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Efficient, Regioselective Copolymerization of Ethylene with Cyclopentadiene by the Titanium Complexes Bearing Two β-Enaminoketonato Ligands

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Introduction. Precise control over functional product structure is an essential requirement for designing and synthesizing polyolefins because the structure of the resultant macromolecule is intimately linked to its material properties, which ultimately determines the potential applications of the polymeric material.[1] The syntheses of the polyolefins bearing pendant double bonds via the copolymerization of olefin with diene have been attracting increasing interest because the pendant double bonds can be easily converted into functional groups and give a broad range of new functionalized polymers with improved performances.[2] However, the approaches of the direct copolymerization of ethylene with aromatic diene or linear diene often face difficulties owing to catalyst poison or cross-linking. In contrast, cyclic dienes are catalyst-innocuous and not easily cross-linking during the polymerization due to their strained structure, unlike aromatic dienes and acyclicdienes.[3] There have been several reports concerning the controlled copolymerization of ethylene with strained cyclicdienes such as dicyclopentadiene (DCPD),[3d,e] 1,3-cyclohexadiene,[3f,g] and norbornadiene.[4] Cyclopentadiene (CPD) is one of the most representative and industrially available cyclic conjugated dienes, and its copolymer might be a promising and attractive candidate for new hydrocarbon−polymeric materials with rigid cyclic units. However, the effective, regioselective copolymerization of ethylene or α-olefin with CPD has never been realized. It is very difficult to copolymerize ethylene or α-olefin with CPD since ethylene and α-olefin trend to polymerize by a coordinating mechanism, while CPD is easily dimerized or polymerized via a cationic mechanism.[5] Although the classical metallocene catalyst Et[Ind]$_2$ZrCl$_2$ and constrained-geometry catalyst (CGC) successfully copolymerized ethylene and CPD, CPD incorporation was limited, and the structures of the resultant copolymers were uncontrollable by the fact that CPD inserted into polymer chain via 1,2- and 1,4-insertion and even DCPD (dimer of CPD) inserted polymer chain via 1,2-insertion.[6] Evidently, the 1,2- and 1,4-insertion of CPD and 1,2-insertion of DCPD are not easily adjusted by these catalysts. Well then, can CPD copolymerize with ethylene via exclusively insertion manner, 1,2- or 1,4-insertion, into a polymer chain by transition metal catalysis via a controlled way? We thus focused on this challenge, though previous catalysts favor an uncontrollable way. Herein, we report the new breakthrough of achieving the precise controllable copolymerization of ethylene with CPD.

Bis(β-enaminoketonato) titanium complexes **1a**−**c** [PhN=C(R$_2$)CHC(R$_1$)O]$_2$TiCl$_2$ (**1a**: R$_1$ = CF$_3$, R$_2$ = CH$_3$, **1b**: R$_1$ = tBu, R$_2$ = CF$_3$, **1c**: R$_1$ = Ph, R$_2$ = CF$_3$) are chosen, for they display excellent ability to polymerize not only ethylene but also ethylene with strained cycloolefins, such as norbornene and cyclopentene, giving polymers with high molecular weight.[7] We explored their copolymerization behaviors toward ethylene and CPD. Metallocene catalyst Et[Ind]$_2$ZrCl$_2$ was also chosen for comparison (Scheme 1a).[6b] The titanium complexes activated with modified methylaluminoxane (MMAO) display unprecedented catalytic performance in excellent regioselectivity and copolymerization ability, which affords the first example of the incorporation of CPD into polyethylene chain via 1,2-insertion exclusively.

