and quaternary carbons of the terminal allyl group of the polymer bonded to Pd. The signals of repeating units and 1-phenylallyl group of the initiating end group of the oligomer are observed at reasonable positions.

The structure of the growing polymer end having π-allyl-Pd bonds is similar to that proposed for the polymerization of 2-aryl-1-methylenecyclopropane promoted by the Pd–diimine complexes. Polymer growth of **2d** with alkoxy group also involves 2,1-insertion of the monomer into the π-allyl-Pd bond and subsequent ring-expansion, as shown in Scheme 10. Although π-allylpalladium complexes show various unique reactions both in organometallic and synthetic organic chemistry, the reactions using π-allylpalladium complexes having alkoxy substituents on the allyl ligand have few precedents.

The polymer growth proceeds via living fashion. Addition of monomer to the growing polymer ([monomer]/[Pd] = 50, $M_n = 5500$, $M_w/M_n = 1.06$) caused the second-stage polymerization to produce the product with higher molecular weight and narrow molecular weight distribution ([monomer]/[Pd] = 100, $M_n = 16\,000$, $M_w/M_n = 1.11$). The living polymerization occurs even in THF containing water impurity under air. By changing the monomer-to-initiator ratio, the molecular weight of the polymer is well controlled. Polymerization of **2d** in the presence of 0.25 mol% of Pd produces the polymer with $M_n = 43\,000$ and $M_w/M_n = 1.11$ (after quenching with NaOH/MeOH). The molecular weight is comparable to the value calculated from the monomer to Pd ratio ($M_{n,calc} = 50\,000$).

Pd-promoted ring-opening polymerization is applicable also to the methylenecyclopropanes listed in Eq. (7), such as those having *tert*-butyl (**2e**), methyl (**2f**), cyclohexyl (**2g**), and methoxymethyl (**2h**) groups and mono- (**2i**), di- (**2j**), and triethylene glycol (**2k**) substituents. Initial polymerization of **2e** ([**2e**]/[Pd] = 50) by **Pd-VI** (quant. conv. in 8 h, $M_n = 4900$, $M_w/M_n = 1.04$) followed by addition of **2d** ([**2d**]/[Pd] = 100) to the living polymer affords the block copolymer (quant. conv. in 21 h, $M_n = 16\,700$, $M_w/M_n = 1.03$) (after quenching with NaOH/MeOH) (Fig. 4). Similar diblock copolymer as well as triblock copolymer with narrow molecular weight distribution can be synthesized by sequential polymerization of 2-alkoxy-1-methylenecyclopropanes by using **Pd-VI**.

Reaction of nucleophilic reagents to the π-allylpalladium complexes cleaves the Pd–C bonds and forms new bonds, which



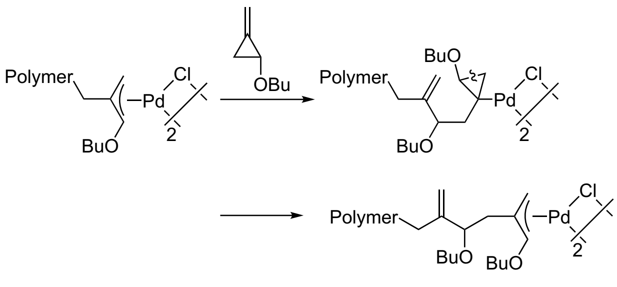
Scheme 9. Polymerization of **2d** initiated by **Pd-VI**.

