



Synthesis of novel poly(ethylene-*ter*-1-hexene-*ter*-dicyclopentadiene)s using bis(β -enaminoketonato)titanium catalysts and their applications in preparing polyolefin-*graft*-poly(ϵ -polycaprolactone)

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ABSTRACT

Novel terpolymers containing ethylene, 1-hexene and dicyclopentadiene (DCPD) were synthesized using bis(β -enaminoketonato)titanium catalysts $[\text{PhN}=\text{C}(\text{R}_2)\text{CHC}(\text{R}_1)\text{O}]_2\text{TiCl}_2$ (**1a**: $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{CF}_3$; **1b**: $\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{CH}_3$). In the presence of modified methylaluminoxane, these catalysts afforded terpolymers with a broad range of monomer compositions and unimodal molecular weight distributions. ^{13}C NMR spectra reveal the exclusive insertion manner of DCPD maintained under various reaction conditions. DSC results show the melting temperature and the glass transition temperature are very sensitive to the terpolymer composition and the morphology can be easily tuned from semicrystalline state to amorphous state. With ethylene/1-hexene/DCPD molar ratio about 67/28/5, the terpolymer exhibits low glass transition temperature ($T_g = -50^\circ\text{C}$) and has a great potential to serve as polyolefin elastomer. Additionally, the terpolymer containing 4.3 mol% 1-hexene and 1.6 mol% DCPD was elated as the “reactive intermediate polyolefin” for PCL graft reaction. The composition of graft copolymer was well controllable and high graft efficiency was observed. The microscopy studies in conjunction with the tensile tests revealed that PCL graft copolymer is the effective compatibilizer for polyethylene/polar polymer blends by improving the interfacial adhesion between separated phases.

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1. Introduction

By far, the most important commercial polyolefin elastomers are EPDM terpolymers, such as poly(ethylene-*ter*-propylene-*ter*-1,4-hexadiene) and poly(ethylene-*ter*-propylene-*ter*-5-ethylidene-2-norbornene), with amorphous structure and low glass transition temperature as well as reactive sites which can effectively form cross-linking networks [1]. Traditionally, the EPDM terpolymers were synthesized by heterogeneous Ziegler–Natta catalysts. However, due to the significant difference in comonomer reactivities and multiple active sites, long crystallizable ethylene sequences and broad molecular weight distributions were observed [2,3]. Chung and his coworkers synthesized elastomers, poly(ethylene-*ter*-1-octene-*ter*-divinylbenzene) and poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene), with relatively narrow molecular weight distributions ($\text{PDI} = 2\text{--}3$) using metallocene catalysts, and demonstrated that higher α -olefin relative to propylene prevents the crystallization of ethylene sequences more effectively

[4,5]. Nevertheless, the copolymerization of α -olefin with divinylbenzene or *p*-methylstyrene often faces difficulties owing to the catalyst poisoning. In contrast, dicyclopentadiene (DCPD) is a very promising cyclic diene, which is catalyst innocuous, industrially available at a low price and its copolymer has many desirable properties such as good transparency [6–16]. Therefore, if DCPD selectively participates in terpolymerization with ethylene and higher α -olefin, the remaining double bonds can be utilized in cross-linking and this novel terpolymer would be a promising elastomer. However, the terpolymerization of ethylene with higher α -olefin and DCPD has not been reported yet. Moreover, cross-linking during polymerization appeared to be a major problem, which was often encountered in metallocene-catalyzed DCPD polymerization [16]. Apparently, in order to achieve ethylene/higher α -olefin/DCPD terpolymerization in a controlled fashion, it is very important to select a proper catalyst system that cannot only have strong terpolymerization ability but also effectively prevent cross-linking during polymerization.

In addition, the remaining double bonds of terpolymer would also be utilized in preparation of well-defined functional polyethylene with improved performances [17–24]. Especially, the use of functional graft polyethylene as interfacial compatibilizer

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established technique to improve interaction and morphology in immiscible polyethylene/polar polymer blends [25–36]. In general, the backbone of functional graft polyethylene used in compatibilized blend is highly crystallized [31–33]. Well then, what about the compatibility of the functional graft polyethylene with low crystallized backbone? If this kind of functional graft polyethylene also has the excellent compatibility, it will be a promising progress.

Herein, we report the novel terpolymerization of ethylene with 1-hexene and DCPD using bis(β -enaminoketonato)titanium catalysts [PhN=C(R₂)CHC(R₁)O]₂TiCl₂ (**1a**: R₁ = Ph, R₂ = CF₃; **1b**: R₁ = CF₃, R₂ = CH₃) (Scheme 1) which have the excellent ability to promote the copolymerization of ethylene with DCPD as well as the copolymerization of ethylene with 1-hexene [8,9,37]. By varying terpolymer composition, the morphology could be easily tuned from semicrystalline state to amorphous state while the exclusive insertion manner of DCPD maintained. The glass transition temperature as low as –50.0 °C was achieved and this terpolymer had a great potential to serve as elastomer. In addition, poly(ϵ -caprolactone) (PCL)-graft-polyolefin proved to be truly miscible with numerous polymers [38–40]. Therefore, PCL graft copolymer with low crystallized backbone was synthesized, and research on its compatibility for different polymer blends was also carried out.

