Synthesis of Cationic Nickel(II) Compounds for Butadiene Polymerization

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ABSTRACT: A series of cationic nickel(II) compounds with various counter ions ($[BF_4]^-$, $[CF_3SO_3]^-$) and N-bearing ligands (1,10-phenanthroline, benzimidazole and terpyridine) were synthesized. The simple compound, $Ni(Phen)_2Cl_2$, was prepared as a reference compound. All title compounds were characterized by elemental analysis, and infrared spectra analyses and compounds, some specific ones, were further examined by X-ray crystallographic analysis. Upon treatment with ethylaluminum sesquichloride, these nickel(II) compounds exhibited high activities (up to 88.5%/4 h) for butadiene polymerization and afforded liquid polybutadiene ($M_w < 30,000$) with a high *cis*-content (up to 92.1%). Various polymerization conditions were investigated in detail, and it was found that less steric hindrance of the ligands enhanced the catalytic activities of the nickel(II) compounds. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40511.

INTRODUCTION

Since the discovery of Ziegler-Natta catalyst, Regio- and/or stereospecific polymerizations of butadiene have been of great interests and importance from viewpoints of polymers design and their applications as polymer materials.[1,2] Depending on the choice of organometallic compound, polymers with specific microstructures could be obtained. Recognizing the strong influence of the compound structure on transition metal catalyst activity and polymer stereoregularity, many scientists have modified the ligands on compounds by changing the substituents on the ligands.[3–7] These modifications adjusted the steric and electronic properties of the ligands and thus control the catalytic activities and microstructure of the products of diene polymerization.

Because of its good chemical resistance, electrical properties, thermal properties, mechanical properties, etc., liquid polybutadiene has had a wide range of applications as a new kind of thermosetting resin during the past decades, for example, as coating and insulation materials.[8,9] Furthermore, a modified polymer could show a high elasticity and high plasticity if high–*cis*−1,4 liquid polybutadiene was connected with a cross-linking agent or other polymers. The higher the *cis*−1,4 content of the liquid polybutadiene is, the lower the viscosity is and the higher iodine value is, which will in turn improve the liquid polybutadiene modification reaction. As catalysts for preparing liquid polybutadiene, organometallic compounds such as butyl-lithium and boron fluoride have been used in the past.[10] These catalysts yield liquid polybutadiene in which the vinyl and *trans*−1,4 configurations predominated, with the *cis*−1,4 configuration making up less than 60%. The stereoselectivity of the butadiene polymerization using nickel-containing catalysts depends on the catalyst composition, and polymers consisting mainly of *cis*−1,4 units, *trans*−1,4 units, and 1,2-vinyl units have been isolated, as well as polymers containing varying proportions of these units.[11–13] Therefore, it would be highly desirable to provide a catalyst that can be usefully employed to produce liquid polybutadiene with high *cis*−1,4 selectivity and a high catalytic activity. Hou and coworkers[14] reported a cationic alkyl rare-earth metal (Y, Yb, and Lu) catalyst species bearing P-ligands and the catalyst that provided extremely high *cis*−1,4 selectivity and high activity for the polymerization of isoprene and butadiene.