provides a useful method to introduce the functional groups to the allyl group [105–107]. These reactions are employed in the polymer synthesis including polycondensation of 1,4-diacetoxybut-2-ene and diethyl malonate [108]. On the other hand, functionalization of alkoxy-substituted π-allylpalladium complexes has only a few precedents [109]. Scheme 11 summarizes the reactions of the nucleophiles with the living polymer and functionalization of the end group. Treatment of poly(**2d**) with a methanol solution of NaOH (1.0 M) affords the polymer with an acetal end group as colorless oil (i). The acetal group is formed probably via nucleophilic attack of MeO anion at the π-allyl carbon bonded to both Pd and OBu group. $^{13}C\{^{1}H\}$ NMR spectrum of the polymer exhibits the acetal carbon at δ 104.1. Relative ^{1}H NMR peak intensity of the acetal CH group to the vinyl CH group indicates that the π-allyl-Pd bond of the living polymer end is converted to the acetal group quantitatively by the reaction. Degree of polymerization (Dp) of the polymer, determined from relative ^{1}H NMR peak intensity ratio of the CH signal of $=CH_2$ group of the polymer chain to the acetal end group, was 17, which was close to the monomer-to-Pd molar ratio in the polymerization (20). Addition of AgOAc to the living polymer converts the polymer end to a hemiacetal ester group (ii). The reaction of $NaCMe(COOEt)_2$ with the living polymer in the presence of PPh_3 produces the polymer having $–CMe(COOEt)_2$ end group (iii). The polymer quenched by addition of NaOH aq. showed the ^{1}H NMR signals at δ 9.51, 6.34, and 6.04 which are assigned to CHO and $=CH_2$ hydrogens of α,β-unsaturated aldehyde group at the polymer end (iv). Initial nucleophilic reaction of OH^- to the π-allyl-Pd end group of the polymer probably forms the polymer with a hemiacetal group, which is isomerized into the more stable aldehyde group.

The polymer having the unsaturated aldehyde end group can be used as a macromonomer. Poly(**2d**) synthesized by the reaction of **2d** with **Pd-VI** ([**2d**]/[Pd] = 20) followed by addition of NaOH aq. (0.14 g, $M_n = 2200$, $M_w/M_n = 1.12$) undergoes copolymerization with styrene (0.11 g) in the presence of AIBN (0.0016 g) as the radical initiator to afford the corresponding copolymer containing the repeating units from **2d** and from styrene in 1:2.2 ratio ($M_n = 9800$, $M_w/M_n = 1.74$). The $C{=}CH_2$ groups of poly(**2d**) remain intact during the radical polymerization. T_g of poly(**2d**) is −57 °C, whereas that of poly(**2d**-*c*-styrene) showed T_g at 31 °C. A similar copolymer is obtained from styrene and poly(**2d**) having an α,β-unsaturated ester group formed by using **Pd-IX** as the initiator.

Dinuclear π-allylpalladium complexes with bridging chloro ligands were reported to undergo photo-initiated coupling of the two allyl groups to form a new C–C bond [110,111]. Analogous coupling of the living polymers of 2-alkoxy-1-methylenecyclopropanes may afford the organic polymers having both terminal groups derived from the π-allyl ligand included in the initiator, as mentioned below. Poly(**2d**) obtained by using **Pd-VI** as the initiator is irradiated by UV light in a solution containing chelating diamines. The GPC trace of the polymer after the irradiation in the presence of TMEDA ([Pd] = 0.78 mM, [**2d**]/[Pd] = 26) shows unimodal elution with narrow molecular weight distribution, and the molecular weight ($M_n = 6200$) agrees well with the value that is twice of the calculated from the monomer-to-Pd ratio (3300). 1,10-Phenanthroline also enhances coupling of the π-allyl ligands and forms the polymer with unimodal GPC elution at 3.1 mM of the monomer concentration. TMEDA completes the coupling even at lower concentration of the polymer. Pyridine, 2,2′-bipyridine, 1,2-diaminocyclohexane do not enhance the photo-assisted coupling.

The partial structure of the polymer resulting from the photo-assisted coupling was investigated by the NMR analyses of poly(**2f**) with a low molecular weight. The living polymer of **2f** ($M_n = 690$, $M_w/M_n = 1.09$) after quenching with PPh_3, is irradiated in the presence of TMEDA for 3 h at 10 °C. The molecular weight of the polymer after the irradiation and subsequent addition of PPh_3 is



Scheme 10. Mechanism of polymerization of **2d** by Pd complexes.