Results and Discussion. The typical results of the copolymerizations are summarized in Table 1. Note that all three complexes can copolymerize ethylene with CPD, affording the copolymers with different molecular weight (MW) and unimodal molecular weight distributions (MWDs). The incorporation and regioselectivity of the conjugated cyclic diene are estimated by ^{1}H and ^{13}C NMR and distortionless enhancement of polarization transfer NMR (dept) and C−H COSY spectra.[8,9] The data in Table 1 indicate that the reaction conditions, such as reaction temperature and comonomer concentration, considerably influence ethylene/CPD copolymerization. Obviously, CPD incorporation and MW of the copolymers were affected by CPD concentration, catalyst structure, and reaction temperature, while the regioselectivity never changed. As observed, increasing CPD concentration can enhance CPD incorporation but decrease the MW of the copolymers. Higher reaction temperature is propitious to increasing catalytic activity and CPD incorporation as well as the MW of the copolymers (entries 2 vs 3 and entries 11 vs 12). The data in Table 1 also indicate that catalytic activity, CPD incorporation, and the MW of the copolymer were significantly influenced by catalyst structure. Under the same polymerization condition, catalyst **1a**, with the least steric hindrance, displays the highest activities and yields the copolymers with the highest CPD incorporation. The enhancement of the catalytic activity and the CPD incorporation may be ascribed to the wider coordination space due to the introduction of the

Scheme 1. Ethylene/CPD Copolymerization and Resultant Copolymer Structure (a) and the Bromination of the 1,2- and 1,4-Insertion Ethylene/CPD Copolymer (b)

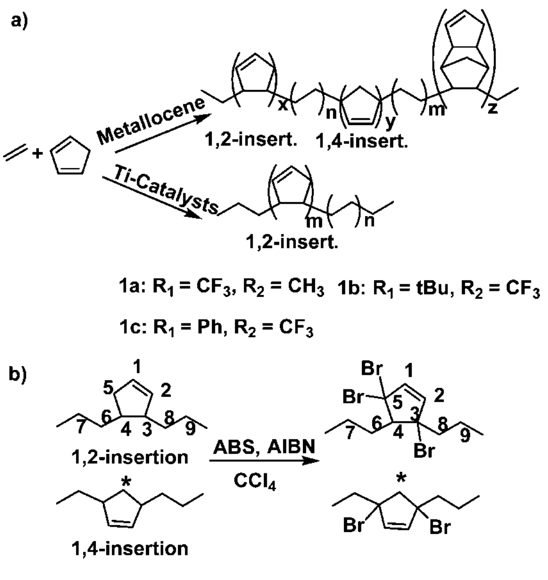

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Table 1. Copolymerization of Ethylene with Cyclopentadiene (CPD) by Bis(β-enaminoketonato)titanium/MMAO Catalytic Systems[a]

entry	cat.	C_{CPD}[b]	temp (°C)	time (min)	yield (mg)	activity[c]	incorp[d] (mol %)	$\bar{M}_n$[e] × 10^4	M_w/M_n[e]	T_m[f] (°C)
1	**1a**	0.4	20	10	390	293	1.8	3.5	2.1	130
2	**1a**	0.8	20	10	287	215	3.1	2.9	2.5	128
3	**1a**	0.8	40	10	543	407	5.8	6.7	2.0	124
4	**1a**	1.2	40	10	685	514	8.9	5.7	2.3	109
5	**1a**	1.8	40	10	360	270	12.2	4.6	1.9	117
6	**1a**	2.4	40	15	283	142	16.0	3.5	1.9	101
7	**1b**	0.4	20	20	192	73	0.7	4.8	2.8	135
8	**1b**	0.8	20	20	trace					
9	**1b**	0.8	40	20	61	23	0.9	3.3	2.6	135
10	**1c**	0.4	20	10	312	234	1.3	7.1	2.6	132
11	**1c**	0.8	20	10	262	197	2.9	5.1	2.6	128
12	**1c**	0.8	40	10	496	372	4.5	5.8	2.0	125
14	**Zr**	0.8	20	10	3875	2901	3.5			121

[a] Conditions: catalyst 8 μmol, ethylene 1 atm, Al/Ti(molar ratio) = 1500, V_{total} = 80 mL. [b] CPD concentration charged (mol/L). [c] Catalytic activity in kg polymer/$\mathrm{mol_{Ti}}$·h. [d] CPD incorporation (mol %) established by ^{13}C NMR spectra. [e] Number-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ vs narrow polystyrene standards. [f] Melt temperatures were measured by DSC.

