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Living Copolymerization of Ethylene with Dicyclopentadiene Using Titanium Catalyst: Formation of Well-Defined Polyethylene-*block*-poly(ethylene-*co*-dicyclopentadiene)s and Their Transformation into Novel Polyolefin-*block*-(functional polyolefin)s

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Living olefin polymerization enables consecutive enchainment of monomer units without termination. Therefore, it can be used to prepare precisely controlled polymers with desired microstructures such as monodisperse polymers, end-functionalized polymers, and block copolymers, all of which are expected to display new or enhanced properties and thus expanded utilities.[1] Recently, it has been reported that several transition metal catalysts can mediate the living coordination polymerization of ethylene, propylene, higher α-olefins, α,ω-nonconjugated dienes, and cyclic olefins.[2,3] However, the syntheses of the ordered copolymers which have either block or alternating sequences, or functional diblock structures, are remaining challenges in transition metal catalyzed living coordination polymerization. Novel polyolefin chain architectures, such as diblock copolymers with semicrystalline PE block and amorphous poly(ethylene-*alt*-cyclic olefin) block, have tremendous potential in various applications since their special properties resulted from their unique structure features. Developing functionalized polyolefin block copolymers containing covalently connected polyolefin and functional polymer blocks is one of extremely attractive recent interests in the living coordination polymerization field.[4] Chung's "reactive polyolefin intermediate" approach has been proved as an effective and facile method of functionalization of polyolefins.[4b] Therefore, the combination of this approach with the living coordination polymerization will be a great breakthrough in the preparation of precisely controlled block copolymers and the well-defined functionalized block polyolefin.

Among "reactive commoners", dicyclopentadiene (DCPD) is a promising and representative cyclic diene, which contains both one norbornene unit and one cyclopentene unit, and is industrially available at a low price.[5a] However, the catalysts suitable for the regioselective copolymerization of DCPD with ethylene or α-olefin are scarce. Usually, titanium catalysts can copolymerize DCPD with alkene, but the reaction is not regioselectivity and cross-linking can not be controlled.[5b] The one successful example is the scandium catalysts reported by Hou and Li, which can incorporate DCPD into polymer chains by enchaining the norbornene unit, and produce alternating E-DCPD copolymers.[5a,5c] If DCPD selectively participates in the copolymerization with ethylene, the remaining double bonds in the resulting copolymers can be easily converted into functional groups and give a broad range of new functionalized polymer with improved performances. Herein, we report the living and regioregular copolymerization of ethylene with DCPD using titanium complex **1** activated by MMAO (Scheme 1), an effective catalyst previously reported for the synthesis of the block copolymers from ethylene and NBE or CPE.[2g,2h] Considering the activities of the titanium catalysts bearing phenoxyimine ligands increase with the number of fluorine atoms, and those with fluorine atom(s) adjacent to the imine nitrogen can promote living polymerization under similar conditions,[5d,5e] we also investigate the copolymerization mediated by fluorinated bis(β-enaminoketonato) titanium complexes **2**−**4**, as a comparison.

Upon treatment with MMAO, complexes **1**−**4** were found to be active for the copolymerization of ethylene with DCPD. At 25 °C in toluene under atmospheric pressure, these activated species, especially **1/MMAO**, proved to be exceptional catalysts for the copolymerization of ethylene and DCPD with regard to both activity and regioselectivity. The typical results including polymer yields, catalytic activities, number-average molecular weights (M_ns), polydispersity indices, and DCPD incorporations are summarized in Table 1.

The DCPD incorporation of the copolymer catalyzed by complex 1 increased with the DCPD content in the feed, and easily reached 46.4−47.7 mol % (Table 1, runs 3−9) although DCPD homopolymerization did not occur under the same conditions,[2g] which is similar to the case of the copolymerization of ethylene with NBE by the same catalyst. Compared with the case of complex **1**, DCPD incorporations of the copolymers catalyzed by complexes **2**−**4** were lower, and the same trend was also observed for catalytic activity. This result might be caused by the steric effect of *o*-fluorine atom(s) of the *N*-aryl moieties of the ligand hindering bulky DCPD from accessing the titanium center.

