Polymer 51 (2010) 3636–3643

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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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A R T I C L E I N F O

Article history:
Received 7 April 2010
Received in revised form
26 May 2010
Accepted 2 June 2010
Available online 9 June 2010

Keywords:
Terpolymer
Functional polyolefin
Compatibilizer

A B S T R A C T

Novel terpolymers containing ethylene, 1-hexene and dicyclopentadiene (DCPD) were synthesized using bis(β-enaminoketonato)titanium catalysts $[PhN{=}C(R_2)CHC(R_1)O]_2TiCl_2$ (**1a**: R_1 = Ph, R_2 = CF_3; **1b**: R_1 = CF_3, R_2 = 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 ($T_g = -50$ °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 served 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.

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 (PDI = 2–3) 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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doi:10.1016/j.polymer.2010.06.006

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(R_2) CHC(R_1)O$]_2$TiCl$_2$ (**1a**: R_1 = Ph, R_2 = CF_3; **1b**: R_1 = CF_3, R_2 = CH_3) (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

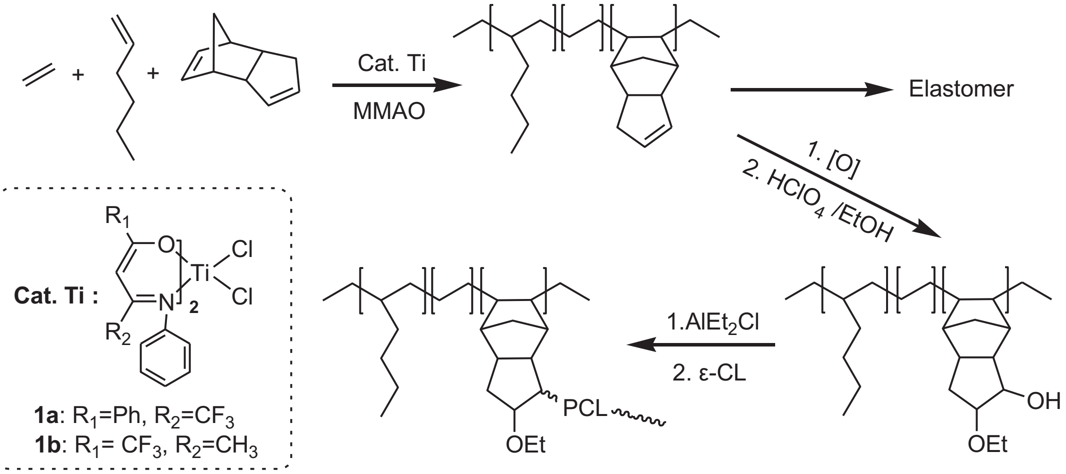
2.1. General

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 ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C) with o-$C_6D_4Cl_2$ as the solvent and all chemical shifts were given in ppm, which referenced to Me_4Si. 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 ^{13}C NMR spectra and calculated according to the formula DCPD mol% = $[2I_{32.9ppm}/(I_{total}-8I_{32.9ppm}-4I_{23.5ppm})]\times 100\%$, HE mol% = $[2I_{23.5ppm}/(I_{total}-8I_{32.9ppm}-4I_{23.5ppm})]\times 100\%$, where I is the peak area of corresponding carbon. PCL content of graft copolymer was determined by ^{1}H NMR spectra and calculated according to the formula PCL mol% = $\{I_{4.09ppm}/[I_{4.09ppm}+(I_{1.50-0.80ppm}-I_{4.09ppm})/2]\}\times 100\%$, 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 μm 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 N_2 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.

2.3. Typical terpolymerization procedure

Terpolymerizations were carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The total volume of the copolymerization solution was 50 mL. The reactor was charged with prescribed volume toluene and the described comonomer under argon atmosphere, and then the ethylene gas feed was started, followed by the toluene solution of the catalyst. After equilibration at the desired polymerization temperature for 10 min, the polymerization was initiated by the addition of MMAO to the reactor. After a desired period of time, the reactor was vented. The resulted copolymers were precipitated from hydrochloric acid/ethanol (2% V), filtered, washed three times with ethanol and acetone, then marinated in acetone for 12 h to remove the unreacted comonomer, and then dried in vacuo at room temperature to a constant weight. The obtained copolymers were conserved in the refrigerator to avoid cross-linking.

2.4. Synthesis of hydroxylated terpolymer

In a 250 mL, three-necked round bottom flask equipped with a magnetic stirrer, an amount of 200 mg of the terpolymer was suspended in 40 mL toluene. The flask was heated to 40 °C and then a toluene solution (10 mL) of *m*-chloroperbenzoic acid (5 eq of the epoxy groups) was added dropwise. The reaction mixture was stirred for 4 h at 40 °C, and then poured into ethanol. The precipitated polymer was filtered, washed with acetone for several times and dried in vacuo at 40 °C to a constant weight.