Therefore, in this work, a series of cationic nickel(II) compounds were synthesized for the first time, and a systematic investigation of the butadiene polymerization initiated by these compounds was carried out. The effects of the catalyst structure (e.g., anionic counter ions and ligands) and reaction conditions on the polymerization behaviors were further studied. In addition, a polymerization mechanism was also proposed to explain the differences between the traditional and cationic nickel-based catalysts.
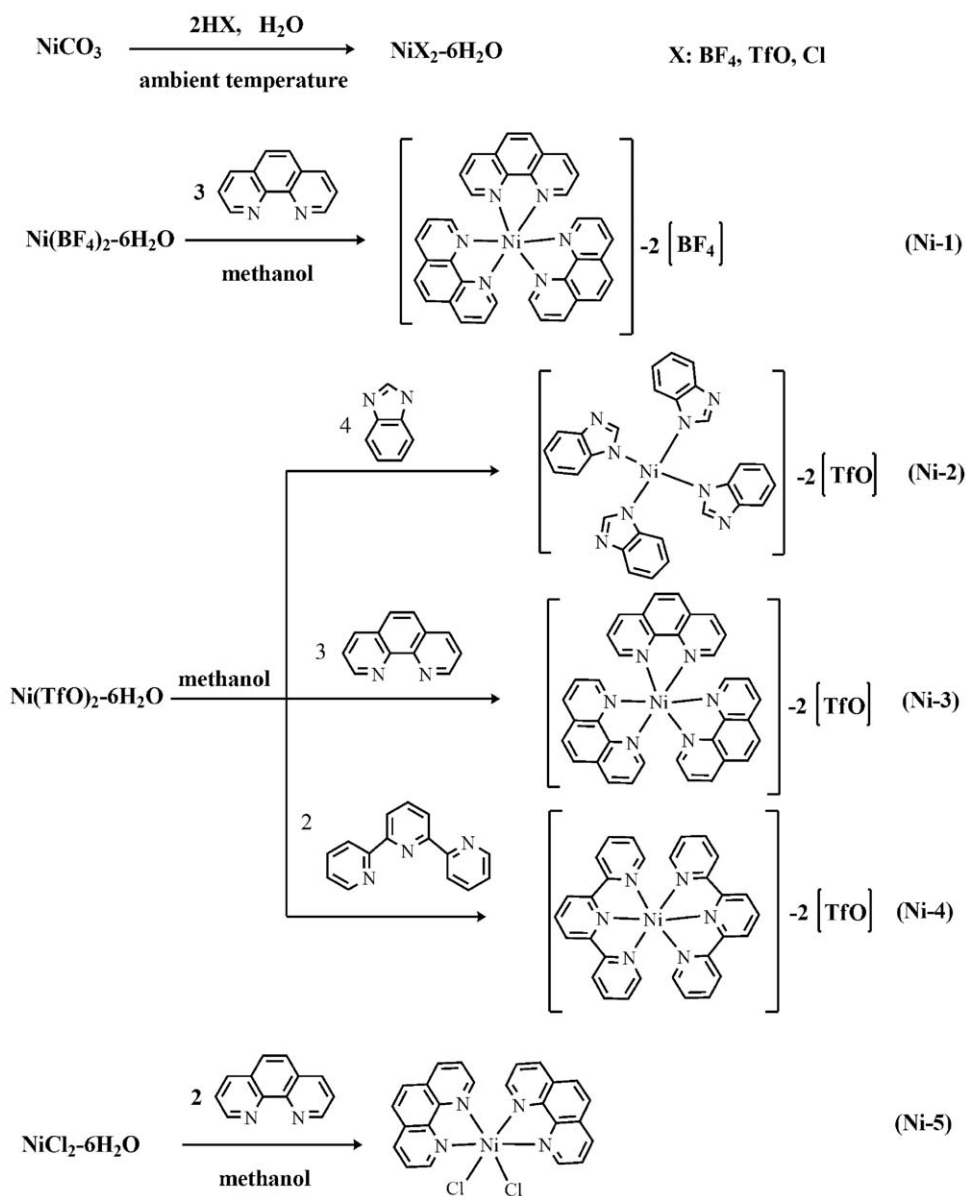
Scheme 1. Syntheses of cationic nickel-based compounds.

EXPERIMENTAL

General Considerations

Nickel carbonate ($NiCO_3$), tetrafluoroboric acid (HBF_4), and trifluoromethanesulfonic acid (HTfO) were available from Alfa Aesar, China. The ligands of 1,10-phenanthroline (Phen), benzimidazole (BZI), and terpyridine (Terpy) were supplied by J&K, China. Ethylaluminum sesquichloride (EASC) was commercially purchased from Akzo Nobel, USA. Polymer-grade butadiene was commercial product from Jinzhou Petrochemical, China and purified by passing through four columns packed with molecular sieves and solid potassium hydroxide. Toluene was distilled by heating to reflux in the presence of sodium and diphenylketyl. Other chemicals were used as received unless otherwise noted. IR spectra were obtained on BRUKER Vertex-70 FT-IR spectrophotometer. Elemental analyses were performed on an elemental Vario EL spectrometer. The proportions of

