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Articles

Addition Polymerization of 2-Aryl- and 2-Ethoxycarbonyl-1-methylenecyclopropanes Promoted by Nickel Complexes

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ABSTRACT: $[Ni(\pi\text{-}C_3H_5)Br]_2$ initiates addition polymerization of 2-aryl-1-methylenecyclopropanes and 2-ethoxycarbonyl-1-methylenecyclopropane, affording the polymers having cyclopropylidene groups. The ^{1}H and ^{13}C NMR spectra of the polymers indicate well-regulated head-to-tail linkage of the monomer units. Quenching of polymerization of 2-phenyl-1-methylenecyclopropane by D_2O forms the polymer with $-CH_2D$ terminal group, which is more consistent with 1,2-insertion of the monomer to the Ni−carbon bond than 2,1-insertion. GPC of the polymer of 2-phenyl-1-methylenecyclopropane prepared at −40 °C shows $M_n = 29\,000$ ($M_w/M_n = 1.59$) based on polystyrene standards. Molecular weight of the polymers of 2-aryl-1-methylenecyclopropane increases with the electron-withdrawing substituent of the aromatic group of the monomer. DSC and TG analyses of the polymer of 2-aryl-1-methylenecyclopropane show glass transition at the temperature range 153−178 °C and 5% weight loss due to thermal decomposition at 352−361 °C. The polymer of 2-ethoxycarbonyl-1-methylenecylopropane has lower T_g and T_{d^5}.

Introduction

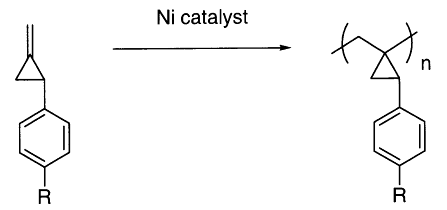
Cyclic olefins such as cyclobutenes, cyclopentenes, norbornenes, and cyclooctenes undergo ring-opening metathesis polymerization promoted by complexes of transition metals such as Ti, Mo, and Ru.[1,2] On the other hand, Pd and Ni complexes promote addition polymerization of norbornene derivatives,[3] dialkyl cyclopropene, cyclobutene, and cyclopentene.[4,5] These polymerization reactions often do not require addition of a cocatalyst such as alkylaluminum which activates the transition-metal complexes. Smooth polymer growth in these reactions is attributed to release of the ring strain of the monomer caused by its incorporation into the polymer and to geometrically unfavorable β-hydrogen elimination of the polymer end.

Methylenecyclopropanes, which have olefinic group attached to the three-membered ring have highly strained structure,[6] and undergo ring-opening polymerization catalyzed by Zr and Pd complexes.[7,8] Addition polymerization of methylenecyclopropanes promoted by transition-metal complexes would produce new polymers with cyclopropylidene group in each structural unit, although such polymerization has not been reported yet.[9] Various methylenecyclopropanes with functional groups are available as the monomer because late-transition-metal complexes in olefin polymerization are tolerant with various functional groups of the monomers, although early-transition-metal complex catalysts are frequently poisoned by such polar functional groups. Norbornene with an ester group was reported to polymerize smoothly in the presence of Pd catalysts.[3]

Herein, we report the polymerization of 2-aryl-1-methylenecyclopropanes and 2-ethoxycarbonyl-1-methylenecyclopropane promoted by Ni complexes. A part of this study was presented in a preliminary form.[10]

Results and Discussion

2-Aryl-1-methylenecyclopropanes with the substituents −OMe, −Me, and −Cl at the phenyl ring undergo addition polymerization in the presence of Ni catalysts to afford the polymers containing cyclopropylidene groups, **Ia**−**Id** (eq 1). Table 1 summarizes the results under various conditions. The reactions promoted by $[Ni(\pi\text{-}C_3H_5)Br]_2$ ([monomer]/[Ni] = 70) at room temperature form the polymer **Ia** with M_n = 4500−6200 (M_w/M_n = 1.88−2.11) in THF, toluene, and NMP (runs 1−3), while the polymerization proceeds smoothly at −40 °C to produce **Ia** with M_n = 8500 (M_w/M_n = 1.95) (run 4). The molecular weight attains to M_n = 29 000 (M_w/M_n = 1.59) in the reaction with [monomer]/[Ni] = 200 (run 5). Since 2-methyl-1-butene is not polymerized



(1)

Ia: R = H
Ib: R = OMe
Ic: R = Me
Id: R = Cl

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Table 1. Polymerization of 2-Aryl-1-methylenecyclopropanes by $[Ni(\pi\text{-}C_3H_5)X]_2$[a]