The subsequent ring opening reaction of epoxidated terpolymer was carried out in a 250 mL, three-necked round bottom flask equipped with a magnetic stirrer. An amount of 200 mg of the epoxidated copolymer was suspended in 80 mL toluene with $HClO_4$ (72%, 0.01 eq of the epoxy group) as a catalyst. The flask was heated to 65 °C, and then the anhydrous ethanol (10 mL) was added dropwise. The reaction mixture was stirred at 65 °C for 6 h, and then poured into ethanol. The precipitated polymer was filtered, washed with 5% aqueous Na_2CO_3 and acetone for several times and dried in vacuo at 40 °C to a constant weight.

2.5. Synthesis of polycaprolactone graft copolymer

In a metalation reaction, 200 mg of the hydroxylated ethylene/H/DCPD terpolymer was dissolved in the dry toluene for 0.5 h at 65 °C and then excess diethylaluminum chloride (5 eq of the hydroxyl group) was slowly added. The reaction mixture was heated to 65 °C and stirred for 6 h to form the aluminum alkoxide. After cooled down to the room temperature, the suspension was filtered and washed with dry hexane for 3 times. Fresh dry toluene was injected to the reaction vessel and heated to 65 °C for 0.5 h. After cooling to the room temperature, 0.5 mL ε-CL was added. The reaction mixture was stirred at room temperature for prescribed time and then terminated by the addition of acidified MeOH. The polymer was isolated by precipitating into MeOH. The polymer mass was extracted with hot THF in a Soxhlet apparatus for 24 h to remove any ε-CL homopolymer.

2.6. Polymer blends

All the blends for SEM were prepared in solution to obtain molecular level mixing. The PE was first dissolved in *o*-xylene inhibited with BHT and kept under a N_2 blanket to prevent oxidation. The PE-*g*-PCL and PCL homopolymer were then slowly added to the hot solution. After the polymer mixture had formed a clear, homogeneous solution, the blend was precipitated into cold hexane. The blend was dried under vacuum before being melt pressed to form a film.

The blends of polarized optical microscopy were dissolved in BHT-inhibited *o*-xylene at 135 °C. The polymer films were then solution cast onto glass microscope slides. After evaporating the *o*-xylene under N_2 purge, the films were covered with a slide cover. The polymer films were then melted in a hot stage at 180 °C for 15 min. The samples were then allowed to cool quiescently in the hot stage to room temperature for 20 min.

3. Results and discussion

3.1. Terpolymerization of ethylene with 1-hexene and DCPD

The terpolymerization involving ethylene, 1-hexene and DCPD initiated by catalysts **1a**–**b** in the presence of MMAO was explored under different experimental conditions. To ensure constant monomer ratio in feed, the polymerization reaction was terminated in 5 min. Note that catalysts **1a**–**b** can effectively terpolymerize ethylene with 1-hexene and DCPD and exhibit high catalytic activity. The data summarized in Table 1 indicate that the copolymerization behavior is considerably influenced by the catalyst structures and the reaction conditions. As observed, compared with **1a**, catalyst **1b** with lower steric effect displayed much higher activity towards the terpolymerization (Table 1, entries 2 *vs* 9 and

Table 1
Terpolymerization of ethylene with 1-hexene and DCPD by bis(β-enaminoketonato)titanium catalysts.[a]

Entry	Cat	Conc.[b](DCPD)	Conc.[b](HE)	Temp.(°C)	Yield (mg)	Activity[c]	Incorp.[d](DCPD)	Incorp.[d](HE)	M_w[e] kg/mol	M_w/M_n[e]	T_g[f](°C)	T_m[f](°C)
1	**1a**	0.0063	0.50	25	450	680	2.7	1.8	67.0	1.08	–	101.0
2	**1a**	0.0042	0.50	40	500	750	1.6	4.3	74.9	1.27	–	78.0
3	**1a**	0.025	0.62	40	460	700	10.0	5.1	45.9	1.30	−13.9	35.9
4	**1a**	0.010	1.12	40	350	530	3.2	7.8	76.8	1.23	−31.2	60.7
5	**1a**	0.020	1.12	40	380	570	5.4	7.0	62.5	1.28	−22.2	37.9
6	**1a**	0.020	1.60	45	400	600	6.0	13.0	43.3	1.48	−27.4	–
7	**1a**	0.017	2.00	45	330	495	5.8	15.2	42.8	1.48	−34.8	–
8	**1a**	0.017	2.00	50	360	540	6.4	23.5	42.0	1.39	−42.6	–
9	**1b**	0.0042	0.50	40	920	1380	2.0	5.0	125.0	1.84	–	74.0
10	**1b**	0.025	0.62	40	800	1200	10.3	6.7	96.3	1.73	−15.0	31.9
11	**1b**	0.020	1.60	45	877	1315	5.8	16.0	65.4	1.84	−34.6	–
12	**1b**	0.017	2.00	50	500	750	6.5	26.0	49.0	2.19	−46.0	–
13	**1b**	0.012	2.00	50	540	810	5.3	27.8	53.3	2.05	−50.0	–

