

(19) (KR)
(12) (A)

(51) . Int. Cl. ⁷ (11) 2002 - 0060989
C08F 4/72 (43) 2002 07 19

(21) 10 - 2002 - 7007308
(22) 2002 06 07
2002 06 07
(86) PCT/US2000/33590 (87) WO 2001/42249
(86) 2000 12 11 (87) 2001 06 14

(54) 15

R₁ArF - ER₂

E

R

C₁ - C₂₀

, 2 R

C₂ - C₂₀R' G - C₂₀

i 0, 1 2

가

[N -

][

(

)]

,

, 15

, 15

"

(noncoordinating anion; NCA)"

EP 0 277 004

5,198,401 [Baird, Michael C. J. Am. Chem. Soc. 1994, 116, 6435 - 6436], 5,312,88
1, 5,668,234 WO 98/03558

가

5,198,401

WO 97/35893

가

()

가

(counter balancing)

5,198,401

[(L' - H)⁺]_d[(M')^{m+} Q₁ Q₂ ... Q_n]^{d-}

, L'

, H

, [(M')^{m+} Q₁ Q₂ ... Q_n]

M

,

Q_n

,

L'

N,N -

WO 97/35893

[L' - H]⁺ [BQ₄]⁻

()

,

B

+3

, Q'

C₁ - C₂₀[L' - H]⁺

(

-)

(

-)

가 H^+ , , , , EP 0 426 637

, i) 가 ii) - - 2

가

가 ,
가 가

13 가

가 ,

$$\begin{array}{ccccccc}
 [A]^- \text{ 가} & & & [L - H]^+ [A]^- & & & \\
 & L & & R_1 ArF - ER_2 & & & , \\
 & , E & & , R & & & ArF \\
 & . & & R^+ & & & \\
 & , 2 & & & & & \\
 & -C & & C_1 - C_{20} & & & \\
 & & & & & & \\
 & & & & R^+ - C_1 - C_2 & & \\
 & & & & & & \\
 & & & & & C_2 - C_{20} & , C
 \end{array}$$

$$\begin{array}{ccc}
 & \text{가} & \\
 \text{가} & \cdot \text{R}' & \text{ArF} - \text{NR}_2 \\
 & & \text{R}
 \end{array}$$

13 4 13

$[L - H]^+ [(M^+)Q_1 Q_2 \dots Q_n]^+$

$[L - H]^+$

M 13 ,

Q $[(M^+)Q_1 Q_2 \dots Q_n]^+$ ()

Q가

Q

, $[(M^+)Q_1 Q_2 \dots Q_n]^+$ 가

NCA

4 20

, 6 20

Q

$C_6 - C_{18}$

5,198,401

, 5,296,433

, 5,278,119

, 5,447,895

, 5,688,634 , 5,895,771 , WO 93/02099 , WO 97/29845 , WO 99/43717 ,

WO 99/42467 , 1999 3 3

09/261,627

WO 99/45052

Q

2 13

$[R^+; ArF - ER_2 - H]^+ [X]^-$

1 2

NCA

1

2 ()

LiCl

Q

, 5,427,991 5,939,347

pKa

11 pKa

가 가

가

1 , 2

, 13

, 5,288,677

5,427,991

, 1999 3 26

09/277,339

WO 99/50311

, WO 98/55518

NCA

WO 91/09882 , WO 93/11172 , WO 96/35726 4,463,135
5,610,115

가
가
3 11
(C₁ - C₁₀)

WO 92/00333

가 , 가
(,)

가
가
EP - A1 - 0 570 982

EP - A - 0 129 368 , 4,871,705 , 4,937,299 , 5,32
4,800 , EP - A - 0 418 044 , EP - A - 0 591 756 , WO - A - 92/00333 ,
WO - A - 94/01471 WO 97/22635

가
(bridge)
3 , 4 , 5

6

가
(
[
4
5,278,264 5,304,614]
30 , 1 5 /
N, S, O,
P, Ge, B Si

()
WO -
A - 92/00333 5,001,205 , 5,198,401 , 5,324,800 , 5,304,614 5,308,
816

[Journal of Org
anometallic Chemistry 369, 359 - 370 (1989)]

4,892,851 , 5,017,714 , 5,296,434 ,
5,278,264 , WO - A - (PCT/US92/10066) , WO - A - 93/19103 , EP - A
2 - 0 577 581 , EP - A1 - 0 578 838 [" The Influence of Aromatic Substituents on the Po
lymerization Behavior of Bridged Zirconocene Catalysts" , Spaleck, W Organometallics 1994, 13, 954 -
963] [" ansa - Zirconocene Polymerization Catalysts with Annulated Ring Ligands - Effects on Catal
ytic Activity and Polymer Chain Lengths" , Brinzinger, H Organometallics 1994, 13, 964 - 970]