As shown in Figure 1, microstructural analysis using ^{13}C NMR technique reveal that the ethylene/DCPD copolymers only contain unreacted CPE units but no unreacted NBE units, suggesting that the copolymerization proceed through enchainment of NBE ring, which is consistent with the fact that the present catalysts are more active toward ethylene/NBE copolymerization than toward ethylene/CPE copolymerization. The DCPD incorporation can be adjusted within a wide range by changing the reaction conditions such as the DCPD content in the feed, but the manner of the regioselective insertion of DCPD remains unchanged. All of the inner double bonds of CPE units were retained near the backbone of the copolymers, and there is no evidence of cross-linking. The copolymers (runs 3−9) all showed similar ^{13}C and ^{1}H NMR spectra and could be assigned to alternating ethylene/DCPD copolymers.[5,6]

Activation of complex **1** with MMAO as a cocatalyst affords ethylene/DCPD copolymers with extremely narrow molecular weight distribution (M_w/M_n about 1.10) under the variational conditions. As shown in Figure 2 and 3(a), MW increased linearly with polymer yield, and M_w/M_n values were consistently low for all the copolymers. As observed (runs 10−12), the copolymerization catalyzed by complexes **2**−**4** also show living feature under the similar condition, and ethylene/DCPD copolymers displayed extremely narrow distribution too. Compared with the case of complex **1**, the molecular weight distributions of the copolymers obtained by complexes **2**−**4** were slight narrower due to the effect of *ortho*-fluorine atom(s) of N-aryl moieties in the ligands.[5d,5e]

Another attractive feature of these catalysts for living polymerizations is their ability to produce well-defined block copolymers via sequential monomer addition. Here, we synthesized

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Scheme 1. Copolymerization of Ethylene with Dicyclopentadiene Using Titanium Catalysts 1−4

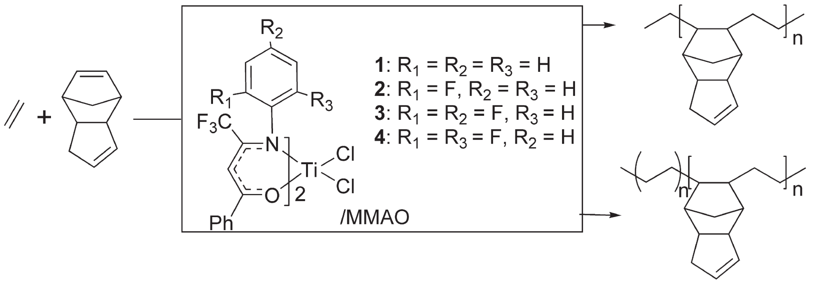

Table 1. Copolymerization of Ethylene and Dicyclopentadiene Using Titanium Catalysts 1-4 [a]

run	catalyst	DCPD (mmol)	time (min)	yield (g)	activity[b]	DCPD incorp.[c](mol %)	M_n[d]	M_w/M_n[d]
1	**1**	2	5	0.31	1.24	9.1	130	1.11
2	**1**	10	5	0.37	1.48	34.5	110	1.07
3	**1**	20	1	0.08	1.60	46.8	25	1.04
4	**1**	20	3	0.28	1.87	47.2	77	1.05
5	**1**	20	5	0.43	1.72	46.7	102	1.07
6	**1**	20	8	0.58	1.45	47.2	155	1.07
7	**1**	20	10	0.68	1.36	47.5	179	1.10
8	**1**	20	15	0.83	1.11	46.4	225	1.13
9	**1**	20	20	0.96	0.96	47.7	284	1.14
10	**2**	20	5	0.02	0.08	25.0	18	1.05
11	**3**	20	5	0.02	0.08	29.4	13	1.06
12	**4**	20	10	0.02	0.04	25.2	27	1.05
13	**1**	0	3	0.16	1.07	0	63	1.12
14[e]	**1**	20	6	0.38	1.27	47.0[f]	139	1.14
15[e]	**1**	20	8	0.48	1.20	47.0[f]	161	1.17