cis−1,4, trans−1,4, and 1,2 units of the polymer were determined from the IR spectra.[15–17] The weight-average molecular weights (M_w) and polydispersities (M_w/M_n) of the resultant polymers were measured at 30°C by a gel permeation chromatograph (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF), and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min. The M_n and M_w/M_n values were determined using the polystyrene calibration. IR spectra were measured with a BRUKER Vertex-70 FTIR spectrophotometer. The proportions of cis−1,4, trans−1,4, and 1,2 units of polymers were determined as reported in the literature.[18] X-ray diffraction data collections was performed at −88.5°C on a BRUKER SMART APEX diffractometer equipped with a graphite-monochromatized Mo Kα source ($\lambda = 0.71073$ Å). The determination of the crystal class and unit cell
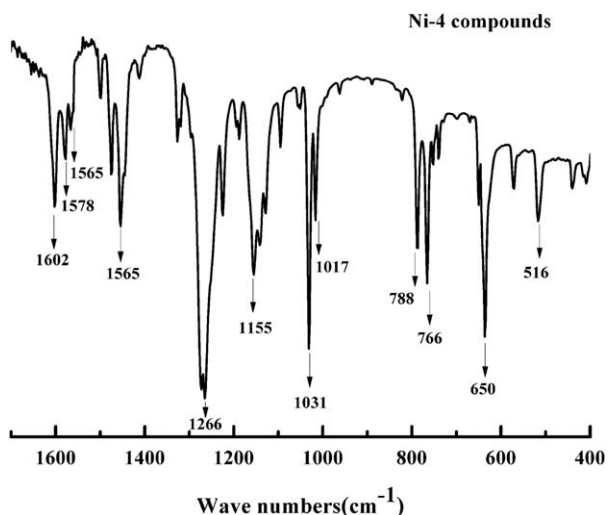
Figure 1. The FT-IR spectra of **Ni-4**.

parameters was carried out using the SMART program package, and the structures were determined by the SHELXTL program. Refinement was performed on F^2 anisotropically for all nonhydrogen atoms using the full-matrix least-squares method. Database: CCDC (**Ni-1**): 873099, CCDC (**Ni-3**):950167, and CCDC (**Ni-4**): 950170.

Syntheses and Characterization of Compounds

The general synthetic route of the nickel-based compounds is shown in **Scheme 1**. The typical synthetic procedures were as follows: Excess nickel carbonate and the corresponding acid (HBF_4, HTfO, HCl) were added to a flask containing distilled water. The mixture was stirred at ambient temperature, and a deep-green suspension was formed. Afterwards, the mixture was filtered through a glass funnel with a filter paper and the filtrate was dried at 70°C under vacuum to obtain the corresponding NiX_2–$6H_2O$ compound.

Tri(1,10-Phenanthroline) Nickel(II) Tetrafluoroborate (Ni-1). A solution was prepared by the reaction of Phen (0.79 g, 4.39 mmol) with nickel(II) tetrafluoroborate hexahydrate (0.5 g, 1.47 mmol) in methanol (20 mL) at 30°C. Then, the reaction system was cooled to ambient temperature. Yellow crystals were obtained from the reaction system by filtration. The resultant compound was dried at 50°C in vacuum and obtained as an air-stable powder. Yellow powder, 90.7% yield. IR (KBr, cm^{-1}): 1626(m), 1605(w), 1583(m), 1518(s), 1496(w), 1426(s), 1341(m), 1305(w), 1224(w), 870(m), 850(s), 724(s), 645(m), 521(m). *Anal.* Calc. for C36H24B2CoF8N6: C, 55.89; H, 3.10; N, 10.87. Found: C, 55.75; H, 3.48; N, 10.82%.

Tetra(benzimidazole) Nickel(II) Trifluoromethanesulfonate (Ni-2). In a manner similar to that described for **Ni-1**. Yellow powder, 90.7% yield. IR (KBr, cm^{-1}): 1628(w), 1598(w),

Table I. Crystal Data and Structure Refinements of Compounds **Ni-1**, **Ni-3**, and **Ni-4**

	Ni-1	Ni-3	Ni-4
Formula	$C_{36}H_{24}B_2F_8N_6Ni$	$C_{38}H_{24}F_6N_6NiO_6S_2$	$C_{32}H_{22}F_6N_6NiO_6S_2$
Molecular weight	772.940	897.46	823.39
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	C2/c	Pbcn
a (Å)	11.1762 (6)	20.8807(16)	16.7734(10)
b (Å)	12.9002 (7)	15.2180(12)	21.2476(13)
c (Å)	14.3060 (7)	16.7599(13)	9.0953(5)
α (deg)	80.844 (1)	90	90.00
β (deg)	75.976 (1)	124.5510(10)	90.00
γ (deg)	68.559 (1)	90	90.00
V (Å^3)	1856.9 (2)	4386.3(6)	3241.5(3)
Z	2	4	4
Dcalcd (mg/m^3)	1.382	1.359	1.687
Absorp. coeff. (mm^{-1})	0.597	0.612	0.819
F(000)	784	1824	1672
Crystal size (mm)	0.27 × 0.13 × 0.09	0.21 × 0.17 × 0.09	0.21 × 0.18 × 0.09
θ range (º)	2.14–26.10	1.79–26.05	2.72–25.92
No. of reflns collected	10357	13485	16574
No. of indep. reflns	7249	4291	3202
No. of data/restraints/params	72496/0/478	4291/1/267	3202/0/242
GOF on F^2	1.065	1.125	1.019
$R1(1 > 2\sigma(1))$	0.0463	0.0731	0.0362
$wR2$	0.1179	0.2231	0.1007