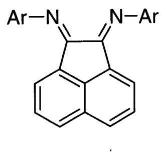
	monomer	Ni complex		condition			product			
run	R[b]	X	ligand	temp (°C)	solvent	time (h)	polymer	yield (%)	M_n[c]	M_w/M_n[c]
1	H	Br		r.t.	THF	3	**Ia**	93	4500	2.02
2	H	Br		r.t.	toluene	3	**Ia**	83	5700	1.88
3	H	Br		r.t.	NMP	3	**Ia**	74	6200	2.11
4[d]	H	Br		−40	THF	12	**Ia**	quant.	8500	1.95
5[e]	H	Br		−40	THF	24	**Ia**	quant.	29 000	1.59
6[d]	OMe	Br		−40	THF	24	**Ib**	95	3600	1.67
7[d]	Me	Br		−40	THF	24	**Ic**	89	6800	1.71
8[d]	Cl	Br		−40	THF	24	**Id**	88	13 000	1.44
9	H	Cl		r.t.	THF	3	**Ia**	93	4500	1.83
10	H	$OCOCF_3$		r.t.	THF	3	**Ia**	74	7500	1.99
11	H	$OCOCH_3$		r.t.	THF	3	**Ia**	26	2300	1.36
12	H	Br	**1**	r.t.	toluene	3	**Ia**	49	4700	1.75
13	H	Br	PPh_3	r.t.	toluene	3	**Ia**	76	3000	1.37
14[f]	H	Br	cod	r.t.	THF	3	**Ia**	quant.	4000	1.79
15[f]	H	Br	cod	−78	THF	3	**Ia**	quant.	20 000	1.81

[a] Reaction conditions: $[Ni(\pi\text{-}C_3H_5)X]_2 = 25$ mM, [ligand]/[Ni] = 1, and [monomer]/[Ni] = 70. [b] R: substituent of aromatic group of the monomer. [c] Determined by GPC based on polystyrene standard. [d] Experiments repeated two or three times show deviation of M_n within 14%. [e] [2-Phenyl-1-methylenecyclopropane]/[Ni] = 200. [f] $AgPF_6$ was added with $[AgPF_6]/[Ni] = 1.2$.

by $[Ni(\pi\text{-}C_3H_5)Br]_2$, the strained cyclopropane ring of the monomer promotes the polymerization.

2-Aryl-1-methylenecyclopropanes with substituents, OMe, Me, and Cl, at the aromatic ring also polymerize at −40 °C to afford the corresponding polymers (**Ib**−**Id**) (runs 6−8). Yields of the polymers obtained at −40 °C are high (>88%), suggesting that the polymerization is not inhibited seriously by these substituents of the monomers. The molecular weight of the polymers (runs 4, 6−8) increase in the order, **Ib** ($M_n = 3600$, $M_w/M_n = 1.67$) < **Ic** ($M_n = 6800$, $M_w/M_n = 1.71$) < **Ia** ($M_n = 8500$, $M_w/M_n = 1.95$) < **Id** ($M_n = 13\,000$, $M_w/M_n = 1.44$), which is related to electron-donating or -withdrawing ability of the substituents, −OMe ($\sigma_p = -0.27$), −Me ($\sigma_p = -0.17$), H ($\sigma_p = 0.0$), and Cl ($\sigma_p = 0.23$). The positive correlation between σ_p and the molecular weights indicates that the relative rate of propagation to that of chain transfer increases by the electron-withdrawing substituent of the monomer.

The reactions using related Ni complexes and additives were conducted. $[Ni(\pi\text{-}C_3H_5)Cl]_2$ and $[Ni(\pi\text{-}C_3H_5)(OCOCF_3)]_2$ bring about smooth polymerization of 2-phenyl-1-methylenecycloropropane (runs 9, 10), although $[Ni(\pi\text{-}C_3H_5)(OCOCH_3)]_2$ is less effective as the catalyst (run 11). Addition of bulky diimine ligand (**1**), whose Ni complex catalyzes the polymerization of ethylene and α-olefins,[11] and of PPh_3 to the complex gave **Ia** in 49 and 76% yields, respectively (runs 12, 13). Other chelating diamine ligands such as bipyridine or *N*,*N*-(dimethylamino)pyridine inhibit the polymerization (yield < 5%). Cationic nickel complexes, prepared in situ from $[Ni(\pi\text{-}C_3H_5)Br]_2$, cod (1,5-cyclooctadiene), and $AgPF_6$, also promoted the polymerization. The reaction at room temperature and −78 °C produces **Ia** with $M_n = 4000$ and 20 000 ($M_w/M_n = 1.79$ and 1.81), respectively (run 14,15).