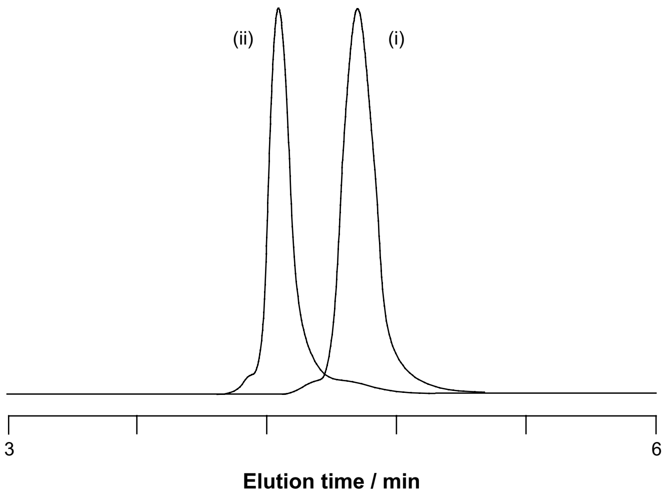
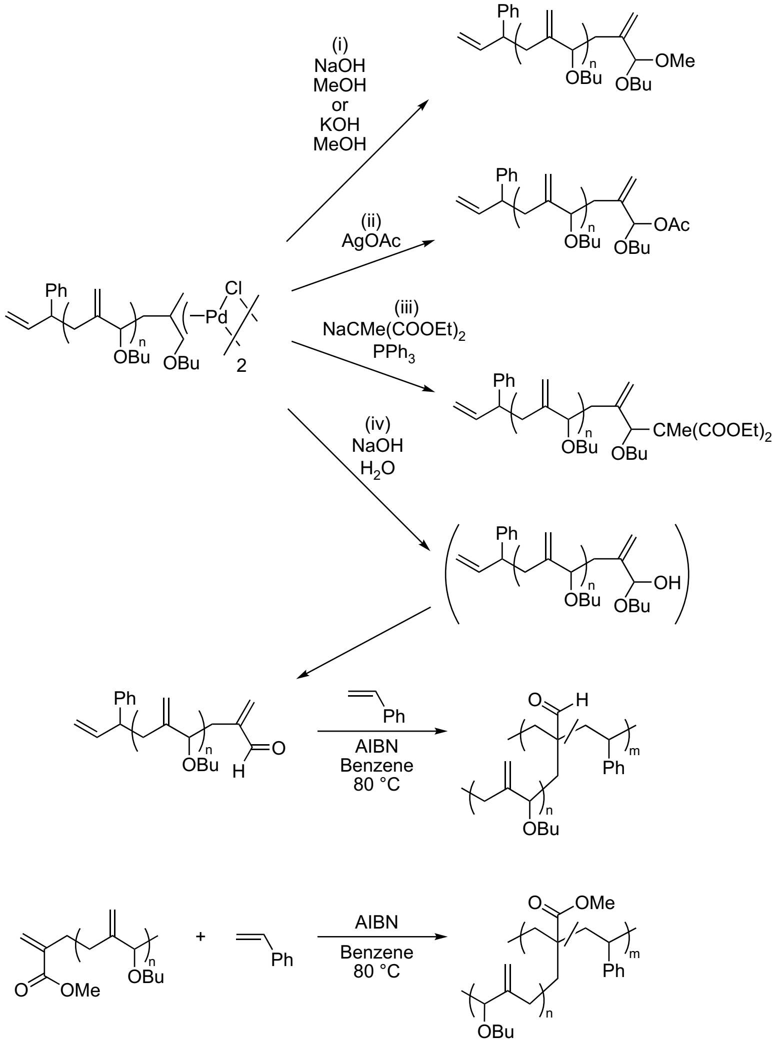


Fig. 4. GPC profile of block copolymer of **2e** and **2d** by **Pd-VI** (i) after addition of the first monomer ([**2e**]/[Pd] = 50) and (ii) after addition of the second monomer ([**2d**]/[[Pd] = 100).



Scheme 11. End-functionalization and graft copolymerization of poly(**2d**).

increased to 1100 ($M_w/M_n = 1.31$). $^{13}C\{^1H\}$, ^1H NMR and ^1H–^{13}C COSY spectra of the reaction mixture indicate that the polymer contains a vinylic ether structure (Chart 3(A)) formed via C–C coupling. Previous studies on similar photo-assisted coupling of the π-allyl group bonded to the Pd centers revealed that the C–C coupling of the monosubstituted allyl ligand formed the structure (B) via head-to-head coupling of the substituted allyl groups as major product [110]. The results of this study indicate that the coupling of the π-allyl ligands with alkoxy substituents form the structure (A) exclusively or form (A), (B), and (C) randomly.