Table II. Selected Bond Distances (Å) and Angles (°) of Cobalt Compounds **Ni-1**, **Ni-3**, and **Ni-4**

	Ni-1		Ni-3		Ni-4	
Bond distance	Ni(1)-N(4)	2.089(2)	Ni(1)-N(1)	2.101(3)	Ni(1)-N(4)	1.998(2)
	Ni(1)-N(1)	2.090(2)	Ni(1)-N(1A)	2.101(3)	Ni(1)-N(2)	2.000(2)
	Ni(1)-N(3)	2.095(2)	Ni(1)-N(2)	2.114(3)	Ni(1)-N(1)	2.1052(16)
	Ni(1)-N(6)	2.096(2)	Ni(1)-N(2A)	2.114(3)	Ni(1)-N(1A)	2.1052(16)
	Ni(1)-N(5)	2.097(2)	Ni(1)-N(3)	2.086(3)	Ni(1)-N(3)	2.1188(17)
	Ni(1)-N(2)	2.099(2)	Ni(1)-N(3A)	2.086(3)	Ni(1)-N(3A)	2.1188(17)
Bond angle	N(4)-Ni(1)-N(1)	92.63(8)	N(3)-Ni(1)-N(3)	80.15(17)	N(4)-Ni(1)-N(2)	180.0
	N(4)-Ni(1)-N(3)	79.58(8)	N(3)-Ni(1)-N(1)	95.70(11)	N(4)-Ni(1)-N(1)	102.23(5)
	N(1)-Ni(1)-N(3)	168.38(8)	N(3)-Ni(1)-N(1)	95.60(12)	N(2)-Ni(1)-N(1)	77.77(5)
	N(4)-Ni(1)-N(6)	171.40(8)	N(3)-Ni(1)-N(1)	95.60(12)	N(4)-Ni(1)-N(1)	102.23(5)
	N(1)-Ni(1)-N(6)	93.84(8)	N(3)-Ni(1)-N(1)	95.69(11)	N(2)-Ni(1)-N(1)	77.77(5)
	N(3)-Ni(1)-N(6)	94.83(8)	N(1)-Ni(1)-N(1)	165.23(16)	N(1)-Ni(1)-N(1)	155.54(10)
	N(4)-Ni(1)-N(5)	94.13(8)	N(3)-Ni(1)-N(2)	96.67(12)	N(4)-Ni(1)-N(3)	77.75(5)
	N(1)-Ni(1)-N(5)	94.64(8)	N(3)-Ni(1)-N(2)	173.77(11)	N(2)-Ni(1)-N(3)	102.25(5)
	N(3)-Ni(1)-N(5)	94.51(8)	N(1)-Ni(1)-N(2)	90.04(12)	N(1)-Ni(1)-N(3)	94.88(6)
	N(6)-Ni(1)-N(5)	79.70(8)	N(3)-Ni(1)-N(2)	79.22(12)	N(1)-Ni(1)-N(3)	90.28(6)
	N(4)-Ni(1)-N(2)	94.25(8)	N(3)-Ni(1)-N(2)	173.77(11)	N(4)-Ni(1)-N(3)	77.75(5)
	N(1)-Ni(1)-N(2)	79.50(8)	N(3)-Ni(1)-N(2)	96.66(12)	N(2)-Ni(1)-N(3)	102.25(5)
	N(3)-Ni(1)-N(2)	92.40(8)	N(1)-Ni(1)-N(2)	79.21(12)	N(1)-Ni(1)-N(3)	90.28(6)
	N(6)-Ni(1)-N(2)	92.50(8)	N(1)-Ni(1)-N(2)	90.04(12)	N(1)-Ni(1)-N(3)	94.88(6)
	N(5)-Ni(1)-N(2)	169.98(8)	N(2)-Ni(1)-N(2)	86.99(17)	N(3)-Ni(1)-N(3	155.51(9)

1467(m), 1355(w), 1226(w), 1176(s), 1116(m), 1030(s), 1011(w), 992(m), 889(m), 751(s), 637(s). *Anal.* Calc. for $C_{30}H_{24}N_8NiF_6S_2O_6$: C, 43.43; H, 2.90; N, 13.51. Found: C, 43.70; H, 3.30; N, 13.65%.