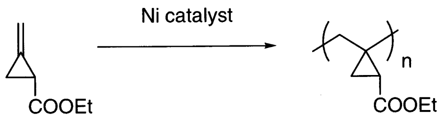
1: Ar = $C_6H_3(^iPr)_2$-2,6

Table 2. Polymerization of 2-Ethoxycarbonyl-1-methylenecyclopropane by $[Ni(\pi\text{-}C_3H_5)Br]_2$[a,b]

	Ni complex		condition		product		
run	ligand	cocat.	solvent	time (h)	yield (%)	M_n[c]	M_w/M_n[c]
1			THF	3	81	18 000	1.20
2			toluene	3	20	7300	1.65
3			CH_2Cl_2	3	66	7100	1.64
4			CH_3CN	12	48	11 000	1.12
5	bipy		THF	12	23	13 000	1.41
6	**1**		THF	12	42	15 000	1.20
7	**1**	AgBARF	THF	12	74	17 000	1.64
8	**1**	NaBARF	THF	10	73	20 000	1.26
9	**1**	$AgPF_6$	THF	24	trace		
10	**2**	AgBARF	THF	12	trace		
11	**3**	AgBARF	THF	12	22	6000	1.54
12	**4**	AgBARF	THF	12	trace		
13	bipy	AgBARF	THF	12	30	14 000	1.32

[a] Reaction conditions: $[Ni(\pi\text{-}C_3H_5)Br]_2 = 25$ mM, [Ni]/[ligand]/[cocat.] = 1/1/1.2, [monomer]/[Ni] = 70 than otherwise stated. [b] $[Ni(\pi\text{-}C_3H_5)Br]_2$/**1** system in the presence of $NaPF_6$, AgOTf, or AgOAc and $[Ni(\pi\text{-}C_3H_5)Br]_2$/AgBARF system in the presence of COD or PPh_3 produced the polymer in low yield. [c] Determined by GPC based on polystyrene standard.

The polymerization of 2-ethoxycarbonyl-1-methylenecyclopropane in the presence of $[Ni(\pi\text{-}C_3H_5)Br]_2$ catalyst ([monomer]/[Ni] = 70) at room temperature produces polymer **II** in 81% yield as shown in eq 2. M_n and M_w/M_n of the product are 18 000 and 1.2, respectively (Table 2, run 1). Table 2 summarizes results of the polymerization under various conditions. The polymerization in toluene, CH_2Cl_2 and CH_3CN produces **II** of lower molecular weights ($M_n = 7100-11000$) in lower yields (20−66%) (runs 2−4). The polymerization in the presence of bipyridine or diimine **1** forms **II** with $M_n = 13\,000$ and 15 000 in 23 and 42% yields, respectively (runs 5, 6). Addition of AgBARF or NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) as the cocatalysts to the reaction using ligand **1** causes increase in the molecular weight and yield of **II** (run 7,8), whereas other additives, $AgPF_6$, $NaPF_6$, and AgOTf, were not effective as the cocatalyst (Table 2, run 9 and footnote *b*). Cationic π-allyl nickel complexes are the probable active species of the catalysis. PF_6^- is much less suited as the coun-



(2)

II

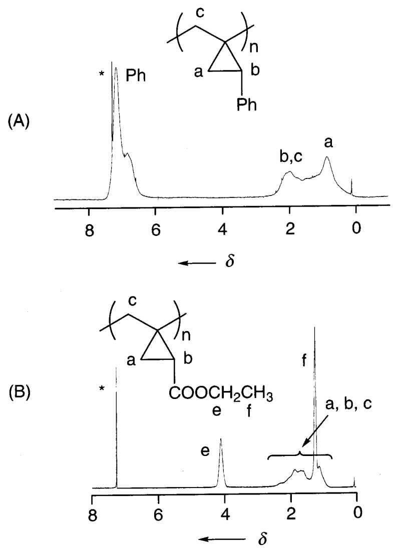
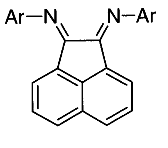
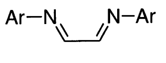


Figure 1. ^{1}H NMR spectrum of (A) **Ia** and (B) **II** in $CDCl_3$ at 25 °C. The signal marked by an asterisk is due to the solvent impurity.

teranion of this polymerization catalyst than BARF$^-$. The catalysts using other ligands such as COD, diimines **2**–**4**, bipyridine, and PPh_3 in the presence of AgBARF,



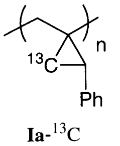
2: Ar = C_6H_4Me-4



3: Ar = $C_6H_3(^iPr)_2$-2,6
4: Ar = C_6H_4Me-4

produce **II** in low yields (0–30%) (runs 10–13).

