Ethylene/Polar Monomer Copolymerization Using (Aza)ferrocenyl(di)imine Nickel(II) Catalysts

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（アザ）フェロセニル（ジ）イミン Nickel（ II ）触媒を用いるエチレン／極性モノマー共重合

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1,1′-Ferrocenyldiimine/$NiBr_2$, 1,2-ferrocenyldiimine/$NiBr_2$, and 2-azaferrocenylimine/$NiBr_2$ were synthesized and employed as catalysts for ethylene polymerization and ethylene/polar monomer copolymerization. 2-Azaferrocenylimine/$NiBr_2$ gave the highest activity for both ethylene polymerization and copolymerization of ethylene with polar monomer such as acrylate among these complexes upon activation with PMAO. The co-catalyst components were also examined and a catalyst system consisting of 2-azaferrocenylimine/$NiBr_2$ and *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate/ethylaluminum sesquichloride was found to be most suitable for the ethylene/acrylate copolymerization to afford an activity of 1.0 kg/Ni•mmol and an incorporation of 1.7 wt % polar comonomer in the obtained copolymer.

1. Introduction

Late-transition-metal catalyzed olefin polymerization has attracted intense research interest in recent years[1)], since Brookhart and DuPont workers showed that nickel(II) and palladium(II) α-diimine complexes can polymerize ethylene into polymers with a branched microstructure[2)]. The less oxophilic nature of late metal system may be suited for the copolymerization of hydrocarbon olefins with polar monomers. Although there have been many reports regarding the polymerization of polar monomers over transition metal catalysts during the past decade[3)], the bulky α-diimine ligating palladium catalyst is the only system with a mechanism that gives random copolymerization of olefins with acrylate esters[3b)]. Recently, the researchers in DuPont have reported α-diimine nickel(II) catalyzed copolymerization of ethylene with acrylate esters under the highly pressurized (>4MPa) conditions at elevated temperatures (> 80℃)[4)].

Ferrocene is known as an electron-rich molecule due to the electron donation from the iron(II) center[5)]. When ferrocene is combined with two imino groups to form ferrocenyldiimines as designed ligand, their complexes with late transition metals can create an electron-rich bidentate coordination environment that is expected to increase poison resistance of transition metals toward polar monomers. Furthermore, azaferrocene itself can coordinate to transition metals directly through its sp^2-hybridized nitrogen[6)]. Combining the azaferrocene molecule with an imino group creates a sterically rigid 5-membered bidentate geometry that is expected to increase not only the poison resistance but also copolymerization activity with polar monomers. We report here the synthesis of 1,1′-ferrocenyldiimine/$NiBr_2$ (1), 1,2-ferrocenyldiimine

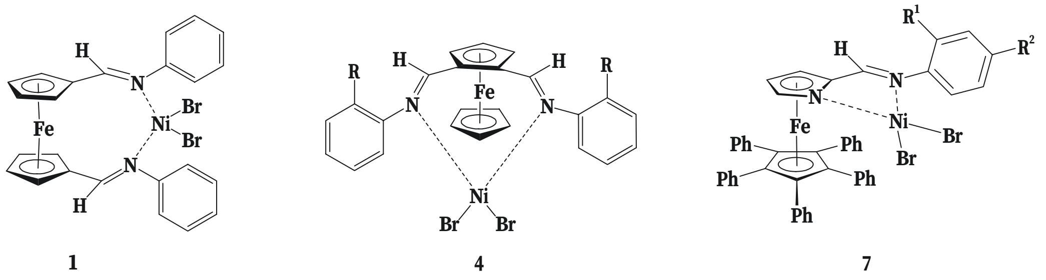


Fig. 1 (Aza)ferrocenyl(di)imine Ni(II) complexes

/$NiBr_2$ (4), and 2-azaferrocenylimine/$NiBr_2$ (7) (**Fig. 1**), and ethylene polymerization and ethylene/acrylates copolymerization using them[7].