Tri(1,10-Phenanthroline) Nickel(II) Trifluoromethanesulfonate (Ni-3). In a manner similar to that described for **Ni-1**. Yellow powder, 87.2% yield. IR (KBr, cm^{-1}): 1627(m), 1607(w), 1520(s), 1497(m), 1427(s), 1343(m), 1223(m), 1155(s), 1105(m), 1032(s), 869(m), 847(s), 777(w), 753(w), 726(s), 637(s), 573(w), 515(m). *Anal.* Calc. for $C_{38}H_{24}N_6NiF_6S_2O_6$: C, 50.84; H, 2.68; N, 9.36. Found: C, 50.80; H, 2.65; N, 9.42%.

Bis(terpyridine) Nickel(II) Trifluoromethanesulfonate (Ni-4). In a manner similar to that described for **Ni-1**. Dark browm powder, 82.3% yield. IR (KBr, cm^{-1}): 1602(s), 1578(m), 1565(w), 1499(w), 1475(s), 1456(s), 1413(w), 1266(s), 1155(s), 1093(m), 1031(s), 1017(s), 788(s), 766(s), 754(w), 739(w), 650(w), 637(s), 573(w), 516(m). *Anal.* Calc. for $C_{32}H_{22}N_6NiF_6S_2O_6$: C, 46.66; H, 2.67; N, 10.21. Found: C, 46.60; H, 2.74; N, 10.35 %.

Bis(1,10-Phenanthroline) Nickel(II) Chloride (Ni-5). In a manner similar to that described for **Ni-1**. Yellow powder, 90.7% yield. IR (KBr, cm^{-1}): 1624(m), 1514(s), 1495(w), 1427(s), 1343(m), 1306(w), 1145(m), 1104(m), 870(w), 728(s), 634(w). *Anal.* Calc. for $C_{24}H_{16}Cl_2CoN_4$: C, 58.80; H, 3.29; N, 11.43. Found: C, 58.86; H, 3.22; N, 11.58%.

Procedure for Butadiene Polymerization. All manipulations were carried out under the dry nitrogen atmosphere. Butadiene

polymerization was conducted as follows: **Ni-4** (0.0152 g, 0.018 mmol) was added as solid to a moisture-free ampoule capped with a rubber septum. Then, a solution of butadiene in toluene (20 mL, 0.1 g/mL) was injected into the ampoule. Catalyst components, EASC (0.62 mL, 1.5 mol/L), was added to the ampoule to initiate polymerization. The polymerization was carried out
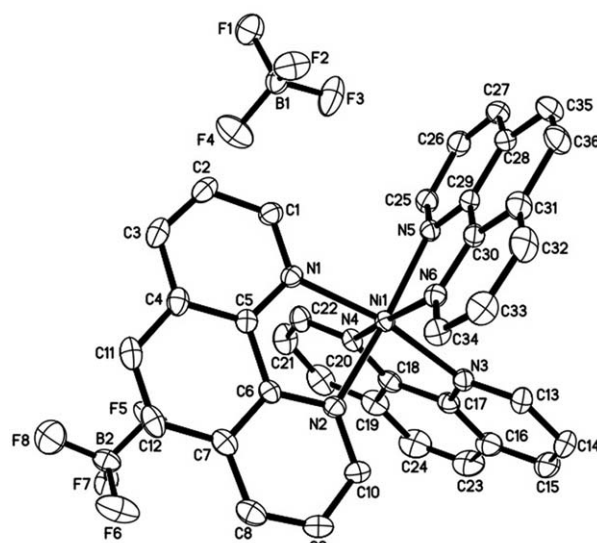