The polymers **Ia**–**Id** and **II** were characterized by ^{1}H and ^{13}C NMR spectroscopy. The structures of the polymers do not vary depending on the polymerization conditions. Figure 1 shows the ^{1}H NMR spectra of **Ia** and **II**. The spectra exhibit a broad signal around δ 1.0, which is characteristic of the CH_2 hydrogens of the three-membered ring. The broad signals at lower magnetic field positions (δ < 2.3) are assigned to CH hydrogen of the cyclopropane ring and CH_2 hydrogens of the polymer chain. The peaks of phenyl hydrogens of **Ia** and of ethyl hydrogens of **II** are observed at reasonable positions. There are no signals at δ 6.5–4.5, the region of olefinic hydrogens, in both spectra. These results indicate that the polymers contain the monomer units with three-membered ring and no olefinic part formed via ring-opening of the monomer during the polymerization. The ^{13}C{^{1}H} NMR spectrum of **Ia** (Figure 2A) shows no signals in the region δ 100–120, due to olefinic groups. CH_2 carbon signal of the polymer chain and that of the three-membered ring at the respective positions, δ 31–48 and δ 12–22, are inverted under DEPT (135° pulse) conditions. Assignment of the latter signal was confirmed by the ^{13}C{^{1}H} NMR spectrum of the polymer obtained from 2-phenyl-1-methylene-3[^{13}C]-cyclopropane (**Ia**-^{13}C) and the peak position with that of 1,1-dimethyl-2-phenylcyclopropane (δ 18.3). Apparent large peak width of the signals is ascribed to existence of the stereoisomers for each monomer unit in the polymer and the rigidity of the polymer chain (vide infra), which makes the circumstances of these carbons varied. Quaternary carbon of the polymer chain is observed at δ 25 as a single sharp signal in the difference spectrum of ^{13}C{^{1}H} and DEPT (45° pulse) spectra, although the ^{13}C{^{1}H} NMR spectrum shows severe overlap of the signal with the CH carbon peaks (δ 23–30). A sharp and intense signal of the quaternary carbon suggests a well-regulated head-to-tail linkage of the monomer units. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **Ib**–**Id** resemble **Ia**. The ^{13}C{^{1}H} NMR signals of **II** are assigned similar to those of **Ia** by using DEPT spectroscopy. The quaternary carbon signal at δ 28.2 is observed clearly in the ^{13}C{^{1}H} NMR spectrum as well as in the difference spectrum of DEPT from ^{13}C{^{1}H} NMR spectra. The CH_2 signal of the polymer chain appears at δ 36.6 which is at a lower magnetic field position than **Ia**.



Ia-^{13}C

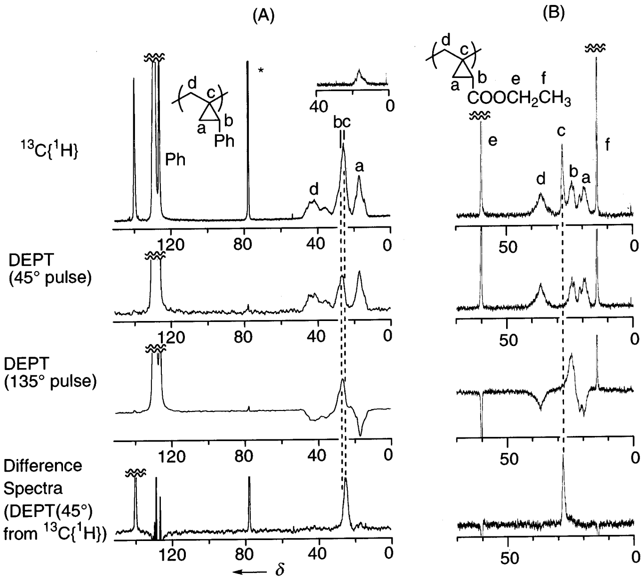
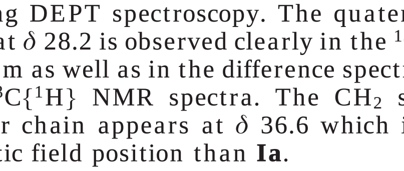


Figure 2. ^{13}C{^{1}H}, DEPT (45 and 135° pulse), and difference spectra (DEPT(45°) from ^{13}C{^{1}H}) of (A) **Ia** and (B) **II** in $CDCl_3$ at 25 °C. The ^{13}C{^{1}H} NMR signal of **I**-^{13}C is shown in the inset. The signal with asterisk is due to the solvent impurity.

The reaction of 2-phenyl-1-methylenecyclopropane with $[Ni(\pi\text{-}C_3H_5)Br]_2$ in a molar ratio of [monomer]/[Ni] = 5, followed by the addition of D_2O, produced the polymer whose ^{2}H NMR spectrum showed a single signal at 1.8 ppm. The signal is assigned to the polymer end with a $-CH_2D$ group (eq 3). The regulated head-to-tail linkage of the monomer units of **Ia**, as revealed by ^{13}C{^{1}H} NMR spectroscopy, and the results of the end group analysis suggest that the polymerization proceeds via successive 1,2-insertion of 2-phenyl-1-methylenecyclopropane to an alkyl–nickel bond of the growing polymer as shown in Scheme 1.[13] The polymer end formed via 1,2-insertion of the monomer has no β-hydrogens and does not undergo chain transfer by



(3)