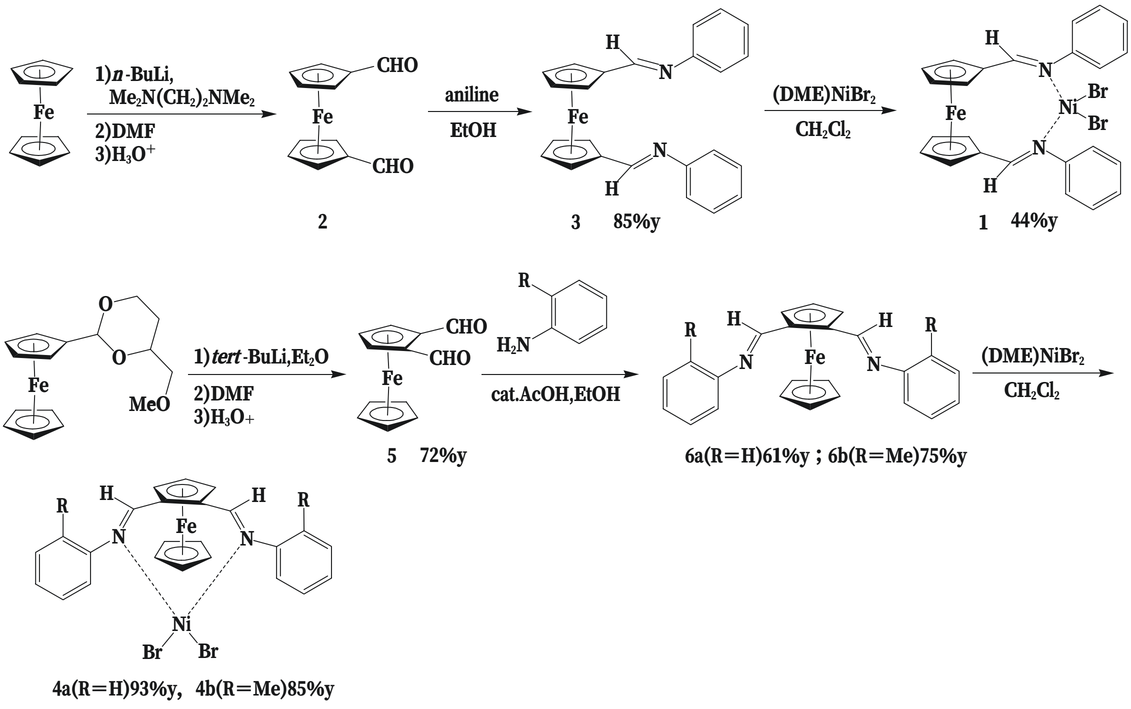
2. Results and Discussion

[1] Synthesis of 1,1'-and 1,2-ferrocenyldiimine/$NiBr_2$

1,1'-Disubstituted ferrocenes can be derived from the reaction of 1,1'-dilithioferrocene with electorophiles. Therefore, 1,1'-diformylferrocene (2)[8] was prepared using *N,N*-dimethylformamide (DMF) as an electorophile. Formation of 1,1'-ferrocenyldiimine (3) was carried out with 2 and aniline in EtOH. The reaction of (DME)$NiBr_2$ with 3 proceeded in CH_2Cl_2 at room temperature to afford the nickel(II) complex 1 in 44% yield. On the other hand, 1,2-diformylferrocene (5)[9] was synthesized by the lithiation of 2-ferrocenecarboxaldehyde methoxymethylacetal followed by acid hydrolysis. 1,2-Ferrocenyldiimines (6a,b) were easily prepared by reacting 5 with aniline and 2-methylaniline in AcOH/EtOH. Formation of the corresponding nickel(II) complexs (4a and 4b) was carried out with these diimines and (DME)$NiBr_2$ in 93% and 85% yields, respectively. Synthetic routes are shown in **Scheme 1**.

[2] Ethylene polymerization and ethylene/methyl acrylate copolymerization using 1,2-ferrocenyldiimine/Ni(II) catalysts

Polymerization of ethylene was examined using 1 and 4 (50 μmol) at 1.0 MPa ethylene pressure upon



Scheme 1 Synthesis of 1,1'-ferrocenyldiimine/$NiBr_2$ (1) and 1,2-ferrocenyldiimine/$NiBr_2$ (4)

activation with PMAO as co-catalysts (Al/Ni ratio = 100) in toluene. Whereas the precatalyst 1 showed no polymerization activity, 4a gave polymerization product (0.07 kg/Ni・mmol,h) as an oil having a molecular weight (M_w) of 5.6 × 10^2 g/mol and a molecular weight distribution of 1.6 by GPC. The GC analysis showed that the product contained no oligomers of C_4-C_{40} content. The catalysts consisting of α-Diimine(*N*-Ph)/$NiBr_2$ and MMAO are known to give oligomers with a Schulz-Flory distribution[10)]. This difference would probably lie on the number of chelating rings and the presence of the ferrocene moiety. The ^{13}C NMR spectrum of the obtained polymer showed that it was highly branched and had the *sec*-butyl group as a branch on branch group (δ = 11.4, 19.2)[11)] (**Fig. 2**). On the other hand, 4b gave no polymer. As 4b was mixed with PMAO, a black precipitate was immediately formed, indicating the reduction of nickel(II) species by PMAO took place.