가 ()
- C=C - 가

$L^A L^B L^C$ MDE

L^A M

L^B L^A

L^A L^B 14

$$\underline{L}^C_i \quad M$$

M 4 5

D E
B

D - M E - M

가,

가

가 D - M
가

E - M

56

가 가

3 11

WO 96/23010, WO 97/48735

(Gibson) [Chem. Comm., pp. 849 - 850(1998)]

8 10

가

WO 97/48735

5 10

5,502,124

5,504,049

5,851,945

5

가

1999 4 29

0

9/302243

PCT/US99/09306

4

9

가

11

가

WO 99/30822

1997 12 16

08/991,160

5,318,935

4

() 4

(D. H. McConville)

[Organometallics 1995, 14, 5478 - 5480]

가, 1 - molecules 1996, 29, 5241 - 5243]

() 4

[Macromo

가

WO 96/40805

WO 98/37109

3

1999 9 29

09/408050

PCT/US99/2

2690

2

2

가

가

가

가

[" The Search for New - Generation Olefin Polymerization Catalysts: Life Beyond Metallocenes"], [Angew. Chem. Int. Ed.38, 428 - 447(1999)]

ging)

가

(scaven

5,153,157, 5,241,025, 5,767,587 WO - A - 91/098
82, WO - A - 94/03506, WO - A - 93/14132 WO 95/07941 13 가

- n -

C₆ - C₂

0

- n -

- n -

- n -

, , , ,
 , , , ,
 가 ,

, (, , , ,)
 ,

, , , ,
 5 10 4 20,
 6 12

,
 382,638 , 5,352,749 , 5,408,017 , 5,436,304 , 5,453,471 , 5,463,999 , 5,767,
 208 WO 95/07942

, 2 20
 , 50 %
 가

1

[1]

	()
A	220
B	40
C	250
D	60
	(bar)
E	2500
F	0.1
G	500
H	1600
I	1.0
J	0.001

(50bar) 40 250
 가 C₃ - C₂₀ , , , (:)
 (100 200 PPM) 2000 3000kPa 60 160
 (0.5 1.2 %) C₂ (25 35 %) 4,543,399 , 4,588,790 , 5,028,67
 0 , 5,405,922 5,462,999 ,
 (- - - - -)
 ,
 10 1000psig(69) 6895kPa ,
 40 160 , ,
 5,001,205
 WO 96/33227 WO 97/22639 ,
 , , , , ,
 , , , , ,
 , , , , ,
 , , , , ,
 5,635,573
 5,763,556 가 1000mer (marcher)

(*ex situ*) 1
가

N - (1 -) ; N - (1 -) ; N - (2,3 -) ; N - (2,4 -)
 ; N - (2,5 -) ; N - (2 - 6 -) ; N - (2 -
 - 6 -) ; N - (3 - -) ; N - (3 -) ; N - (3 -
) ; N - (3 - -) ; N - () ; N - () ; N - ()
 ; N - () ; N - (1 -) ; N - (1 -) ; N - (2,3 -)
 ; N - (2,4 -) ; N - (2,5 -) ; N - (2 - 6 -) ; N - (3 - -) ; N - ()
 - () ; N - () ; N - () ; N - () ; N - ()
 ; N - () ; N - () ; N - () ; N - (1 -)
 ; N - (1 -) ; N - (2,3 -) ; N - (2,4 -) ; N -
 N - (2,5 -) ; N - (2 - 6 -) ; N - (3 - -) ; N - (3 -
 -) ; N - (3 -) ; N - () ; N - () ; N - ()
 ; N - () ; N - (1 -) ; N - () ; N - () ; N - (1 -)
 4 -) ; N - (2,5 -) ; N - (2 - 6 -)

13

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 - 5 -
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 (1 -
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 (N - (

, %

가

(differential refractive index: DRI)

(Mw) (Mn)
(low angle light scattering; LS)
(Waters) 150

PC Gel

B

- 3

1.2.4 -

(135)
[" Liqu

id Chromatography of Plastics and Related Materials III" J. Cazes current regime Ed., Marcel Dekker, 1981, page 207] . (spreading) , [: National Bureau of Standards Polyethylene 1475] Mw/Mn 0.2 .

1

2

$\text{C}_6\text{F}_5 - \text{N}(\text{CH}_2\text{CH}_2)_2\text{HCl}$: $\text{C}_6\text{F}_5 - \text{N}(\text{CH}_2\text{CH}_2)_2$ (1.55g) (100Mℓ) HCl 가 . HCl
 | 가 가 . HCl 가 . HCl
 가 . HCl 가 . HCl
 .
 : = 1.48g, 82%. ^1H NMR(CDCl_3 , 25) : 12.9(s, 1H), 3.71(m, 4H), 2.17(m, 4H).