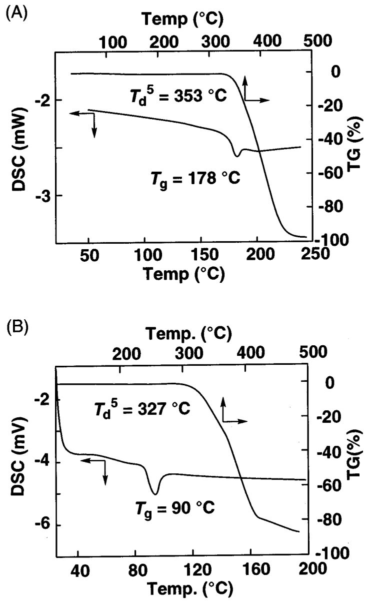
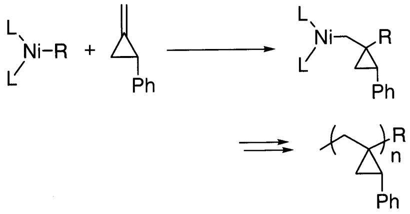


Figure 3. DSC and TG profiles of (A) **Ia** (Table 1, run 5) and (B) **II** (Table 2, run 1).

Scheme 1



β-hydrogen elimination. The chain transfer of the polymerization without addition of water may arise from β-alkyl elimination causing ring-opening of the three-membered ring (vide infra) or by 2,1-insertion of the monomer into the Ni–C bond, followed by β-hydrogen elimination of the growing polymer end.[14] Polymerization of 2-phenyl-1-methylenecyclopropane at −40 °C leads to the polymer with higher molecular weight than that formed at room temperature. These results suggest that raising the temperature enhances the chain transfer reaction more significantly than the polymer growth.

Figure 3A depicts DSC (differential scanning calorimetry) analysis of **Ia** (obtained in run 5 of Table 1), which revealed a glass transition temperature (T_g) of 178 °C. It is higher than those of many other known hydrocarbon polymers, such as thermally resistant syndiotactic polystyrene.[15] The polymer with cyclohexenediyl moiety in the main chain has been reported to show the highest glass-transition temperature among hydrocarbon polymers (231 °C).[16] T_g of **Ia** with M_n = 5700 is 163 °C. T_g of **Ia**–**Id** increases in the following order: **Ib** (153 °C) < **Ia** (163 °C) < **Ic** (168 °C) < **Id** (193 °C). It appears to correlate with electron donating or withdrawing character of the susbsituents although the high T_g of **Id** may be partly due to the higher moelcular weight than the others. The polymers decompose higher temperature than 300 °C in the thermogravimetric (TG) analysis of **Ia** (Figure 3A). Thermal weight loss of **Ia** (obtained in run 5 of Table 1) in 5% is observed at 353 °C. Thus, the produced polymer has good thermal stability. In contrast to **Ia**, DSC analysis of **II** shows T_g at 90 °C, which is close to T_g of PMMA (Figure 3B). Thermoglavimetric analysis of **II** showed that the polymer is stable up to 300 °C (Figure 3B). The polymers show high thermal stability despite the presence of three-membered ring in the monomer unit. It is presumably due to the rigid structure of the polymer chain.

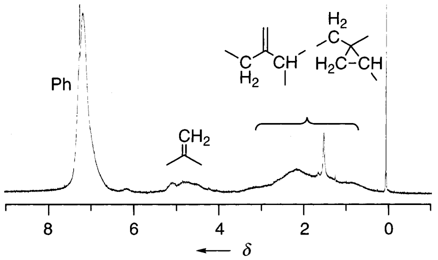
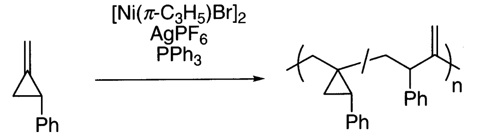


Figure 4. ^{1}H NMR spectrum of **III** in $CDCl_3$ at 25 °C. **III** was obtained by $[Ni(\pi\text{-}C_3H_5)Br]_2/AgPF_6/PPh_3$ system ([Ni]/[Ag]/[PPh_3] = 1/1.2/2).

