Ethylene Copolymerization with Vinyl Naphthalene, Vinyl Biphenyl Using Aryloxo-Modified Half-Titanocene Catalysts

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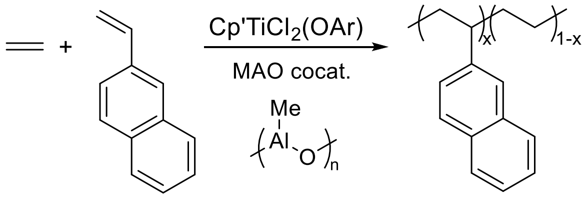
Abstract: Ethylene copolymerization with 2-vinyl naphthalene (VN) proceeded with efficient VN incorporation in the presence of (^{t}BuC$_5$H$_4$)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) – MAO catalyst, affording high molecular weight copolymers with uniform compositions, whereas the other Cp analogues [Cp' = 1,2,4-Me$_3$C$_5$H$_3$ (**2**), indenyl, Cp* in place of ^{t}BuC$_5$H$_4$] showed negligible VN incorporation or afforded polymers with two compositions. Complex **1** showed more efficient VN incorporation than reported [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ conducted under the same conditions; the VN content increased upon increasing the initial VN concentration charged without decrease in the M_n values. Efficient ethylene copolymerization with 4-vinylbiphenyl proceeded by **1**,**2** – MAO catalysts affording high molecular weight polymers with uniform compositions.

Keywords: Olefin Polymerization, Half-titanocene, Ethylene/Vinyl-aromatics Copolymerization.

1. Introduction

Transition metal catalyzed olefin polymerization is a core technology in chemical industry for production of polyolefins that covers almost 50 % of commercialized synthetic polymers. Synthesis of new polymers that cannot be (or are very difficult to be) prepared by ordinary catalysts has been considered as an important subject in this research field.[1,2] Ethylene/styrene copolymers, which cannot be prepared by free radical or ordinary Ziegler-Natta processes, are interesting materials, because the introduction of styrene results in drastic changes in both the viscoelastic behavior and thermo-mechanical properties of the material.[3] Although there are many reports for ethylene/styrene copolymerization,[4] examples for the copolymerization with the other aromatic vinyl monomers have been limited so far.[5] Since the resultant copolymers should have promising applications as the functional materials, we thus herein demonstrate that an efficient 2-vinyl naphthalene (VN) incorporation has been achieved in the ethylene copolymerization by using half-titanocene catalyst, (^{t}BuC$_5$H$_4$)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**).[6]



Scheme 1. Ethylene/2-vinyl naphthalene copolymerization.

2. Experimental

All experiments were carried out under nitrogen atmosphere in a drybox. Half-titanocene complexes, Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$ C$_6$H$_3$) [Cp' = ^{t}BuC$_5$H$_4$ (**1**), 1,2,4-Me$_3$C$_5$H$_2$ (**2**), indenyl (**3**), Cp* (**4**)] were prepared according to the published method. Ethylene copolymerizations were conducted in toluene in the presence of d-MAO prepared by removing toluene and AlMe$_3$ from the commercially available methylaluminoxane (TMAO, Tosoh Finechem Co.). Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (GPC) in *o*-dichlorobenzene at 140 °C, and the microstructural analysis was explored by ^{13}C NMR spectra.

3. Results and discussion

Table 1 summarizes results in ethylene polymerization in the presence of 2-vinyl naphthalene (VN) using a series of Cp'Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$) – d-MAO catalysts. The results using linked half-titanocene, [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC),[5] are also placed for comparison. It turned out that the ^{t}BuC$_5$H$_4$ analogue, (^{t}BuC$_5$H$_4$)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**), afforded high molecular weight copolymers with uniform compositions confirmed by DSC (Differential scanning calorimetry) thermograms. In contrast, both 1,2,4-Me$_3$C$_5$H$_2$ (**2**) and the indenyl analogues (**3**) afforded a mixture of the copolymer and polyethylene (confirmed by DSC thermograms), the Cp* analogue (**4**) showed negligible VN incorporation (confirmed by DSC thermograms). Therefore, **1** only afforded the copolymers with uniform compositions. It also turned out that the VN content in the resultant copolymer by **1** increased upon increasing the VN concentration charged without significant decrease in the M_n values. The activity increased at higher ethylene pressure (from 4 to 6 atm) with decrease in the VN content in the copolymer.

