New Monodisperse Ethylene–Propylene Copolymers and a Block Copolymer Created by a Titanium Complex Having Fluorine-Containing Phenoxy-Imine Chelate Ligands

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New monodisperse ethylene–propylene copolymers and a block copolymer, highly syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene), were synthesized with a titanium complex having fluorine-containing phenoxy-imine chelate ligands, an FI Catalyst, using methylalumoxane (MAO) as a cocatalyst. Analysis using transmission electron microscopy (TEM) suggests that the well-defined block copolymer possesses high potential as a compatibilizer.

Recently, research on living olefin polymerization catalysts has been intensive since living olefin polymerizations can be used for the preparation of precisely-controlled polymers such as monodisperse polymers, terminally functionalized polymers, and block copolymers, all of which are expected to display novel properties and uses. Recent advances in the rational design of high performance living olefin polymerization catalysts have enabled the synthesis of many of the before mentioned precisely-controlled polymers.[1] However, the preparation of ethylene-based monodisperse ethylene–α-olefin copolymers and block copolymers consisting of crystalline and amorphous segments remains a challenge. Previously, we found, as a result of ligand-oriented catalyst design research, that group 4 transition metal complexes featuring a pair of non-symmetric phenoxy-imine chelate ligands, named FI Catalysts, display high catalytic performance for olefin polymerization.[2] Recently, we discovered and applied for a patent in which titanium FI Catalysts having fluorine(s) in the ligand promote unprecedented living olefin polymerization resulting in the production of monodisperse polymers and copolymers, and various block copolymers from ethylene and α-olefins.[3] Therefore, in this paper, we would like to describe the synthesis of ethylene-based monodisperse ethylene–propylene copolymers and a highly syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene) block copolymer, a block copolymer consisting of crystalline and amorphous segments, using a titanium FI Catalyst possessing *N*-(3-*tert*-butylsalicylidene)pentafluoroaniline ligands. In addition, we would also like to report evaluation results of the well-defined block copolymer using transmission electron microscopy (TEM) for the first time.

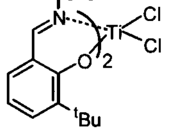

Figure 1. Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**1**).

The FI Catalyst employed in this study is bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (complex **1**, Figure 1). The synthesis of complex **1** has already been reported.[3f,3g] Preparation of monodisperse ethylene–propylene copolymers requires a catalyst which displays high performance for the living polymerization of both ethylene and propylene. Since, as reported previously,[3] complex **1** promotes living polymerization of ethylene and propylene, exhibiting high performance, we tried to synthesize monodisperse ethylene–propylene copolymers.

Table 1. Ethylene/propylene copolymerization results using complex **1** / MAO catalyst system

Entry	E/P feed /L h^{-1}	Time min	Yield g	M_n[a] /10^4	M_w/M_n[a]	P[b] mol%
1	5/95	20	0.95	1.96	1.07	47.9
2	10/90	30	3.55	5.23	1.11	38.2
3	30/70	10	2.69	4.25	1.08	28.9
4	50/50	5	2.85	4.27	1.08	21.1
5	80/20	5.3	5.25	8.36	1.13	14.7

Conditions: 25 °C, 0.1 MPa pressure, toluene; 250 mL, complex **1**; 0.05 mmol, MAO (Albemarle); [Al]=5.0 mmol. [a]M_w, M_n values; GPC analysis. [b]Propylene contents; IR analysis.

Copolymerizations of ethylene with propylene were carried out under atmospheric pressure at 25 °C with complex **1** using methylalumoxane (MAO) as a cocatalyst (Table 1). In all cases, ethylene–propylene copolymer having extremely narrow polydispersity (M_w/M_n: 1.07–1.13) was obtained. The produced copolymers possess propylene contents in the range of 14.7 to 47.9 mol%. These are the first examples of the syntheses of ethylene-based monodisperse ethylene–propylene copolymers. These results together with our previous results[3] indicate that complex **1** is capable of generating monodisperse polymers, ranging from polyethylenes, ethylene–propylene copolymers with various propylene contents to highly syndiotactic polypropylenes, making it possible to create block copolymers having a variety of segments and thus compositions.