The polymerization of 2-phenyl-1-methylenecyclpropane by cationic nickel complexes with addition of phosphine ligands afforded the polymer with a low molecular weight and different structures from **Ia**–**Id** and **II**. The reaction promoted by $[Ni(\pi\text{-}C_3H_5)Br]_2$ in the presence of additives, $AgPF_6$ and PPh_3 ([Ni]/[Ag]/[PPh_3] = 1/1.2/2), produces the polymer **III** with M_n = 1600 in 61% yield (eq 4). The ^{1}H NMR spectrum of **III** is shown in Figure 4. The broadened ^{1}H NMR signals at δ 4.5, 4.9, and 5.4 are characteristic of the $=CH_2$ hydrogens of olefinic group. The $^{13}C\{^1H\}$ NMR spectrum also shows the signals at δ 107–115, which are at similar positions to the polymer prepared by ring-opening polymerization of 2-phenyl-1-methylenecyclopropane.[8] The cyclopropylidene group is also contained because the polymer exhibit the NMR signals at high-field positions. All these results indicate that the polymer contains both the repeating units formed via addition polymerization and the ring-opened repeating unit. The content of ring-opened repeating unit is estimated from ^{1}H NMR spectrum to be 45%. The reaction at −40 °C afforded the polymer with M_n = 3700 and increased the rate of the ring-opened unit ratio (63%). The polymerization also proceeded in CH_2Cl_2, toluene, and CH_3CN, although yield of the polymer became low. $P(C_6H_4Cl\text{-}4)_3$ and $P(C_6H_4F\text{-}4)_3$ were usable as the ligand, whereas $P(OPh)_3$, $P(2\text{-furyl})_3$, and $P(C_6H_4\text{-}Me\text{-}2)_3$ were not effective for the polymerization.



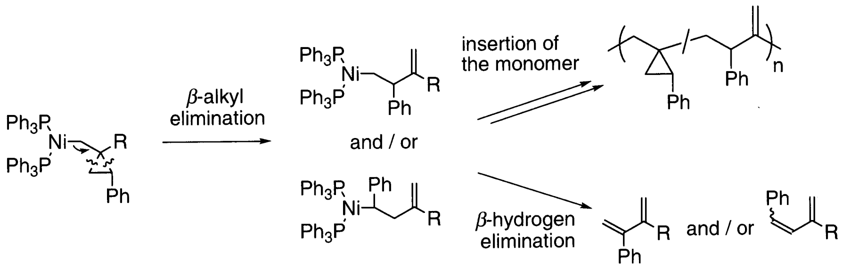
(4)

III

Since the catalyst prepared form $[Ni(\pi\text{-}C_3H_5)Br]_2$ and PPh_3 produces **Ia** without ring-opening (Table 1, run 13), the structure of **III** is due to a cationic Ni–PPh_3 complex formed by addition of $AgPF_6$ to the complex.[17] Scheme 2 depicts a possible pathway for formation of the ring-opened monomer units. β-Alkyl elimination of the three-membered ring of the polymer end produces the polymer end with a $=CH_2$ group at γ-position.[18] Although it undergoes further insertion of the monomer into the Ni–C bond, it would allow facile β-hydrogen elimination which results in the products with low molecular weight.

In summary, this study revealed the Ni-complex-catalyzed polymerization of 2-aryl- and 2-ethoxycarbonyl-1-methylenecyclopropanes. The polymers are formed

Scheme 2



via successive 1,2-insertion of the monomers into the Ni−C bond of the growing polymer and are free from ring-opening of the three-membered ring during the polymerization. This mechanism is in contrast to the ring-opening polymerization of 2-phenyl-1-methylenecyclopropane by Pd complexes, where the polymerization proceeds via 2,1-insertion of the monomer to π-allyl−Pd bond and accompanying C−C bond cleavage of the three-membered ring.[8] Addition of PPh_3 and $AgPF_6$ to the reaction promoted by the Ni complex leads to incorporation of the units formed via ring-opening during polymerization.

Experimental Section

General Methods. Manipulations of nickel complexes were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. Anhydrous THF and toluene were refluxed over sodium benzophenone ketyl and fractionally distilled in an Ar atmosphere. CH_2Cl_2 was washed successively with concentrated H_2SO_4, water, and brine, dried over $CaCl_2$, and distilled over CaH_2 under Ar. Dry CH_3CN was used as received. $[Ni(\pi\text{-}C_3H_5)Br]_2$, $[Ni(\pi\text{-}C_3H_5)Cl]_2$, $[Ni(\pi\text{-}C_3H_5)(OCOCF_3)]_2$, and $[Ni(\pi\text{-}C_3H_5)(OCOCH_3)]_2$ were prepared according to the reported procedure.[19] 2-Phenyl-1-methylenecyclopropane was purchased from Lancaster Co., Ltd. 2-Aryl-1-methylenecyclopropanes and 2-ethoxycarbonyl-1-methylenecyclopropane were prepared according to the reported procedure.[20] 2-Phenyl-1-methylene-3[^{13}C]-cyclopropane was synthesized according to the previously reported procedure.[21] Diimine ligands, NaBARF, and AgBARF were prepared according to the reported procedure.[22,23]

NMR (^1H and ^{13}C) spectra were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer. The peaks were referenced to $CHCl_3$ in the $CDCl_3$ solvent (δ 7.26) for ^1H and $CDCl_3$ (δ 77.0) for ^{13}C. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using THF as eluent at a flow rate of 0.6 mL min^{-1} with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated based on polystyrene standards. DSC and TG were recorded on Seiko DSC6200R and Seiko TG/DTA6200R.