The copolymerization of ethylene/methyl acrylate was conducted with 4a/PMAO catalyst and the results were summarized in **Table 1**. Although the activity was quite low, the analysis of ^{13}C NMR spectrum (**Fig. 3**) of the obtained polymer implied that copolymerization proceeded from the chemical shifts of carbonyl groups[2b)] (δ = 172-176).

[3] Synthesis of 2-azaferrocenylimine/$NiBr_2$

As described above, we have found the 1,2-ferrocenyldiimines nickel(II) complex was capable of building the ethylene/methyl acrylate sequence in the obtained polymer. This finding encouraged us to further pursue the investigation of ethylene/acrylate ester copolymerization. Because the rigid 5-membered chelation structure is considered to be critical not only to improve catalytic activity but also to increase molecular weights, we attempted to exploit azaferrocenylimine nickel(II) complexes. The synthesis

Table 1 Ethylene/methyl acrylate copolymerization using 1,2-ferrocenyldiimine/$NiBr_2$ (4a)[a]

run	catalyst	4a [mmol]	methyl acrylate [mL, mmol]	yield [g]	activity [g/Ni・mmol]	acrylate incorporation [wt%][b]	M_w[c] [×10^{-3}]	M_w/M_n
1	4a/PMAO	0.113	5.0, 55	2.08	18.4	18.6	1.0	1.8
2	4a/PMAO	0.110	15.0, 165	1.60	14.5	24.8	1.0	1.9

[a] Polymerization conditions: ethylene pressure; 1 MPa, 0.5 L of toluene, 24 h, Al/Ni ratio 100. temperature 25℃, time 24 h. [b] Determined by ^{1}H NMR. [c] Determined by GPC relative to polystyrene standards.