Figure 2. X-ray structure of **Ni-1**. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.
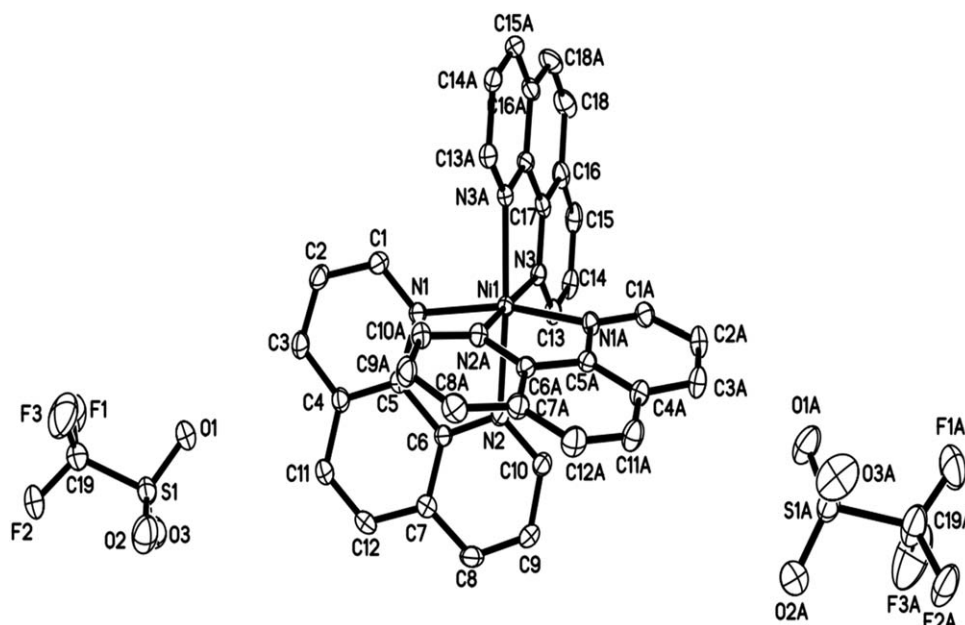
Figure 3. X-ray structure of **Ni-3**. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

at 25°C for 4 h and quenched by adding ethanol containing 2,6-di-tert-butyl-4-methylphenol(1.0% v/v) as a stabilizer. Polybutadiene was obtained after being dried in vacuum at 50°C to constant weight (yield: 1.63 g, 81.5%).

RESULTS AND DISCUSSION

Preparation and Characterization of Compounds

As shown in **Scheme 1**, cationic nickel-based compounds were readily prepared by the reaction of nickel tetrafluoroborate or nickel trifluoromethanesulfonate with various N-bearing ligands in methanol. The resultant products were isolated as air-stable powders in good yields and were characterized by IR spectroscopy and X-ray analysis. The C=N stretching bands of the free ligands appeared at 1561–1618 cm^{-1}. In the compounds, the C=N stretching vibrations were obviously shifted toward lower frequencies and were greatly reduced in intensity, indicating an effective coordination interaction between the nitrogen atoms and the metal ion. Typical FT-IR spectra of the **Ni-4** compound are shown in **Figure 1**. The IR spectral peaks of the obtained nickel compounds and found to be in good agreement with the literature values.[19–21] The molecular structures of compounds **Ni-1**, **Ni-3**, and **Ni-4** were further confirmed by X-ray crystallographic study. However, no structural information was obtained for **Ni-2**, which limits the discussion regarding this compound. The crystallographic data together with the collection and refinement parameters are summarized in **Table I**. Selected bond distances (Å) and angles (°) of cobalt compounds were shown in **Table II** and their crystal structures are depicted in **Figures 2–4**. All the compounds mentioned above consisted of one cation and two noncoordinating counter ions, and the coordination geometries at the nickel metal center could be best described as slightly distorted octahedron. The distances between the nickel centers and counter ions influence the elec-

tropositivity of the coordinated metal. The Ni...B distances in Ni-1 (Ni...B(1) = 5.795 Å, Ni...B(2) = 8.204 Å) are shorter than the Ni...S distances in Ni-3 (Ni...S(1) = 9.245 Å, Ni...S(1A) = 9.245 Å), and the Ni...S distances in **Ni-4** (Ni...S(1) = 6.048 Å, Ni...S(1A) = 6.048 Å) are shorter than the Ni...S distances in **Ni-3** (Ni...S(1) = 9.245 Å, Ni...S(1A) = 9.245 Å).

In the traditional nickel(II) compound, the Ni...Cl bond distance is about 2.5 Å (shorter than that in the cationic nickel-based compound). These results indicated that the metal centers
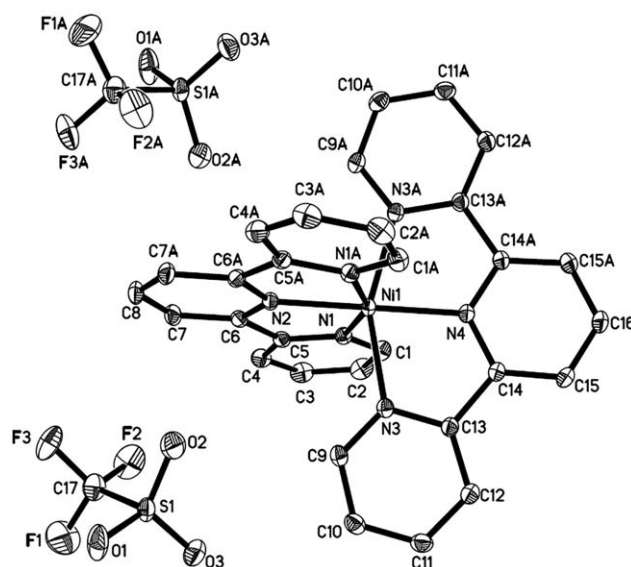

Figure 4. X-ray structure of **Ni-4**. Displacement ellipsoids are drawn at the 50% probability level. Displacement ellipsoids are drawn at the 50% probability level.