An A–B diblock copolymer, highly syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene), from propylene and ethylene was prepared using complex **1** / MAO catalyst

Table 2. Preparation of *s*PP-*b*-poly(ethylene-*co*-propylene) and its segments

Entry	Time /min	Monomer	Yield g	M_n[a] /10^4	M_w/M_n[a]	P[b] mol%
1[c]	300→40	P→E/P	2.53	16.1	1.51	40.3
2	300	P	0.55	2.7	1.13	100[d]
3	40	E/P	2.50	17.0	1.12	32.4

Conditions: 25 °C, 0.1 MPa pressure, complex **1**; 0.02 mmol, MAO (Albemarle); [Al]=5.0 mmol. Toluene (250 mL) saturated with propylene was employed as a solvent. [a]M_w, M_n values; GPC analysis. [b]Total propylene contents in the resulting polymers; IR analysis. [c]After propylene (100 L/h) polymerization, the feeding gas was changed from propylene to ethylene (1.5 L/h, 40 min). [d]rr=87%.

system under atmospheric pressure at 25 °C (Table 2). Thus, after the preparation of syndiotactic polypropylene (*s*PP) segment (propylene: 100 L/h, 5 h), the propylene gas feed was stopped and, at the same time, the ethylene gas feed (1.5 L/h, 40 min) was initiated to create a sequential poly(ethylene-*co*-propylene) segment. An overlay of the monomodal GPC elution curves for the *s*PP A block (M_n: 27000, M_w/M_n: 1.13) and the final *s*PP-*b*-poly(ethylene-*co*-propylene) A–B diblock (M_n: 161000, M_w/M_n: 1.51)[4] indicates a shift towards higher molecular weight range while retaining reasonably narrow polydispersity (Figure 2), demonstrating the creation of the desired block copolymer. The poly(ethylene-*co*-propylene) segment of the block copolymer is estimated to possess a propylene content of 31.8 mol%. The peak melting temperature (T_m) of the produced block copolymer is 127 °C, the value being lower than the corresponding *s*PP (rr = 87%, T_m = 137 °C, Table 2, entry 2). The decrease in T_m of the block copolymer is probably ascribed to the fact that the crystalline state is disturbed by the segregation process of incompatible components comprised of *s*PP and poly(ethylene-*co*-propylene) segments which are chemically linked, further confirming the formation of the block copolymer. This is probably the first synthesis of a highly syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene) block copolymer as introduced in the patent,[3a] though very recently the preparation of a similar block copolymer using a similar FI Catalyst has been reported.[5]

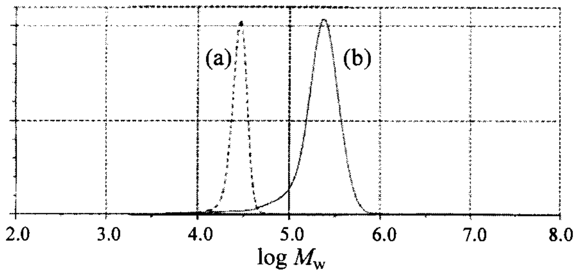

Figure 2. GPC traces of the polymers; (a) *s*PP, (b) *s*PP-*b*-poly(ethylene-*co*-propylene).

TEM was used to investigate the morphology of the press-sheets made of the *s*PP-*b*-poly(ethylene-*co*-propylene) [Table 2, entry 1] and *s*PP [Table 2, entry 2] / poly(ethylene-*co*-propylene) [Table 2, entry 3] blend polymer. The TEM micrograph of the block copolymer shows well-defined morphology of micro phase separation compared with that of the blend polymer (Figure 3). In Figure 3 (A), white domains corresponding to the *s*PP segment form a very fine and uniform nanostructue, while those of the blend polymer (Figure 3 (B)) display coarse and non-uniform domains. Therefore, the well-defined block copolymer is suggested to have a high potential as a compatibilizer.

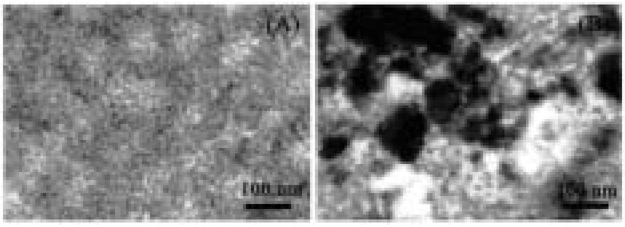

Figure 3. TEM micrographs of (A) *s*PP-*b*-poly(ethylene-*co*-propylene) and (B) *s*PP and poly(ethylene-*co*-propylene) blend polymer (blend conditions; toluene, 100 °C, 1 h).

In summary, new monodisperse ethylene–propylene copolymers and a block copolymer, highly syndiotactic polypropylene-*b*-poly(ethylene-*co*-propylene), have been synthesized from propylene and ethylene using an FI Catalyst. As anticipated, TEM analysis indicates that the block copolymer possesses a high potential as a compatibilizer. Thus, the usefulness of the FI Catalyst living polymerization technology has been demonstrated.

References and notes

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4 A somewhat wide polydispersity is probably derived from the non-homogeneity of the polymerization system because of high molecular weight and insoluble polymers.

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