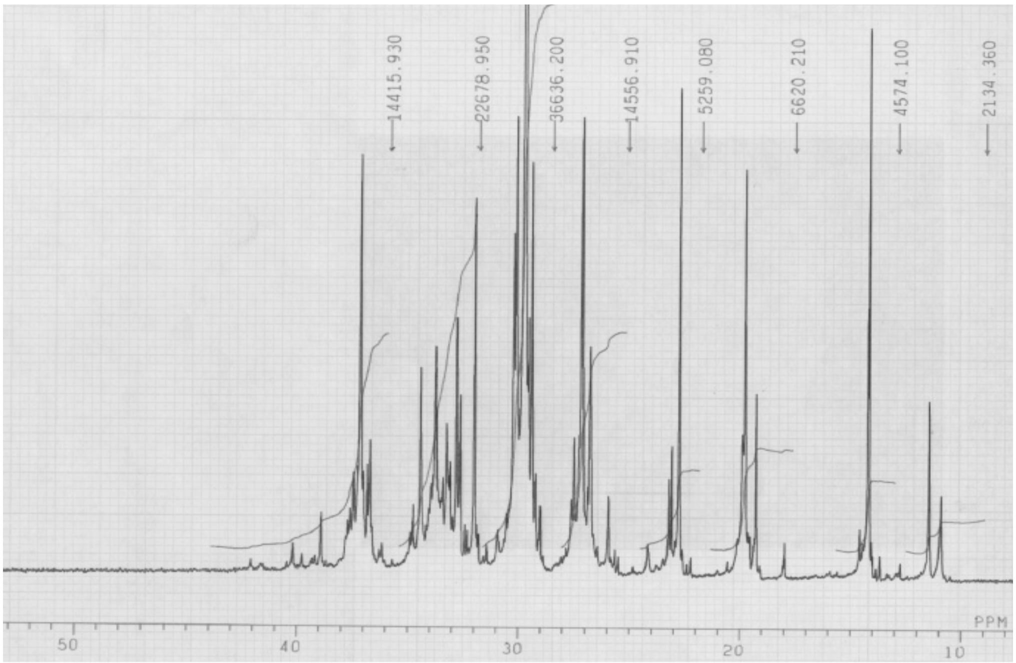


Fig. 2 ^{13}C NMR spectrum of obtained polyethylene

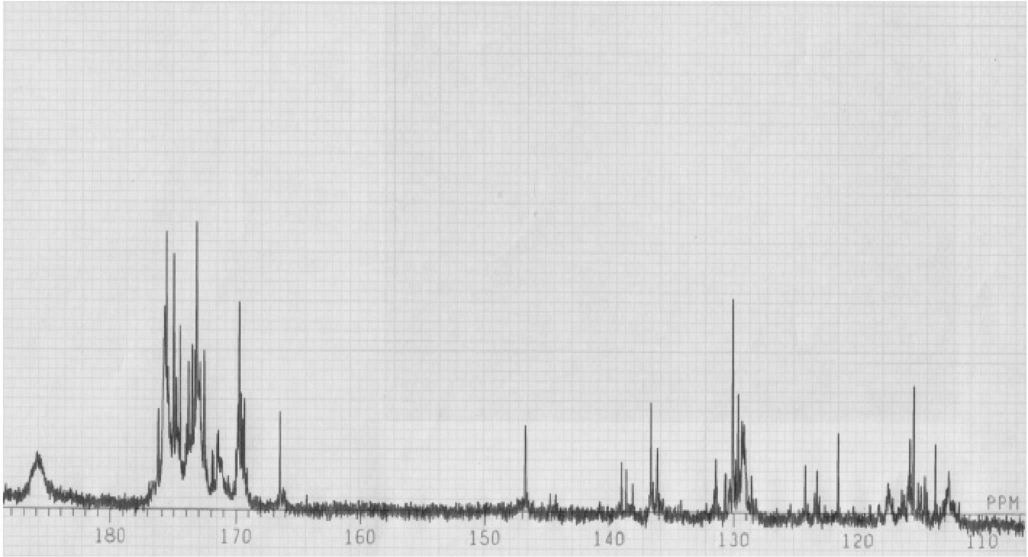
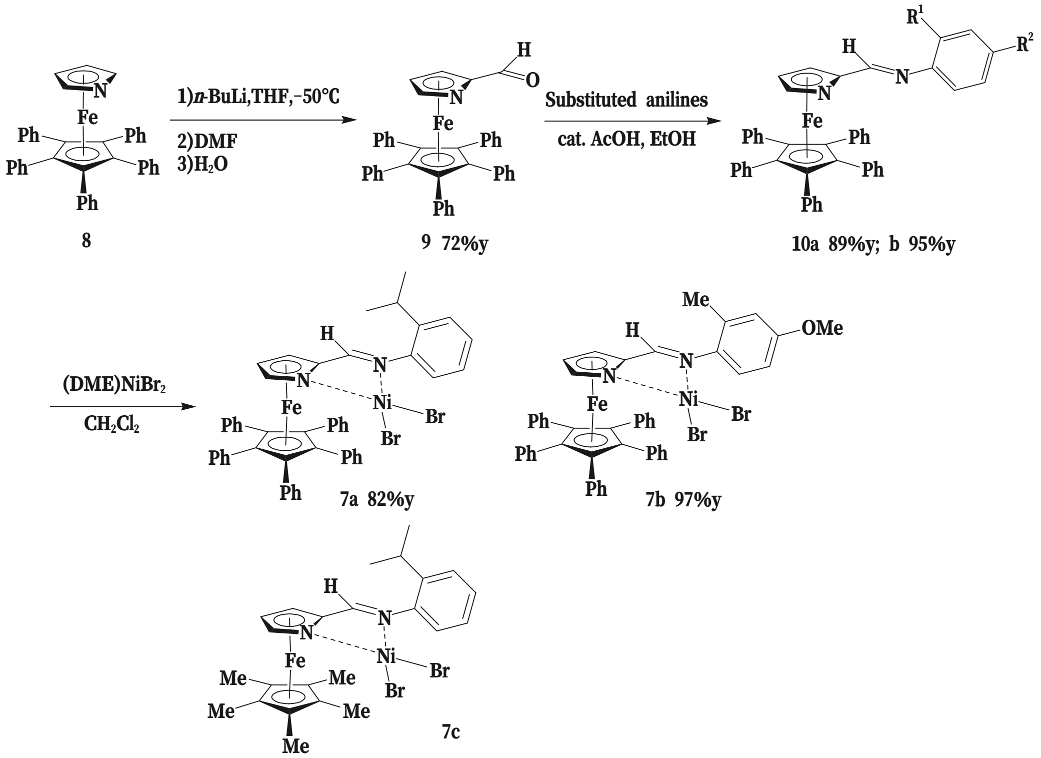