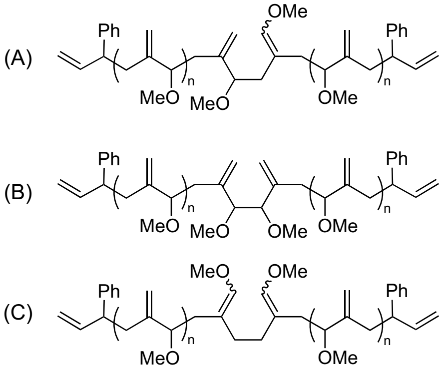
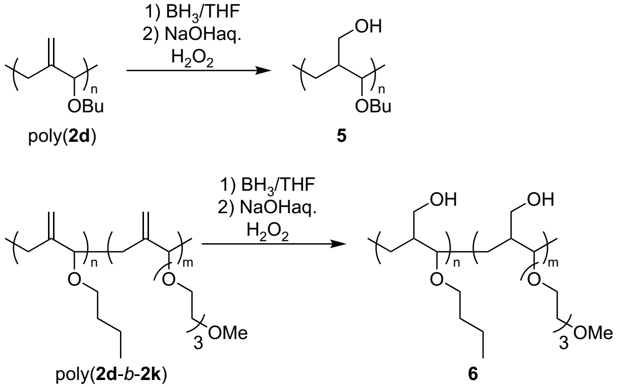


Chart 3. Possible structures of poly(**2f**) after photo-irradiation.

The polymers obtained by the ring-opening polymerization contain a vinylidene group in every structural unit and are able to react with the chemical reagent that adds to a C=C double bond of organic compounds. Polymer reactions using hydroboration of C=C double bond were reported by Yamaoka and Tomita [112,113]. We conducted hydroboration of the polymers with BH_3–THF and succeeded in the introduction of OH groups to the repeating units. Addition of a THF solution of excess BH_3–THF to poly(**2d**) and poly(**2d**-*b*-**2k**) at 0 °C, followed by quenching the reaction mixture with NaOH aq. and H_2O_2 aq (30%), produced the polymers with hydroxymethyl group in every structural unit, **5** and **6**, respectively, as shown in Scheme 12. Polymer **5** is obtained as a colorless solid in 91% yield after purification by reprecipitation from hexane.

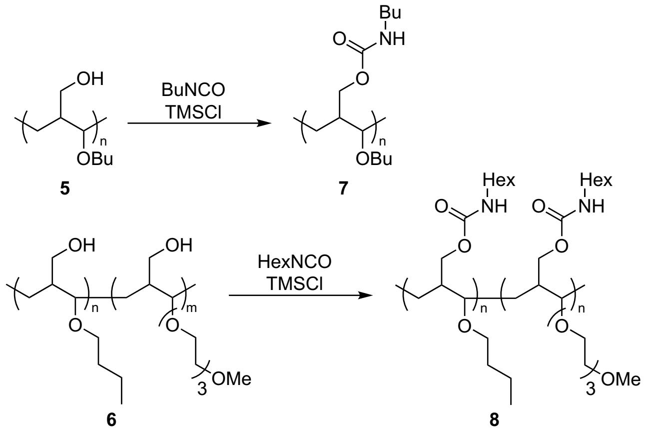
$^{13}C\{^1H\}$ NMR spectrum of **5** displays the signal of hydroxymethyl carbon at δ 63, which is assigned by comparison of the chemical shift with the corresponding signals of 3-ethoxy-2-methyl-1-butanol (δ = 64.8 (erythro) and 66.3 (threo)) [114]. The signal is broadened due to the presence of erythro and threo sequence of the repeating units randomly. Molecular weights of **5** ($M_n = 5300$, $M_w/M_n = 1.19$) and **6** ($M_n = 7800$, $M_w/M_n = 1.16$) by GPC are smaller than the respective prepolymers, poly(**2d**) ($M_n = 8100$, $M_w/M_n = 1.04$) and poly(**2d**-*b*-**2k**) ($M_n = 15\,100$, $M_w/M_n = 1.05$). Decrease of the molecular weight and slight increase of



Scheme 12. Hydroboration of poly(**2d**) and poly(**2d**-*b*-**2k**).