Table III. Butadiene Polymerization with Various Ligands and Anions

Entry[a]	Cat.	Yield (%)	Microstructure[b]			M_w[c] ($\times 10^{-4}$)	M_w/M_n[c]
			Cis−1,4 (%)	Trans−1,4 (%)	1,2 (%)		
Ni-1	[Ni(Phen)$_3$][BF$_4$]$_2$	8.0	90.7	5.5	3.8	2.2	2.0
Ni-2	[Ni(BZI)$_4$][TfO]$_2$	57.0	78.6	18.9	2.5	1.7	2.6
Ni-3	[Ni(Phen)$_3$][TfO]$_2$	30.5	92.1	4.6	3.3	1.9	2.0
Ni-4	[Ni(Terpy)$_2$][TfO]$_2$	81.5	81.8	16.5	1.6	2.1	3.1
Ni-5	[Ni(Phen)$_2$]Cl$_2$	42.9	85.5	11.1	3.4	2.0	2.2

[a] Polymerization conditions: [Bd] = 0.1 g/mL, [Bd]/[Ni] = 2000, [Al]/[Ni] = 50, toluene, 25°C, 4 h.
[b] Determined by FTIR.
[c] Determined by GPC.

of these new nickel compounds were cationic in nature, unlike those in nickel chloride. We tentatively believe that such compounds probably catalyze butadiene polymerization more effectively and rapidly in terms of both chain initiation and propagation.

Butadiene Polymerization Behaviors of Compounds Activated by Alkylaluminium Chlorides

The polymerization of 1,3-butadiene was conducted using the title compounds combined with ethylaluminum sesquichloride as a cocatalyst. To investigate the effects of different ligands on the catalytic activity and properties of the resultant polymers, we conducted a series of experiments by changing the N-bearing ligands and counter ions. For comparison, the simple compound [Ni(Phen)$_2$]Cl$_2$ was also conducted. The results are summarized in **Table III**. Compounds **Ni-1** and **Ni-3**, which contain anionic groups, exhibited relatively lower catalytic activities than **Ni-5**. The lower activity could perhaps be attributed to the steric hindrance due to the bulky Phen (two Phen ligands on **Ni-5** and three Phen ligands on **Ni-1** and **Ni-3**) around the nickel active center. In addition, the cis−1,4 contents of the resultant polybutadiene samples obtained using **Ni-1** and **Ni-3** were similar, but slightly higher than that of the sample

obtained using **Ni-5**. For compounds of **Ni-2**, **Ni-3**, and **Ni-4**, the catalyst activities of the compounds with various ligands was in the following order: Terpy > BZI > Phen, while the cis−1,4 content was not so sensitive to anion type (**Ni-1** vs. **Ni-3**). It is notable that the Ni-3 compound with Phen ligands produced polybutadiene with the highest cis−1,4 content (92.1%). The high cis−1,4 selectivity of **Ni-3** is because the Ni...S distances in **Ni-3** (Ni...S(1) = 9.245 Å, Ni...S(1A) = 9.245 Å) is the longer, and the electropostivity of central metal in **Ni-3** is the stronger among the five compounds, which led to center metals have the strong buckle coordination ability to monomer. The M_w and polydispersity of the obtained polybutadiene were ~2.0 × 10^4 and 2.0–3.1.

In most cases, the best result was obtained for the compound **Ni-4** and the effects of the polymerization conditions (polymerization temperature, polymerization time, and [Al]/[Ni] molar ratio) on the butadiene polymerization of **Ni-4** were examined as listed in **Table IV**. It was found that the catalyst activity increased with the polymerization temperature from 0 to 25°C, and then decreased from 25 to 70°C. As the polymerization temperature increased, the cis−1,4 content of the resultant polybutadiene decreased and the trans−1,4

Table IV. Effects of Polymerization Temperature and Time and [Al]/[Ni] Ratio with **Ni-4** Compound[a]