Table 1. Copolymerization of ethylene with 2-vinly naphthalene (VN) using Cp'$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) [Cp' = $^tBuC_5H_4$ (**1**), 1,2,4-$Me_3C_5H_2$ (**2**), indenyl (**3**), Cp* (**4**)], [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC) – MAO catalysts (toluene, 25 ºC).[a]

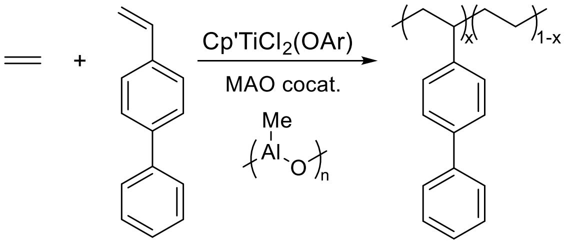
cat. / µmol	ethylene / atm	VN[b] / M	activity[c]	M_n[d] $\times10^{-4}$	M_w/ M_n[d]	cont.[e] / mol%	T_g (T_m)[f]
1 (2.0)	4	0.30	689	4.36	1.39	17.0	7
1 (2.0)	4	0.50	393	3.33	1.35	22.4	25
1 (2.0)	6	0.50	626	4.02	1.42		11
1 (2.0)	4	0.87	249	2.73	1.33	28.0	48
1 (2.0)	6	0.87	399	3.15	1.37		35
2 (2.0)	4	0.50	537	4.00	1.39	-	26 (123)
2 (2.0)	4	0.87	442	3.76	1.28	-	44 (123)
3 (2.0)	4	0.50	2940	6.05	1.52	-	-8 (124)
3 (2.0)	4	0.87	2240	4.52	1.78	-	11 (123)
4 (2.0)	4	0.50	59.1	2.75	1.28	trace	(133)
4 (2.0)	4	0.87	15.9	2.17	1.26	trace	(131)
CGC (2.0)	4	0.50	298	9.14	1.86	4.7	(103)
CGC (2.0)	4	0.87	274	-	-	8.6	(91)

[a]Conditions: Toluene 10 mL, 25 ºC, 10 min, MAO 3.0 mmol. [b]Initial VN concentration in mmol/mL. [c]Activity in kg-polymer/mol-Ti·h. [d]GPC data in *o*-dichloro benzene *vs* polystyrene standards. [e]VN content estimated by ^1H NMR spectra. [f]By DSC thermogram.

It also turned out that linked half-titanocene (CGC)[5] showed less VN incorporation under the same conditions. The cyclohexyl (Cy) analogue, [$Me_2Si(C_5Me_4)(NCy)]TiCl_2$, which showed better styrene incorporation in the ethylene copolymerization,[7] afforded a mixture of the copolymer and polyethylene. Therefore, **1** showed the most efficient VN incorporations among these catalysts.

Microstructural analysis for poly(ethylene-*co*-VN)s prepared by **1** reveals that the resultant polymer possesses head-to-tail VN repeating units in addition to isolated and alternating VN incorporations; resonances ascribed to head-to-head VN incorporation were also observed. The observed characteristics are similar to those in poly(ethylene-*co*-styrene)s prepared by **1** – MAO catalyst.[8]

Moreover, it also turned out that efficient ethylene copolymerization with 4-vinyl biphenyl proceeded by using **1**,**2** – MAO catalysts (Scheme 2), affording the copolymers with unimodal molecular weight distributions and with uniform compositions. More details will be introduced in the conference.



Scheme 2. Ethylene/4-vinyl biphenyl copolymerization.

4. Conclusions

We have shown that ethylene copolymerization of with 2-vinyl naphthalene (VN) proceeded with efficient VN incorporation in the presence of ($^tBuC_5H_4$)Ti(O-2,6-$^iPr_2C_6H_3$) (**1**) – MAO catalyst, affording the high molecular weight copolymers with uniform molecular weight distributions as well as compositions. As far as we know, this is the first demonstration of an efficient VN incorporation in the ethylene copolymerization that cannot be achieved by ordinary catalysts. The catalysts also showed efficient 4-vinyl biphenyl incorporation in the ethylene copolymerization with high catalytic activity.

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