2. Experimental

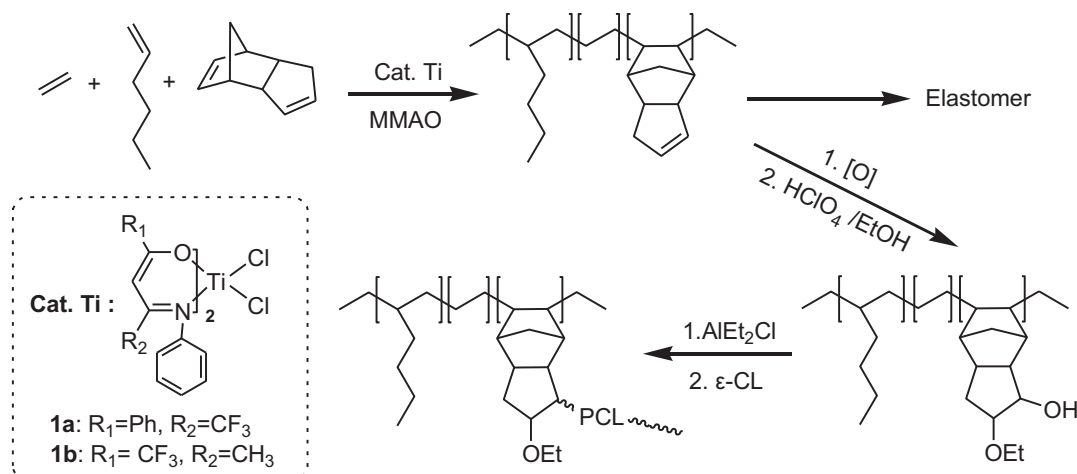
2.1. General

All work involving air- and/or moisture-sensitive compounds were carried out in an MBraun glovebox or under an argon atmosphere by using standard Schlenk technique. Anhydrous toluene was purified by Solvent Purification System purchased from an MBraun SPS system. Modified methylaluminoxane (MMAO, 7% Aluminum in heptane solution) and diethylaluminium chloride were purchased from Akzo Nobel Chemical Inc and Albemarle Corporation, respectively, and both of them were used without further purification. DCPD, 1-hexene and ϵ -caprolactone (ϵ -CL) were purchased from Aldrich. 1-Hexene was stirred over sodium for 3 days and distilled under argon atmosphere prior to use. DCPD dried over sodium, vacuum-transferred, and degassed by two freeze-pump-thaw cycles to remove the cyclopentadiene. ϵ -CL was purified by drying over calcium hydride and distilling under reduced pressure. Catalysts **1a–b** were synthesized by the method described in the literature [37].

2.2. Characterization

All ¹H and ¹³C NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (399.65 MHz for ¹H, 100.40 MHz for ¹³C) with *o*-C₆D₄Cl₂ as the solvent and all chemical shifts were given in ppm, which referenced to Me₄Si. All spectra were acquired at 398 K with 90° pulse width (P1) of 5.7, sweep width (SW) of 25,062 Hz and relaxation delay (D1) of 7.7 s. The monomer contents of terpolymer were determined by ¹³C NMR spectra and calculated according to the formula DCPD mol% = $[2I_{32.9\text{ppm}}/(I_{\text{total}} - 8I_{32.9\text{ppm}} - 4I_{23.5\text{ppm}})] \times 100\%$, HE mol% = $[2I_{23.5\text{ppm}}/(I_{\text{total}} - 8I_{32.9\text{ppm}} - 4I_{23.5\text{ppm}})] \times 100\%$, where *I* is the peak area of corresponding carbon. PCL content of graft copolymer was determined by ¹H NMR spectra and calculated according to the formula PCL mol% = $\{I_{4.09\text{ppm}}/[I_{4.09\text{ppm}} + (I_{1.50-0.80\text{ppm}} - I_{4.09\text{ppm}})/2]\} \times 100\%$, where *I*_{4.09ppm} is the peak area of corresponding hydrogen and *I*_{1.50–0.80ppm} is the total peak area from 1.50 ppm to 0.80 ppm (Since contents of 1-hexene and DCPD are far lower than the contents of ethylene sequence and PCL segment in graft copolymer, the units of 1-hexene and DCPD in terpolymer are omitted for simple calculation). The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatography with three PL-gel 10 μ m Mixed-B LS columns equipped by the light scattering detector. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard Easi-Cal PS-1 (PL Ltd). The differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris 1 DSC instrument under N₂ atmosphere. The samples were heated at a rate of 10 °C/min and cooled down at a rate of 20 °C/min.

The polarized optical microscopy observations of the thin films were performed using a Leica DMLP microscope equipped with CCD camera. The morphologies of the fracture surfaces of the blends were examined with an XL30 environmental scanning electron microscope with a field-emission gun (FEI Co., Eindhoven, Netherlands). The samples were frozen well in liquid nitrogen and quickly broken off to obtain a random brittle-fractured surface. A layer of gold was sputter coated uniformly overall the fractured surfaces before SEM observations. Tensile tests were performed on a 8.9 kN, screw-driven universal testing machine (Instron 1211, Canton, MA) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at room temperature using a cross-head rate of 5 mm/min. All tests were carried out according to the ASTM standard, and the data reported were the mean and standard deviation from five determinations.



Scheme 1. The structure of catalysts and the synthetic route for terpolymer elastomer and functional graft polyolefin copolymer.

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