Polymerization. To a 25 mL Schlenk flask containing a THF solution (1 mL) of $[Ni(\pi\text{-}C_3H_5)Br]_2$ (0.025 mmol Ni, 0.0044 g) was added 2-phenyl-1-methylenecyclopropane (0.228 g, 1.75 mmol) by a syringe at room temperature. Heat evolution and change of color of the reaction mixture from deep red to dark red were observed. The mixture was stirred for 3 h at room temperature and the viscous reaction mixture was quenched by adding MeOH. The produced polymer was isolated by pouring a chloroform solution of the polymer into a large amount of methanol. The formed white precipitates were collected and dried in vacuo at 25 °C.

Ia (93%). ^1H NMR ($CDCl_3$): δ 0.0−2.5 (5H, br, CH, CH_2), and 6.3−7.5 (5H, br, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12−22 (CH_2 (cyclopropylidene)), 23−30 (C, CH), 31−48 (CH_2), 125.8 (*p*-Ph), 128.0, 128.8 (*o*-, *m*-Ph), and 139.5 (*ipso*-Ph). T_g: 178 °C. T_d:[5] 353 °C.

Polymerizations of 2-aryl-1-methylenecyclopropanes and 2-ethoxycarbonyl-1-methylenecyclopropane were performed analogously.

Ib. ^1H NMR ($CDCl_3$): δ −0.2−2.9 (5H, br, CH, CH_2), 3.8 (3H, s, CH_3), and 6.0−7.4 (4H, br, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12−22 (CH_2 (cyclopropylidene)), 23−31 (C, CH), 36−50 (CH_2), 55.2 (CH_3), 113.4 (*m*-C_6H_4), 126.9, 129.8, 131.5 (*ipso*-, *o*-C_6H_4), and 157.6 (*p*-C_6H_4). T_g: 153 °C. T_d:[5] 352 °C.

Ic. ^1H NMR ($CDCl_3$): δ −0.1−2.6 (8H, br, CH, CH_2), 2.31 (3H, s, CH_3), and 6.2−7.3 (4H, br, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12−20 (C, CH_2 (cyclopropylidene)), 21.1 (CH_3), 25 (CH), 32−47 (CH_2), 128.7 (*o*-, *m*-C_6H_4), and 134.8, 136.4 (*ipso*-, *p*-C_6H_4). T_g: 168 °C. T_d:[5] 346 °C.

Id. ^1H NMR ($CDCl_3$): δ −0.3−2.5 (5H, br, CH, CH_2), and 6.0−7.5 (4H, br, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12−21 (C, CH_2 (cyclopropylidene)), 21−31 (CH), 31−46 (CH_2), 128.4 (*m*-C_6H_4), 129.9 (*o*-C_6H_4), 132.0 (*ipso*-C_6H_4), and 137.3 (*p*-C_6H_4). T_g: 193 °C. T_d:[5] 361 °C. **II**: ^1H NMR ($CDCl_3$): δ 0.9−2.7 (8H, br, CH, CH_2, CH_3), and 4.12 (2H, s, OCH_2). $^{13}C\{1H\}$ NMR ($CDCl_3$): δ 14.3 (CH_3), 19.8 (CH_2 (cyclopropylidene)), 24.5 (CH), 28.2 (C) 36.6 (CH_2), 60.3 (OCH_2), and 172.5 (CO). T_g: 90 °C. T_d:[5] 327 °C.

The polymerization of 2-phenyl-1-methylenecyclopropane by $[Ni(\pi\text{-}C_3H_5)Br]_2/AgPF_6/PPh_3$ system was performed as follows: To a 25 mL Schlenk flask containing a THF solution (1 mL) of $[Ni(\pi\text{-}C_3H_5)Br]_2$ (0.025 mmol Ni, 0.0044 g) was successively added PPh_3 (0.05 mmol, 0.013 g) and $AgPF_6$ (0.03 mmol, 0.076 g). After being stirred for a few minutes, 2-phenyl-1-methylenecyclopropane (0.228 g, 1.75 mmol) was added and the mixture was stirred for 3 h at room temperature. The polymer was quenched by adding MeOH. The product was isolated by pouring chloroform solution of the polymer into a large amount of methanol. The formed white precipitates were collected and dried in vacuo at 25 °C.

III (61%). ^1H NMR ($CDCl_3$): δ 0−3.7 (br, CH, CH_2), 4.5, 4.9, 5.4 (br, $=CH_2$), and 6.3−7.9 (br, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13−61 (CH, CH_2), 108, 111, 114 ($=CH_2$), 124−130 (*p*-, *o*-, *m*-Ph), 132−141 (*ipso*-Ph), and 141−154 (C=). Content of the ring-opened repeating unit is estimated to be 45% from the ^1H NMR signal intensity ratio between δ 0−3.7 and δ 3.7−5.4.