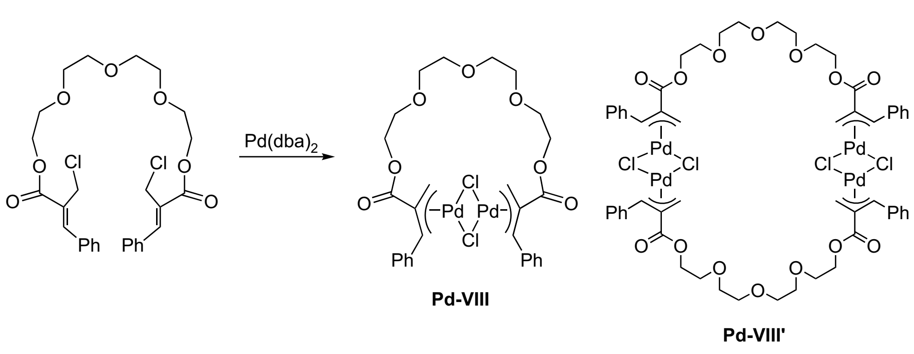
the polydispersity by the reaction suggest cleavage of the polymer chain in part. Polymers **5** and **6** with hydroxymethyl groups in the repeating units react with alkylisocyanate to form the polymer having urethane group as the side groups of the polymers, as shown in Scheme 13. Reaction of *N*-butylisocyanate with **5** produces the polymer with urethane group, **7**, which shows the $^{13}C\{^1H\}$ NMR signals due to carbonyl group (δ 157) and the NH–Bu group (δ 41, 32, 20, and 14). Polymer reaction in Scheme 12 results in the water miscible copolymers, while the water insoluble copolymers are obtained from the reactions in Scheme 13.

The ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes was applied to synthesis of the cyclic polymer by using a cyclic dinuclear π-allylpalladium complex as the initiator [115]. Attempts to prepare the cyclic initiator **Pd-VIII** by oxidative addition of tetraethylene glycol bis{α-(chloromethyl) cinnamate} to $Pd(dba)_2$ (dba = dibenzylideneacetone) lead to the formation of a mixture of the cyclic Pd complexes (Scheme 14). CSI-MS (coldspray ionization mass spectroscopy) showed a large peak at $m/z = 728$ and a small peak at $m/z = 1492$, which corresponds to [**Pd-VIII**–Cl] and [**Pd-VIII′**–Cl], having a ring with double size of **Pd-VIII** (Scheme 14), respectively [116]. Direct polymerization of **2d** by using the mixture of **Pd-VIII** and **Pd-VIII′** as the initiator ([**2d**]/[Pd] = 70) forms the product with a bimodal GPC pattern. The molecular weight of the higher elution peak top (29 000) is almost double of the lower one (15 000), indicating that the fractions with higher and lower molecular weight are formed from **Pd-VIII′** and **Pd-VIII**, respectively. Addition of excess PPh_3 to the polymer solution changes the bimodal elution pattern to unimodal one with the molecular weight ($M_n = 16\,000$, $M_w/M_n = 1.05$), which is close to that calculated from the **2d**-to-Pd molar ratio ($M_{n,calc} = 18\,000$). All these results suggest that polymerization initiated by **Pd-VIII** and **Pd-VIII′** takes place separately in a living fashion and that coordination of PPh_3 to Pd converts the cyclic polymers to the linear one having two $Pd(Cl)PPh_3$ end groups.