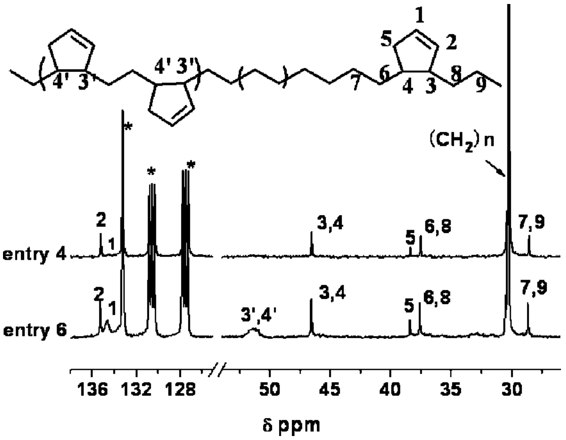

Figure 1. ^{13}C NMR spectra of poly(E-*co*-CPD)s (entries 4 and 6 with CPD incorporation 8.9 and 16.0%, respectively) synthesized by catalyst **1a**.

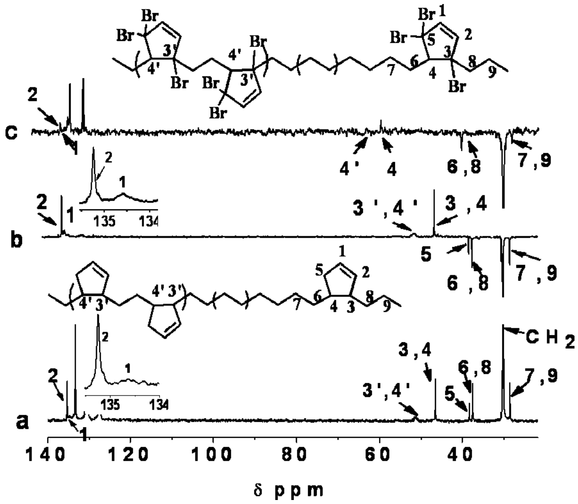

Figure 2. Comparison of the ^{13}C NMR (dept) spectra of poly(E-*co*-CPD)s (entry 5 with CPD incorporation of 12.2%) before (a, b) and after (c) brominated.

smaller trifluoromethyl substituent at the R_1 position, which could make CPD insert more easily. Therefore, the CPD incorporation can be adjusted in a wide range by varying the polymerization conditions.

The microstructures of the poly(E-*co*-CPD)s were established by ^{1}H and ^{13}C NMR (dept) spectra with the assistance of 2D H−H COSY and C−H HMQC technology. The typical ^{13}C NMR spectra are shown in Figure 1. It is very exciting to see that the CPD was incorporated into polymer chain via 1,2-insertion manner without 1,4-insertion. Taking the chemical shift into account, the signals at 135.24 and 134.66 ppm of curve entries 4 and 6 are assigned to carbons 2 and 1, respectively, which correspond to the reserved double bond of the inserted CPD. Absorption peaks at 38.36 ppm are assigned to carbon 5, the secondary carbon in the CPD unit. The peaks presented at 46.52 ppm are assigned to carbons 3 and 4, the tertiary carbon connected to ethylene chain. Furthermore, alternating E−CPD blocks presented in the polymer backbone can be approved by the presence of a broad absorption peak at 50.2 to 52.3 ppm in curve entry 6 (with CPD incorporation of 16%). The unprecedented microstructural features can be proved with the help of DEPT (135) spectra. As shown in Scheme 1b, the 1,2-insertion manner of CPD was also affirmed via the *N*-bromosuccinimide (NBS) bromination of the copolymers. A comparison of the ^{13}C NMR and DEPT (135) spectra of the copolymer (entry 5) before and after being brominated is shown in Figure 2. Taking the chemical shift into account, the signals at 135.21 and 134.66 ppm of curves a and b as well as the signals at 133.2 and 132.2 of curve c are assigned to tertiary carbon, which correspond to the reserved double bond of the 1,2-inserted CPD unit. These signals can be observed in all ^{13}C NMR spectra of the E/CPD copolymers.[8] The positive peaks at 51.3−51.4 and 46.52 ppm of curves a and b are assignable to the tertiary carbon corresponded to the carbons connected to main chain. After being brominated, carbons 4 and 4′ are reserved and can be observed in the DEPT spectra (curve c) as positive peaks at 61.96 and 58.72 ppm, respectively. Because all H atoms of carbons 3(3′) and 5 have been replaced by Br atom, the signals correspond to carbons 3(3′) and 5 disappeared in curve c (CH_2 groups display negative peaks, CH and CH_3 show positive peaks). Thereby, the 1,4-insertion of CPD can be completely excluded for the characteristic signal of methylene in the CPD (marked as * in Scheme 1b) cannot be observed in curve c.