References and Notes

(1) Ring-opening metathesis polymerization of norbornenes: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(2) Ring-opening polymerization of dialkyl cyclobutene by transition-metal catalysts: Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459.

(3) Addition polymerization of norbornenes: (a) Mathew, J. P.; Reinmuth, A.; Melia, J.; Swords, N.; Risse, W. *Macromolecules* **1996**, *29*, 2755. (b) Sacchi, M. C.; Sonzogni, M.; Losio, S.; Forlini, F.; Locatelli, P.; Tritto, I.; Licchelli, M. *Macromol. Chem. Phys.* **2001**, *202*, 2052.

(4) Addition polymerization of cyclobutene by Ziegler−Natta catalyst: (a) Dall'Asta, G. *J. Polym. Sci., Part A-1* **1968**, *6*, 2397. (b) Kormer, V. A.; Poletayeva, I. A.; Yufa, T. L. *J. Polym. Sci.*, A-1 **1972**, *10*, 251.

(5) Addition polymerization of cyclopropenes: (a) Rush, S.; Reinmuth, A.; Risse, W.; O'Brien, J.; Ferro, D. R.; Tritto, I. *J. Am. Chem. Soc.* **1996**, *118*, 12230. Polymerization of cyclopentene by Pd and Ni complexes has also been reported: (b) McLain, S. J.; Feldman, J.; McCord, E. F.;

Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705.

(6) The ring strain relieved upon hydrogenation of double bond in methylenecyclopropane has been reported to be 53.6 kcal mol^{-1}: Binger, P.; Büch, H. M. *Top. Cur. Chem.* **1987**, *135*, 77.

(7) Jia, L.; Yang, X.; Seyam, A. M.; Albert, I. D. L.; Fu, P.-F.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 7900.

(8) Takeuchi, D.; Kim S.; Osakada, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2685.

(9) Reaction of Ni complexes with methylenecyclopropane: Binger, P.; Brinkmann, A.; McMeeking, J. *Liebigs Ann. Chem.* **1977**, 1065. Recently, nickel complexes with a diimine ligand were found to bring about addition polymerization of cyclopentene. See ref 5b.

(10) Takeuchi, D.; Osakada, K. *Chem. Commun.* **2002**, 646.

(11) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(12) de Souza, R. F.; Mauler, R. S.; Simon, L. C.; Nunes, F. F.; Vescia, D. V. S.; Cavagnolli, A. *Macromol. Rapid Commun.* **1997**, *18*, 795.

(13) The results of the deuterium labeling study are more consistent with 1,2-insertion of the monomer than 2,1-insertion, but they do not exclude the mechanism of polymer growth via 2,1-insertion completely. Polymer growth mainly via 2,1-insertion and preferential hydrolysis of the polymer end via 1,2-insertion, which occurs much less frequently than 2,1-insertion, may also account for the results. Regioregularity of this polymerization, however, suggests that 1,2-insertion is more favorable than the above mechanism of polymer growth. The bulky monomer structure is suited for 1,2-insertion rather than 2,1-insertion.

(14) The structure of the end group was not determined by NMR spectroscopy. The latter chain transfer mechanism is less plausible because of severe ring strain of the polymer end formed via β-hydrogen elimination of the growing polymer end.

(15) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.

(16) Natori, I.; Imaizumi, K.; Yamagishi, H.; Kazunori, M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1657.

(17) (a) Taube, R.; Gehrike, J.-P.; Schmidt, U. *Makromol. Chem., Makromol. Symp.*, **1986**, *3*, 389. (b) Ascenso, J. R.; Dias, A. R.; Gomes, P. T.; Romão, C. C.; Tkatchenko, I.; Revillon, A.; Pham, Q.-T. *Macromolecules* **1996**, *29*, 4172.

(18) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

(19) (a) Phillips, J. R.; Rosevear, D. T.; Stone, F. G. A. *J. Organomet. Chem.* **1964**, *2*, 455. (b) Dawans, F.; Marechal, J. C.; Teyssie, Ph. *J. Organomet. Chem.* **1970**, *21*, 259.

(20) (a) Arora, S.; Binger, P. *Synthesis* **1974**, 801. (b) Lai, M.-T.; Liu, L.-D.; Liu, H.-W. *J. Am. Chem. Soc.* **1991**, *113*, 7388.

(21) (a) Kim S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2002**, *124*, 762. (a) Kim S.; Takeuchi, D.; Osakada, K. *Macromol. Chem. Phys.*, in press.

(22) (a) Kliegman, J. M.; Barnes, R. K.*J. Organomet. Chem.* **1970**, *35*, 3140. (b) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. (c) van Asselt, R.; Elsevier, C. J.; Smeets, E. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas.* **1994**, *113*, 88.

(23) (a) Buschmann, W. E.; Miller, J. S. *Chem.—Eur. J.* **1998**, *4*, 1731. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (c) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.

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