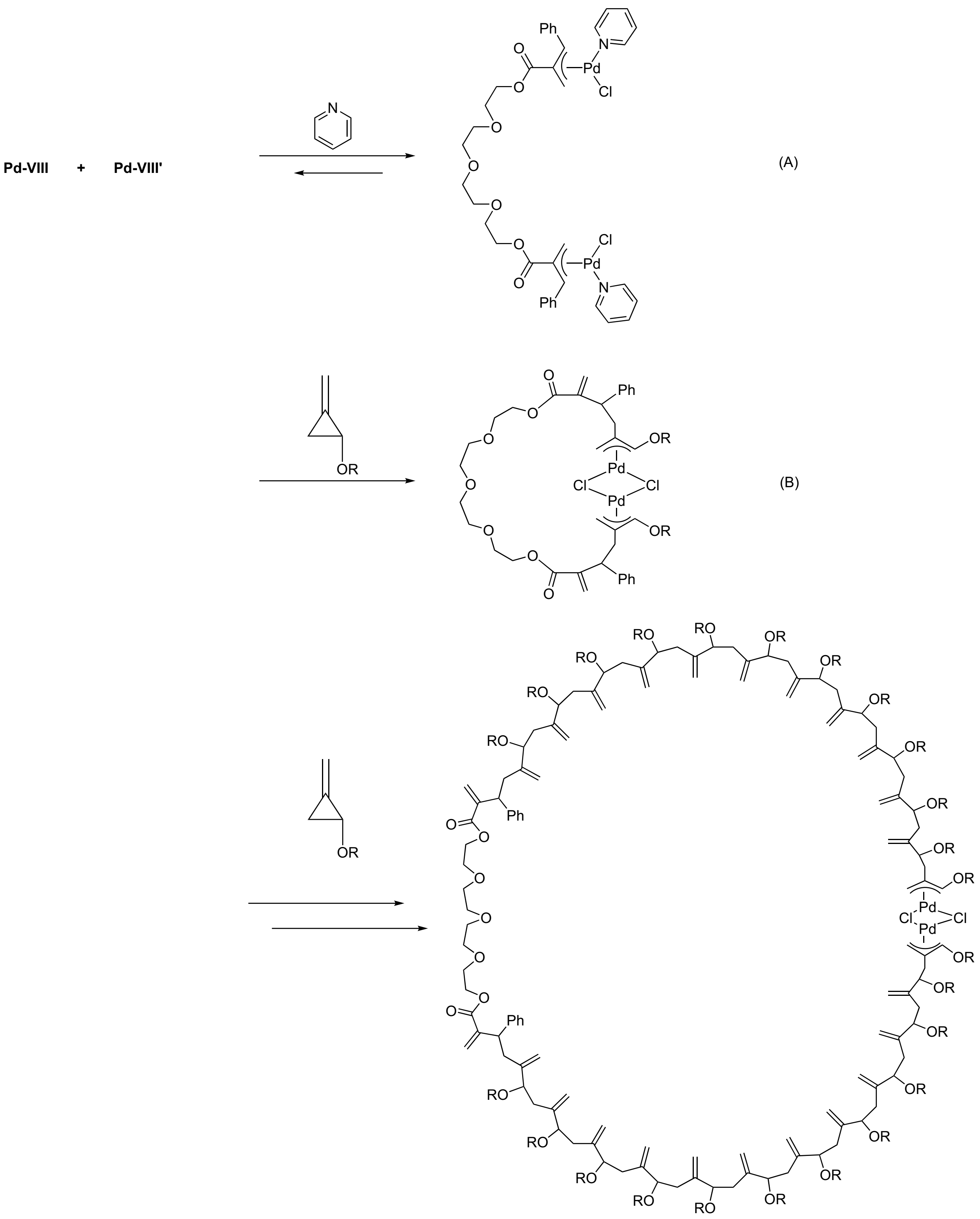


Scheme 13. Reaction of alkyl isocyanates with **5** and **6**.