[a] Conditions: catalyst 3 μmol, ethylene 1 atm, Al/Ti(molar ratio) = 2000, V_{total} = 80 mL, T = 25 °C. [b] Activity: 10^6 g polymer/mol_{Ti}·h. [c] DCPD incorporation established by ^{13}C NMR spectra. [d] Number-average molecular weight (kg/mol) and polydispersity index were determined by GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ vs polystyrene standards. [e] After reaction with ethylene for 3 min, 20 mmol of DCPD was added and reacted for 3 (run 14) or 5 (run 15) min, respectively. [f] DCPD incorporation of the second block established by ^1H NMR spectra.

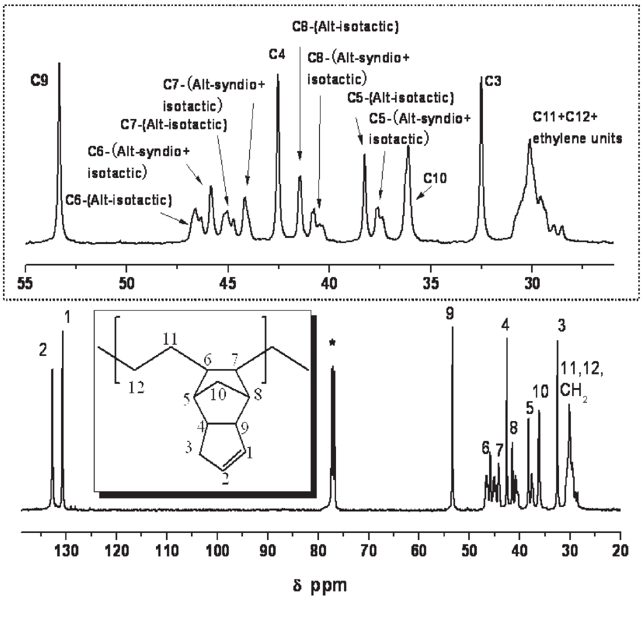

Figure 1. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) for poly(E-*co*-DCPD) (run 4, DCPD content = 47.2 mol %) prepared by catalyst **1**.

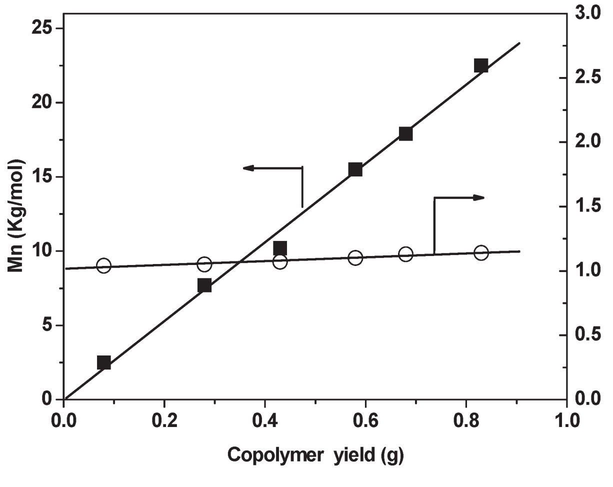

Figure 2. Plots of M_n (■) and polydispersity index (○) as a function of yield using **1**/MMAO at 25 °C, determined by GPC at 150 °C.

novel polyethylene-*block*-poly(ethylene-*alt*-DCPD) diblock copolymers with a semicrystalline PE block and an amorphous poly (ethylene-*alt*-DCPD) block using catalyst **1** (run14, 15).

As presented in Figure 3(b), both the initial PE block (M_n = 63 kg/mol) and the final diblock copolymer (M_n = 139 kg/mol) showed low M_w/M_n values (1.14 and 1.17, respectively). The DCPD incorporation of the second block is about 47 mol % determined by ^1H NMR. Atomic force microscopy (AFM) and transmission electron micrograph (TEM) characterization of the diblock copolymers runs 14 and 15 demonstrate that they are microphase-separated,[6] thus further confirming the block architecture in scheme 1, at the same time, and also demonstrate the high potential of the block copolymer as a new material composed of semicrystalline polyethylene and amorphous poly(ethylene-*alt*-DCPD) that are chemically linked.