3

[C₆F₅ - N(CH₂CH₂)₂(H)][(C₆F₅)₄B] : [Li()₂][(C₆F₅)₄B] (1.52g) (100Mℓ)
 C₆F₅ - N(CH₂CH₂)₂HCl(0.5g) . 가
 1 . , LiCl .
 10Mℓ 가 , 15 .
 . : = 1.480g. ¹H NMR(CD₂Cl₂, 25 ℃): 7.95(bs, 1H),
 4.32(bt, 2H), 3.94(bt, 2H), 2.68(bt, 2H), 2.43(bt, 2H). ¹⁹F NMR(CD₂Cl₂, 25 ℃): -133.8(m, 8F), -145.2(m, 1F), -145.5(m, 2F), -155.3(m, 2F), -163.9(t, 4F), -168.0(m, 8F).

0.5L 500psig 150
() ,
가 ,
가 60 , (125Mℓ)
TIBAL (20Mℓ, 25 %) 가 (125Mℓ)
가 60 가 (40Mℓ)
가 ,
16 , 60 ,
가

2 (H)

(B)

[2]

^a	(g)	()	(g/mmol × m in)	Mw	Mn	Mw/Mn
A()	16.63	15	1288	191,751	112,002	1.77
A()	11.56	15	896	324,379	182,802	1.77
			1092			
B	24.58	10	2583	252,314	223,296	1.77
B	27.86	10	2940	223,296	123,895	1.80
			2762			

(57)

1.

114

$$[R'_iArF - ER_2 - H]^+ [An]^-$$

,

ArF

,

E

C₁ - C₂₀

, 2 R

[XII] .

2.

1

[An]⁻ 가

• 100 •

■

3.

1

ArF가

3

, 3

4.

1 ,

- R₂ - γ C₂ - C₂₀

5.

1 4 ,

- Eγ

6.

1 ,

iγ 1 , Ar R'γ Ar

7.

(a) - - - (b) , ,

R ArF - ER₂

,

ArF ,

E ,

R C₁ - C₂₀, 2 R
C₂ - C₂₀,

R' G - C₂₀,

i 0, 1 2 .

8.

7 ,

ArFγ , , , , , , 3
3

9.

7 ,

- R₂ - γ C₂ - C₂₀

10.

6 9

E가

11.

1

i가 1 , Ar R'가 Ar

12.

1

$$[\text{ArF} - \text{NR}_2 - \text{H}]^+ [\text{An}]^-$$

,

ArF

R $C_1 - C_{20}$

[An]⁻

13.

13

ArF가 3 . , , , , , 3

14.

12 13 ,

15.

14 ,

ArF - NR₂ 가 N -

16.

(a) (i)

(ii)

가

가

(b) (i) - - 2 [, , , ,
 , 3 3] (ii) 13

17.

16

[R₁ArF - ER₂ - H]⁺ [(M⁺)Q₁Q₂...Q_n]⁻

ArF

E ,
 R C₁ - C₂₀ , 2 R
 C₂ - C₂₀ ,

R' G - C₂₀ ,

i 0, 1 2 ,

M' 13 ,

n 1 ,

Q M , [(M⁺)Q₁Q₂...Q_n]⁻ 가

18.

17 ,

Q 가 [, ,
]

19.

18 ,

Q 가 (pendant) 5 20

20.

18 ,

Q 가 .

21.

17 18 , , N - - , N - , N - 3
 R ; ArF - ER₂ 가 N - , N - , N - , N - , N - 3
 , N - , N - , N - , N - , N - , N -
 , N - - , N - , N - 3 , N - , N -
 , N - , N - 3 , N - , N - , N -
 , N - 3 , N - , N - , N -
 N - 3 .

22.

16 20 , ,
 가 3 11 .

23.

21 , ,
 가 3 11 .

24.

22 , ,
 3 6 :
 .

L^A L^B L^C MDE

,
 L^A M

,
 L^B M

, L^A L^B 14 ,
 .

L^C M [, i 0 3],
 .

M 3 6 ,
 .

D E M , , L^A L^B , D E
 M M 가 , 가 ,
 M - E .

25.

24

M, $L^B \models M$

26.

24

M, $L^B \models M$

27.

(a) ; \models

(b) - - 2 ;

(c) 13

28.

16 20 27

29.

(a) ; \models

(b) (i) - - 2 (ii) 13

30.

29 ,

Q가 ,

31.

29 30 ,

가 3 11

32.

29 30 ,

30 300 0 2000bar , , ,

33.

32

, ,

34.

13

2

35.

- - - 2

13

36.

- - - 2

13