Fig. 3 ^{13}C NMR spectrum of obtained ethylene/methyl acrylate copolymer

of azaferrocenylimine/NiBr$_2$ (7) was carried out by a synthetic method similar to 1,2-ferrocenyldiimine/NiBr$_2$ (4) (**Scheme 2**). Pentaphenylazaferrocene (8), prepared from Ph$_5$CpLi, FeCl$_2$ and potassium pyrrolide in one pot manner, underwent lithiathion by *n*-BuLi followed by formulation by DMF to afford 2-formyl azaferrocene 9 in 72% yield. Formation of imines 10a (R^1=*i*-Pr, R^2=H) and 10b (R^1=Me, R^2=OMe) was carried out with anilines in AcOH/EtOH. Nickel(II) complexes 7a and 7b were prepared from 10a,b and (DME)NiBr$_2$ in CH$_2$Cl$_2$. The Cp* derivative 7c was also prepared similarly.

[4] Ethylene/acrylate ester copolymerization using 2-azaferrocenylimine/Ni(II) catalysts

A highly active ethylene polymerization catalyzed by



Scheme 2 Synthesis of 2-azaferrocenylimine/NiBr$_2$ (7)

azaferrocenylimine/NiBr$_2$ was revealed upon activation with PMAO[7)]. The activity was as high as 7.0 kg/Ni・mmol,h at 1.0 MPa of ethylene pressure. The α-diimine-nickel(II) catalyzed copolymerization of ethylene/2-phenoxyethyl acrylate was reported to take place in the presence of a large excess of tris(pentafluorophenyl)borane and tetrakis (pentafluorophenyl)borate salt[4)]. Detailed ^{1}H NMR characterization of the obtained copolymer and acrylate homopolymer was shown in that literature. Therefore, we conducted the copolymerization of ethylene/2-phenoxyethyl acrylate catalyzed by 2-azaferrocenylimine/NiBr$_2$ at 4 MPa of ethylene pressure (**Table 2**). When PMAO was used as an activator for the nickel(II) complex 7a (Ni/Al ratio = 1/100), the activity of 0.11 kg/Ni・mmol was obtained at 25℃ (run 1), but it decreased to 0.02 kg/Ni・mmol at 50℃ (run 2). One needs to take into consideration the fact that unfavorable concomitant reduction of nickel(II) active species competes especially at higher temperature. Therefore, the catalyst containing a borate component was examined. When trimethylaluminum was combined with *N*,*N*-dimethylanilinium tetrakis (pentafluorophenyl)borate(DAN・FABA)(Ni/B/Al ratio = 1/5/100), the comparable activity (0.15 kg/Ni・mmol) was obtained even at higher temperatures (80℃, run 3). Surprisingly, the cocatalyst consisting of ethylaluminum sesquichloride and DAN・FABA exhibited approximately ten-times higher activity (run 4). Halogenated alkylaluminums are thought to be suited for activating the nickel (II) precatalyst and suppressing the reduction of nickel(II) active species. When lithium tetrakis (pentafluorophenyl)borate was used as an additive (20 equiv. to Ni)[4)], it gave a negative effect on the activity (run 5). On the other hand, although the complex 7b bearing an electron-donating methoxy group on the *N*-aryl group was less active than 7a, it led to higher incorporation of acrylate comonomer (run 6). When this catalyst system was heated to 100℃, the activity slightly decreased to 0.35 kg/Ni・mmol (run 7). A plausible explanation for the higher incorporation of acrylate comonomer would be the increased electron density around the nickel center of 7b enaugh to attract an electron-poor acrylate. The Cp* derivative 7c was extremely less active (run 8) as compared with 7a, although its incorporation of acrylate ester became more than doubled. Thus, the pentaphenyl cyclopentadienyl moiety in the complexes was indispensable for the copolymerization of ethylene-acrylate esters.