The most attractive feature of the resultant ethylene/DCPD diblock copolymers is their unique structure, in which abundant pendant reactive C═C double bonds of the second block can be readily transformed into various functional groups such as epoxy,

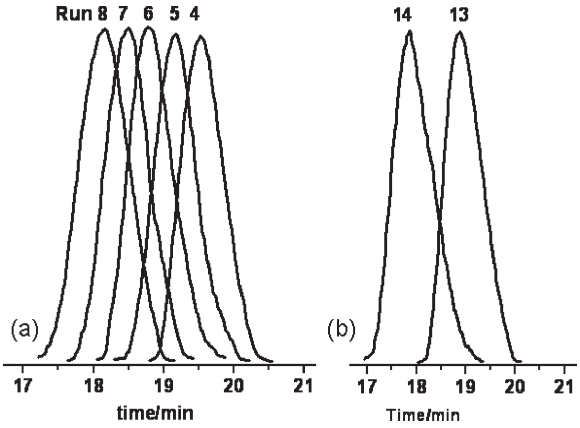

Figure 3. GPC profiles of (a) E/DCPD copolymer: (4) 3 min, M_n 77 K, PDI 1.05; (5) 5 min, 102 K, 1.07; (6) 8 min, 155 K, 1.07; (7) 10 min, 179 K, 1.10; (8) 15 min, 225 K, 1.13; (b) PE (run 13, 63 K, 1.12) and the block copolymer (run 14, 139K, 1.14) obtained by catalyst **1**/MMAO.

hydroxyl, and amino groups, thus the novel diblock copolymer with nonfunctional-*block*-functional feature can be easily created. This unique approach for the preparation of functional diblock copolymers was easily to control and enabled the synthesis of functional polyolefins with narrow distributed and well-defined structures. For instance, we demonstrated the preparation of diblock dual-functional copolymers containing epoxy or hydroxyl groups in the functional block. The epoxidation of the copolymers can be easily achieved by using *m*-chloroperbenzoic acid as an oxidant. The inner olefinic groups were completely converted into epoxy groups at 50 °C in toluene. Benefiting from Chung's approach for terminal olefins,[7] the hydroboration of the inner double bonds was successfully achieved by treating with 9-borabicyclononane (9-BBN) and subsequently oxidated into the hydroxyl groups. Therefore, novel block copolymers with unprecedented structures were obtained via this facile way.

These functional diblock copolymers are attractive and promising in the field of polyolefin functionalization. The high efficacy of the transforming reactions must be due to the high surface area of the reacting sites, despite the some copolymers were suspended in the solvent during the functional reactions. FT-IR spectra further demonstrated that the new epoxidated or hydroxylated copolymers were successfully obtained.[6] These dual-functional diblock copolymers are fascinating and will have potential use in the functional polyolefin field.

In summary, the present report serves to unequivocally establish, to the best of our knowledge, the first demonstration of highly efficient living ethylene/DCPD copolymerisation using a series of titanium complexes bearing two trifluoromethyl-containing enaminoketonato chelate ligands activated with MMAO. The catalyst systems can produce high molecular weight copolymers with narrow molecular weight distribution ($M_n > 200$ kg/mol, $M_w/M_n < 1.15$) and well-defined block copolymers from ethylene and DCPD. By varying the reaction conditions such as the monomer feed concentrations, the composition of the copolymers can be controlled within a wide range. New diblock copolymer with both block and alternate structure was obtained under the mild conditions, and served as double bond containing "reactive intermediate" in the subsequent functionalization, in which novel diblock copolymers with nonfunctional-*block*-functional feature were successfully prepared. Diblock copolymers with different compositions and various functional structures of the dual-functional diblock copolymers are expected to be created in the near future.

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Supporting Information Available: Text giving general experimental procedures and figures showing selected ^{1}H NMR, ^{13}C NMR, and FT-IR spectra as well as AFM and TEM characterization for the resultant (co)polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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