This exclusive regioselectivity may be due to the special electronic effect and the stereo hindrance of the titanium catalysts, which is different from metallocene and CGC catalysts. In addition, DCPD units were also not observed in all poly(E-*co*-CPD)s produced by the titanium catalysts. The analyses of the microstructure of the resultant copolymers prove that the poly(E-*co*-CPD)s possess isolated CPD sequences, while no consecutive sequences of CPD are found. Furthermore, alternating CPD−E−CPD sequences could be found for the copolymers with CPD incorporation over 12 mol %. In contrast with the controlled and regioselective E/CPD copolymerization catalyzed by the titunium catalysts, not only CPD (1,2- and 1,4-

insertion) but also DCPD (1,2-insertion) were incorporated into the copolymer chain when Et[Ind]$_2$ZrCl$_2$ was employed as a catalyst even under lower temperature, lower CPD concentration, or shorter reaction period. The copolymerization ability and regioselectivity of the zirconocene catalyst are poor compared with its high catalytic activity. In other words, both CPD incorporation and CPD inserted manner are controllable in ethylene/CPD copolymerization using titanium complexes **1a**−**c** as the catalysts.

The poly(E-*co*-CPD)s bearing abundant double bonds are the promising and attractive candidates for the preparation of functional polyolefin materials. Here we demonstrate that they can be functionalized by epoxidation as a typical example. The epoxidation of the copolymers can be easily achieved by using *m*-chloroperbenzoic acid as an oxidant, which completely converted the olefinic groups into the epoxy groups. ^{13}C NMR spectra (peaks assignable to the epoxy group newly appear at 59 ppm, accompanied by a complete disappearance of the peaks attributed to the C═C double bonds), and FT-IR spectra (new absorption at 839 cm^{-1}) indicate that the new epoxidated copolymers were successfully obtained.[8]

In summary, the bis(β-enaminoketonato)titanium complexes activated with MMAO showed unprecedented behaviors in the controlled copolymerization of ethylene and CPD, in which CPD can be regioselectively incorporated into polymer chains as the only comonomer inserted via previously undiscovered 1,2-insertion fashion. Unprecedented microstructural features of alternating CPD−E−CPD sequences presented in the backbone of the copolymers are also observed. Reactive double bonds are reserved in the resultant copolymers without cross-linking. Introduction of polar functionality under mild conditions has been achieved by adopting this promising approach. On the basis of the unique characteristic of this catalysis, studies on evolution of the new polyolefins with excellent properties by introducing various functionalities via the controlled way, as well as on the copolymerization of CPD with α-olefins by related transitional-metal complexes, are in progress.

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Supporting Information Available: Text giving general experimental procedures; selected ^{1}H and ^{13}C NMR (dept) spectra for the resultant (co)polymers. This material is available free of charge via Internet at http://pubs.acs.org.

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(8) Experimental procedures, selected ^{1}H and ^{13}C NMR (dept) spectra, and FTIR and DSC curves of the copolymers are shown in the Supporting Information.

(9) The CPD incorporations were estimated on the basis of the ratio of total integration values of CPD vs ethylene at each resonance in the ^{13}C NMR spectra. The amounts of the CPD and triads in the ethylene backbone were calculated by ^{13}C NMR with the following equations (C = CPD and E = ethylene): [EEE] = $I_{\mathrm{CH2}}/2$; [EEC + CEE] = 2 [ECE]; [ECE] = $(I_3 + I_4 + I_6 + I_8)/4$; [CEC] = $(I_{3'} + I_{4'})/4$, where I_x is the normalized integral of peak *x* shown in Figure 2. On the basis of these equations, the amounts of CPD and ethylene in the copolymers were calculated as follows: [E] = [EEE] + [EEC + CEE] + [CEC]; [C] = [ECE] + [CCC] + [ECC + CCE] + 2[CEC]. Hence, the ratio of [C] to ([C] + [E]) reflected the CPD incorporation in the copolymers: CPD incorporation: CPD (mol %) = [C]/([C] + [E]).

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