Characterization of the incorporation of acrylate monomer was carried out by measuring ^{1}H NMR spectra of the obtained polymers. The typical spectrum of a polymer from run 4 was shown in **Fig. 4**. The chemical shift around 4.37 to 4.45 ppm was assigned to the phenoxyethyl moieties in the copolymer but the

Table 2　Ethylene/2-phenoxy acrylate copolymerization using 2-azaferrocenylimine/NiBr$_2$ (7)[a]

run	catalyst	7 [μmol]	temp. [℃]	time [h]	yield [g]	activity [kg/Ni・mmol]	a. i. [wt%][b]	M_w[c] [×10^4]	M_w/M_n	T_m[d] [℃]	ΔH [J/g]
1[e]	7a/PMAO	22.1	25	30	2.62	0.11	1.7	2.9	3.7	57.7	28.1
2[e]	7a/PMAO	12.8	50	12	0.29	0.02	1.2	1.7	3.3	48.3	25.3
3[f]	7a/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Me$_3$Al	5.5	80	20	0.72	0.15	0.7	1.9	3.7	30.9 74.8	40.0
4[f]	7a/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Et$_3$Al$_2$Cl$_3$	5.7	80	10	5.73	1.00	1.7	2.2	3.1	44.8 83.7	55.5
5[f,g]	7a/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Et$_3$Al$_2$Cl$_3$	5.5	80	10	2.99	0.54	0.9	2.0	3.3	42.0 85.0	56.3
6[f]	7b/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Et$_3$Al$_2$Cl$_3$	10.0	80	10	4.51	0.45	2.1	1.4	3.7	33.2 81.0	62.7
7[f]	7b/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Et$_3$Al$_2$Cl$_3$	5.0	100	10	1.75	0.35	2.5	0.9	3.5	35.0 69.5	53.1
8[f]	7c/Ph(Me)$_2$NH・B(C$_6$F$_5$)$_4$ /Et$_3$Al$_2$Cl$_3$	6.9	50	10	0.03	0.004	5.7	0.2	2.6	55.3	75.0

[a] Polymerization conditions: ethylene pressure; 4 MPa, 0.5 mL (2.86 mmol) of 2-phenoxyethyl acrylate, 30 mL of toluene. [b] Acrylate incorporation, determined by ^{1}H NMR. [c] Determined by GPC relative to polystyrene standards. [d] Determined by DSC. [e] Al/Ni ratio 100. [f] Ni/B/Al ratio 1/5/100. [g] 20 equiv. of Li・B(C$_6$F$_5$)$_4$ to the Ni complex was added as additive.

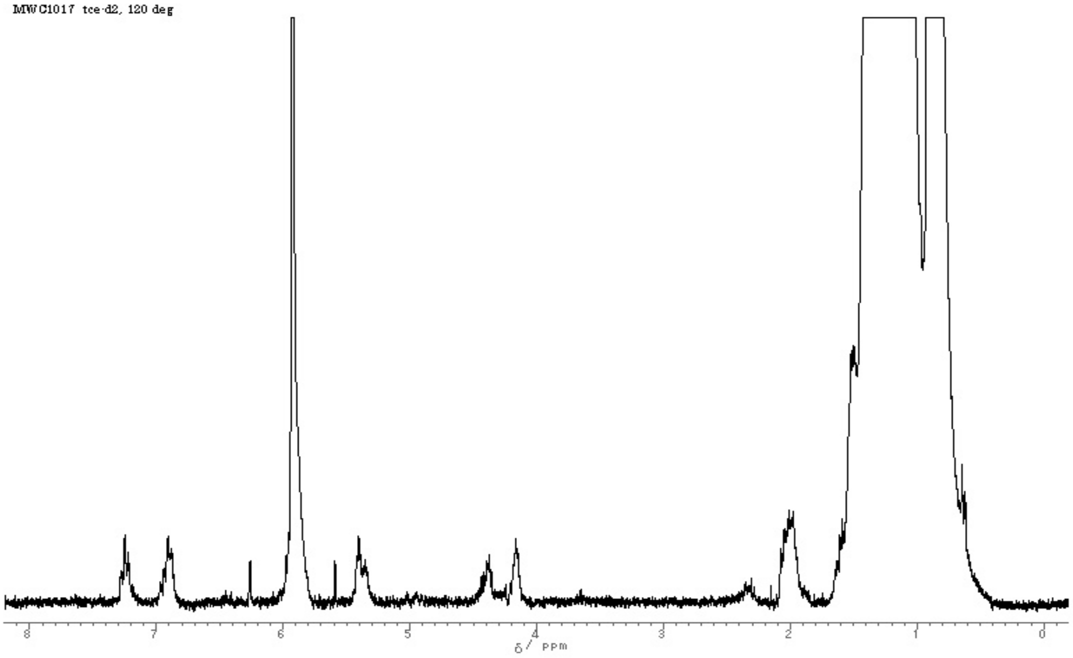


Fig. 4 ^{13}C NMR spectrum of obtained ethylene/2-phenoxyethyl acrylate copolymer

peak due to acrylate homopolymer (δ = 4.31) were not observed$^{4)}$. All polymers obtained in **Table 2** were consistently characterized by ^{1}H NMR analysis as the expected copolymers.

