Efficient Cyclooctene Incorporation in Ethylene Copolymerization Using Half-Titanocene Catalysts

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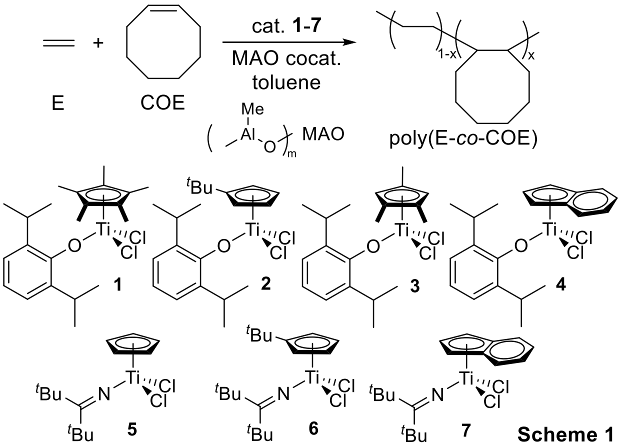
Abstract: Ethylene/*cis*-cyclooctene (COE) copolymerizations using a series of half-titanocene catalysts, Cp'$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) [Cp' = Cp* (**1**), $^tBuC_5H_4$, 1,2,4-$Me_3C_5H_2$, indenyl], Cp'$TiCl_2$(N=C$^tBu_2$) [Cp' = Cp, $^tBuC_5H_4$, indenyl], have been explored in the presence of MAO cocatalyst. Complex **1** exhibited high catalytic activity and efficient COE incorporation, and the resultant polymers were amorphous materials and the glass transition temperature was dependent upon the COE content. It turned out that the copolymerization behaviors were affected not only by the substituents on the cyclopentadienyl group, but also by the anionic donor ligands.

Keywords: Olefin Polymerization, Half-titanocene, Cyclic Olefin Copolymers.

1. Introduction

Transition metal catalyzed olefin polymerization is a core technology for production of polyolefins that covers almost 50 % production of commercialized synthetic polymers in the world. In this research field, considerable attention has been paid recently to the synthesis of new polymers that cannot be (or are very difficult to be) prepared by ordinary catalysts such as Ziegler-Natta, ordinary metallocene, linked-half metallocene (so called constrained geometry, CGC), and so called non-metallocene catalysts.[1,2] Certain cyclic olefin (co)polymers are amorphous materials, highly transparent in the UV-vis region, endowed with high humidity-, and thermal-resistance, high glass transition temperature (T_g).[3-7] They are mostly prepared by coordination copolymerization of ethylene with cyclic olefins (called COC), or ring-opening metathesis polymerization of multi-cyclic olefins and subsequent hydrogenation (called COP). The copolymerization approach is promising in terms of modification of the compositions, microstructures.[3-7] There have been may reports for the ethylene copolymerization with norbornene,[3-7] and reports on the copolymerization with cyclopentene[8,9] have also been known. In contrast, reports for the copolymerization with cyclohexene[10,11] and cyclooctene (COE)[12] still have been limited so far. We thus herein report that COE has been incorporated rather efficiently in the ethylene copolymerization especially using aryloxo-modified half-titanocene catalyst (Scheme 1).[13]



Scheme 1

2. Experimental

All experiments were carried out under nitrogen atmosphere in a drybox. Half-titanocene complexes, Cp'$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) [Cp' = Cp* (**1**), $^tBuC_5H_4$ (**2**), 1,2,4-$Me_3C_5H_2$ (**3**), indenyl (**4**)], Cp'$TiCl_2$(N=C$^tBu_2$) [Cp' = Cp (**5**), $^tBuC_5H_4$ (**6**), indenyl (**7**)] 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 MAO (TMAO, Tosoh Finechem Co.). Molecular weights and their distributions for the resultant polymers were measured by gel permeation chromatography (GPC) in o-dichlorobenzene at 140 °C, and their microstructural analysis was explored by ^{13}C NMR spectra.