[Al]/[Ni]	T (°C)	t (h)	Yield (%)	Microstructure[b]			M_w[c] ($\times 10^{-4}$)	M_w/M_n[c]
				Cis−1,4 (%)	Trans−1,4 (%)	1,2 (%)		
50	0	4	76.5	83.6	14.3	2.1	2.3	2.9
50	25	4	81.5	81.8	16.5	1.6	2.1	3.1
50	50	4	71.0	76.2	22.3	1.6	1.5	3.0
50	70	4	51.8	72.9	25.5	1.7	1.2	2.8
50	25	1	71.0	84.5	13.4	2.1	1.8	2.4
50	25	2	78.0	85.0	12.9	2.1	2.0	2.7
50	25	6	84.0	84.8	13.9	1.3	3.0	3.3
70	25	4	82.5	80.6	17.9	1.5	1.9	2.8
100	25	4	88.5	77.5	21.3	1.3	2.1	3.3

[a] Polymerization conditions: [Bd] = 0.1 g/mL, [Bd]/[Ni] = 2000, toluene.
[b] Determined by FTIR.
[c] Determined by GPC.
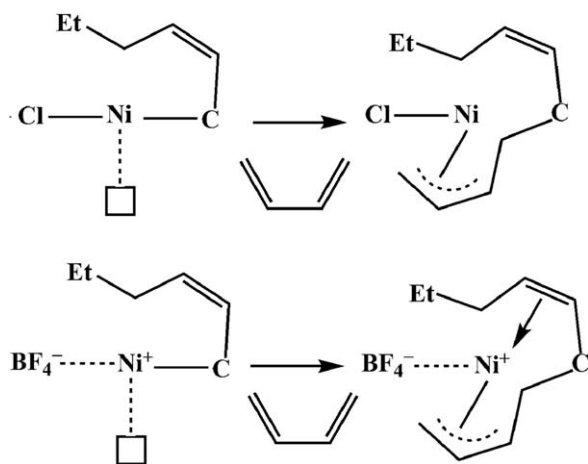
Scheme 2. The proposed polymerization mechanism for liquid butadiene polymerization with traditional nickel-based catalyst and cationic nickel-based catalyst.

CONCLUSION

In summary, a series of nickel compounds with cationic active center were successfully synthesized and used to initiate butadiene polymerization in combination with EASC. The resultant products were liquid polybutadiene ($M_w \sim 2 \times 10^4$) with a high $cis-1,4$ content (92.1%). The $cis-1,4$ selectivity in butadiene polymerization of the synthesized cationic compounds was superior to that of nickel chloride compounds. In addition, by introducing steric bulky ligands to the nickel atom, it was found that the catalyst activity increased in the following order: Terpy > BZI > Phen.

content increased correspondingly, which could be because the higher temperature facilitates anti-syn isomerization.[22] The M_w of the obtained polybutadiene was found to decrease gradually with increasing the polymerization temperature, which indicates that a higher chain transfer rate was obtained at a higher temperature.[23] As expected, the $cis-1,4$ selectivity of the catalyst was less affected by the polymerization time. As the polymerization time increased from 1 to 6 h, the M_w of the resultant polybutadiene increased from 1.8×10^4 to 3.0×10^4 without any change in polydispersit. In addition, elevation of the [Al]/[Ni] molar ratio from 50 to 100 led to a slightly decrease in $cis-1,4$ content from 81.8% to 77.5%.

Mechanism for Butadiene Polymerization

Cationic nickel-based catalysts tend to produce liquid polybutadiene with mostly the $cis-1,4$ structure. The proposed polymerization mechanisms of the traditional nickel(II) compound catalyst (**Ni-5**) and the cationic nickel(II) compound catalysts are shown in **Scheme 2**, where all ligands and anions were omitted for clarity. The polymerization occurs via two steps after the catalyst is activated by the cocatalyst. In the first step, the coordination of a butadiene monomer to the active center occurs, followed by migratory insertion of the coordinated monomer into the nickel–carbon bond. In the migratory insertion step (second step), a vacant coordination site is regenerated, which enables further chain propagation. Compared with the traditional nickel(II) compound catalyst (**Ni-5**), the cationic nickel(II) compound catalyst (**Ni-1–4**) has an active center with a very strong negative electron affinity. Therefore, the coordination and insertion rates of the butadiene monomers increase (diene is a weak Lewis base).[12,13,24,25] In addition, we speculate that the cationic nature of the nickel center (electron deficiency) would lead to an attractive force toward the C=C double bond of the penultimate monomer unit. Therefore, the polybutadiene provided by the cationic nickel-based catalyst would have a higher $cis-1,4$ content (**Ni-1** and **Ni-3**) compared with the polybutadiene prepared by the traditional catalyst (**Ni-5**).

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