3. Conclusion

1,1′-Ferrocenyldiimine/NiBr$_2$ (1), 1,2-ferrocenyldiimine/NiBr$_2$ (4), and 2-azaferrocenylimine/NiBr$_2$ (7) were synthesized, and used as catalyst for the ethylene polymerization and ethylene/acrylates copolymerization. Although 1 had no polymerization activity for ethylene, 4 was found to work as catalyst for both ethylene polymerization and ethylene/acrylates copolymerization. The polymerization method was extended to use the complexes 7a-c. The catalytic activity towand ethylene polymerization was 7 > 4 in accordance with the size of chelation sphere. We have also found that the catalyst system consisting of 7, ethylaluminum sesquichloride and borate drastically improved the activity for ethylene/acrylate copolymerization. Compared to the method of ethylene/acrylate copolymerization by DuPont, our copolymerization method is more practical on the economical point of view because it needs only small amounts of highly expensive borate cocatalyst.

4. Experimental

[1] General

Ethylene/acrylate ester copolymerization was performed in a 0.15 L stainless steel autoclave. NMR spectra were recorded on a JEOL GSX-270WB (270 MHz) spectrometer. Chemical shifts for ^{1}H NMR spectra were referenced to internal solvent references and reported as parts per million relative to tetramethylsilane. ^{1}H-NMR spectra of ethylene/2-phenoxyethyl acrylate copolymers were measured in [D$_2$]1,1,2,2-tetrachloroethane at 120℃. ^{13}C NMR spectra of polymers (about 15% (w/v) solutions of sample) were measured in CDCl$_3$ at 25℃ using a 10-mm sample tube. Chemical shifts were referenced to the major backbone methylene carbon resonance, which was taken as 30.00 ppm downfield from tetramethylsilane. High-temperature gel permeation chromatography (GPC) was performed in 1,2,4-

trichlorobenzene at 140℃ using a Tosoh HLC-8121GPC/HT apparatus with TSKgel GMHhr-H(20)HT (× 3) columns. A calibration curve was established with polystylene standards. Differential scanning calorimetry was recorded on a Seiko Instruments DSC200. A 8.7% Al (wt %) solution of polymethylaluminoxane (PMAO) in toluene and a 20.3% solution of ethylaluminum sesquichloride in toluene were purchased from Tosoh-Finechem Co. 2-Phenoxyethyl acrylate was purchased from Tokyo Kasei Kogyo Co., was degassed by repeated freeze-pump-thaw cycles and dried over Zeolite.

[2] Typical ethylene/acrylate ester copolymerization procedure

A 0.15 L stainless steel autoclave with a magnetic stirrer bar was heated at 100℃ under vacuum for 1 h and then cooled and repeated pressuring with nitrogen to 0.7 MPa and venting three times. A suspension of precatalyst (5-6 μmol) in toluene (15 mL) was injected into autoclave via a cannula at room temperature. Then, the autoclave was pressurized with ethylene to 1 MPa and vented. Ethylaluminum sesquichloride (20.3%, 1.48 M (Al) toluene solution, 0.5 mL, 0.74 mmol) and *N,N*-dimethylanilinium tetrakis(pentafluorophenyl) borate (29.0 mg, 0.0361 mmol) in toluene (15 mL) were added. And then, after 2-phenoxyethyl acrylate (0.5 mL, 2.86 mmol) was added, the autoclave was immediately pressurized with ethylene to 4 MPa, shaken, and placed in an oil bath at 80℃. The mixture was stirred at 80℃ for 10 h. Then the autoclave was vented and the reaction mixture was poured into ethanol (200 mL) with stirring to precipitate the polymer, which was filtered and dried in a vacuum oven at 50℃. The obtained polymers were characterized by ^{1}H NMR, GPC and DSC.

5. References

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