3. Results and discussion

Table 1 summarizes results in ethylene (E) copolymerization with *cis*-cyclooctene (COE) using a series of half-titanocenes (**1**-**7**) in the presence of MAO. It turned out that the ketimide-modified half-titanocenes (**5**-**7**) exhibited the high activities affording high molecular weight copolymers with unimodal molecular weight distributions, and their compositions were uniform confirmed by DSC (Differential scanning calorimetry) thermograms. Both the Cp (**5**) and $^{t}BuC_5H_4$ (**6**) analogues showed better COE incorporations than the indenyl analogue (**7**). The activities increased upon increasing ethylene pressure with decrease in the COE content (estimated by ^{13}C NMR spectra and/or DSC thermograms).

It should be noted that the Cp*-aryloxo analogue (**1**) exhibited moderate catalytic activity with efficient COE incorporation in the copolymerization, affording the copolymers with uniform molecular weight distributions and compositions. In contrast, the other aryloxo-modified half-titanocenes (**2**-**4**) afforded low molecular weight polymers, and the compositions were not uniform. Therefore, only **1** showed efficient COE incorporation among these complex catalysts (**1**-**7**). Both the activity and the COE content in the copolymer were affected by the COE concentration and ethylene pressure employed, and the M_n value was not strongly affected by the Al/Ti molar ratios. Attempts for the copolymerizations using $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ afforded a mixture of homo and copolymers, and the similar attempt by Cp_2ZrCl_2 afforded polyethylene without (or with negligible) COE incorporation.

^{13}C NMR spectra in the resultant poly(E-*co*-COE)s revealed that COE was incorporated in 1,2-insertion mode and resonances ascribed to 1,3- (due to isomerization before incorporation of subsequent monomers) were not observed. The microstructure of the copolymers prepared by **1** – MAO catalysts possessed resonances ascribed to isolated and alternating COE insertions. However, it seemed difficult to prepare the copolymer with high COE content even by **1** under high COE concentration conditions. More details will be introduced in the conference.

Table 1. Copolymerization of ethylene (E) with *cis*-cyclooctene (COE) by half-titanocenes (**1**-**7**) – MAO catalysts.[a]

cat. (μmol)	ethylene / atm	COE / M	activity[b]	M_n[c] ×10^{-4}	M_w/ M_n[c]	cont.[d] / mol%	T_g (T_m)[e] / °C
1 (0.5)	2	5.0	1660	23.9	1.57	28.0	32
1 (0.5)	4	2.5	6850	86.3	1.89	16.1	-15 (32)
2 (1.5)	2	5.0	231	2.07	1.61	-	44 (127)
3 (1.5)	2	5.0	251	4.17	1.31	-	22 (125)
4 (1.0)	2	5.0	602	0.57	1.18	-	18 (125)
5 (0.03)	2	7.5	29700	121	2.3	20.2	-5
6 (0.02)	2	7.5	35800	254	2.15	20.4	-5.5
7 (0.01)	4	5.0	110000	179	2.05	2.6	(102)
7 (0.01)	2	7.5	59300	105	2.3	7.2	(76)

[a] Conditions: toluene+COE total 10 mL, 25 °C, 10 min, MAO 3.0 mmol. [b] Activity in kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [d] COE content (mol%) estimated by ^{13}C NMR spectra. [e] By DSC thermograms.

4. Conclusions

We have shown that the aryloxo-modified half-titanocene, $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**1**), incorporated *cis*-cyclooctene (COE) efficiently in the ethylene copolymerization in the presence of MAO cocatalyst. It turned out that COE incorporation was affected not only by the substituents on the cyclopentadienyl group, but also by the anionic donor ligands as well as basic catalyst structures. The resultant copolymers are promising amorphous materials, and the glass transition temperature was dependent upon the COE content.

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