The polymerization of **2d** starting from the mixture of **Pd-VIII** and **Pd-VIII′** in the presence of pyridine ([**2d**]/[Pd] = 70, [pyridine]/[Pd] = 1.5), however, results in the polymer with a unimodal elution pattern in GPC ($M_n = 14\,000$, $M_w/M_n = 1.09$), and addition of PPh_3 to the solution does not change the molecular weight of the polymer by GPC to $M_n = 15\,000$ ($M_w/M_n = 1.07$). The molecular weights before and after quenching with PPh_3 are relatively close to double of that calculated from the monomer to Pd ratio ($M_n = 18\,000$). These results as well as comparison of the polymerization starting from **Pd-VI** indicate that the cyclic polymer with a unimodal GPC pattern is formed and that the reaction of PPh_3 with a $Pd(\mu\text{-}Cl)_2Pd$ core converts it into the linear polymer with little change of the molecular weights. Scheme 15 depicts the mechanism for the initiation and propagation of the living polymerization, affording the cyclic polymer. Coordination of pyridine to palladium converts the mixture of **Pd-VIII** and **Pd-VIII′** into the linear complex with two PdCl(pyridine) ends (**A**), and the reaction occurs reversibly. Insertion of a monomer into the Pd-π-allyl bonds produces the cyclic dinuclear Pd complex (**B**), predominantly, with loss of the pyridine ligand. Dinuclear complex $[(\pi\text{-allyl})PdCl]_2$ was reported to be in equilibrium with monomeric (π-allyl)PdCl(pyridine) in the presence of pyridine, whereas introduction of electron-donating group at the π-allyl ligand shifts the equilibrium to formation of the dinuclear complex [117]. Complexes **Pd-VIII** and **Pd-VIII′** have electron-withdrawing Ph substituent at the π-allyl ligand and tend to react with pyridine to yield (**A**) partly. Complex B, formed by insertion of the monomer into the Pd-allyl bonds, have electron-donating OR groups at the ligand, and does not cause ring-opening even in the presence of pyridine. Successive insertion of the monomer into the Pd-allyl bonds affords the macrocyclic polymer with $Pd(\mu\text{-}Cl)_2Pd$ core.



Scheme 14. Synthesis of cyclic Pd complexes.



Scheme 15. Mechanism of formation of cyclic polymer with controlled molecular weight.

The polymerization of **2d** starting from the mixture of **Pd-VIII**, **Pd-VIII′** and pyridine ([pyridine]/[Pd] = 1.5) ([**2d**]/[Pd] = 35, $M_n = 5000$, $M_w/M_n = 1.07$) and further addition of **2k** as the second monomer ([**2k**]/[Pd] = 35) lead to increment of the molecular weight keeping narrow molecular weight distribution ($M_n = 12\,000$, $M_w/M_n = 1.13$). Glass transition temperature of the cyclic poly(**2d**) ($T_g = -65.3$ °C) and poly(**2k**) ($T_g = -91.7$ °C) is lower than that of the corresponding linear polymers, poly(**2d**) ($T_g = -55.3$ °C) and poly(**2k**) ($T_g = -74.3$ °C). The cyclic polymers in this study show small difference of the GPC hydrodynamic volume from the linear polymers composed of the same repeating unit (<10%) and lower T_g than the linear ones.

5. Summary

The late transition metal (Fe, Co, Pd) complexes in this study were already known to polymerize ethylene and α-olefins. These complexes, on the other hand, have potentiality in converting dienes and related molecules into the other compounds via π-allyl complexes of the metals as the intermediate. We succeeded in applying the catalysis to polymerization of α,ω-dienes and methylenecyclopropanes and in preparing new functionalized polymers, as described in this review article. The cyclopolymerization of 1,6-heptadiene shows *trans*- or *cis*-selectivity in the cyclization depending on the metal center, and the selectivity is controlled by kinetic and thermodynamic stability of the intermediates. Selectivity of the reaction is much better than the conventional cyclopolymerization catalyzed by early transition metal complexes. The Co complex with tridentate chelating ligand promotes vinyl polymerization of the methylenecyclopropane derivatives via 1,2-insertion of the monomers as well as their alternating copolymerization with ethylene, although it does not polymerize α-olefins. The polymers with bulky cyclic groups in the structural units show optical transparency, similar to the polymers of cyclic olefins, as already mentioned by the other research groups. Pd complexes promote ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes via insertion of the monomer molecule into the π-allyl-palladium bond and ring-opening of the three-membered ring of the growing polymer end. The polymer end structure having π-allyl ligand bonded to Pd center are stable enough for the living polymerization even under air. The unique reactivities toward monomer insertion and the nucleophilic addition of several compounds enabled living polymerization and end functionalization of the polymer. The macrocyclic polymer of the monomer is also synthesized. All these selective reactions of the diene derivatives produce unique polymers, and have further potentiality toward new polymer materials with strictly regulated structures with various functional groups.

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