[a] Conditions: catalyst 8 μmol, ethylene 1 atm, Al/Ti(molar ratio) = 1500, V_{total} = 50 mL, reaction time = 5 min.
[b] Comonomer concentration charged (mol/L).
[c] Catalytic activity: kg polymer/mol_{Ti} h.
[d] comonomer incorporation (mol%) established by ^{13}C NMR spectra.
[e] Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ *vs* narrow polystyrene standards.
[f] Melt temperatures and glass transition temperatures were measured by DSC.

entries 6 *vs* 11) and produced the terpolymer with slightly higher 1-hexene incorporation. In addition, elevating reaction temperature was also propitious to enhance the catalytic activity and monomer incorporation while the molecular weight of terpolymer decreased slightly (Table 1, entries 7 *vs* 8). Overall, catalysts **1a**–**b** show a preference for incorporating DCPD to 1-hexene, which is consistent with the fact that these catalysts are more active for ethylene/DCPD copolymerization than ethylene/1-hexene copolymerization [8,37]. Nevertheless, the incorporation of 1-hexene was enhanced by elevating the reaction temperature or increasing 1-hexene concentration (Table 1, entries 5 *vs* 6 and entries 7 *vs* 8). The high 1-hexene incorporation up to 27.8 mol% has been achieved at 50 °C by catalyst **1b** (Table 1, entry 13).

The terpolymer composition can also be predicted quantitatively by reactivity ratios. However, the catalysts used in our work can only promote ethylene/DCPD and ethylene/1-hexene copolymerization but are incapable of DCPD/1-hexene copolymerization, DCPD or 1-hexene homopolymerization. Therefore, the conventional equation used for determining the composition is unsuitable in this work as it requires all the monomer reactivity ratios to have finite values [41]. Thus, for this special terpolymerization where monomer M_2 and monomer M_3 cannot add to themselves or to one another, following modified equation was used to predict the terpolymer composition [42,43]:

$$\begin{aligned} m_1/m_2 &= 1 + r_{12}[M_1]/[M_2] + r_{12}[M_3]/r_{13}[M_2], \\ m_1/m_3 &= 1 + r_{13}[M_1]/[M_3] + r_{13}[M_2]/r_{12}[M_3], \\ m_2/m_3 &= r_{13}[M_2]/r_{12}[M_3]. \end{aligned} \tag{1}$$

m_1/m_2, m_1/m_3 and m_2/m_3 are the molar ratios of the three monomer units in terpolymer, $[M_1]$, $[M_2]$ and $[M_3]$ are the concentrations of three monomers in feed and the parameters r_{ij} are related to corresponding monomer reactivity ratios. The resultant reactivity ratios, the data used to calculate Fineman-Ross plots and the comparison of experimental and calculated compositions was provided in Supporting Information. An approximate agreement was observed between experimental composition and calculated composition. For instance, molar ratios of m_E/m_{DCPD}, m_E/m_{HE} and m_{DCPD}/m_{HE} calculated by reactivity ratios are 24.2, 11.5 and 0.47 mol %, respectively (catalyst **1a**; 40 °C; DCPD = 0.10 mol/L; 1-hexene = 1.12 mol/L). Under the same conditions, molar ratios of m_E/m_{DCPD}, m_E/m_{HE} and m_{DCPD}/m_{HE} determined by ^{13}C NMR spectra are 27.8, 11.4 and 0.41 mol% respectively, which were basically consistent with the calculated composition.

The typical GPC profiles of terpolymers produced by catalysts **1a**–**b** are presented in Fig. 1. The curves are all unimodal with relatively narrow molecular weight distributions, which are consistent with the single homogeneous catalytic species. Especially, catalyst **1a** produced the terpolymer with relatively narrow molecular weight distributions (PDI < 1.5), which is the predominance of non-metallocene catalyst because the metallocene catalyst usually produces the polymer with molecular weight distribution in the range of 2–3. Even at high reaction temperature (50 °C), the terpolymer produced by catalyst **1a** has the PDI as low as 1.39 (Table 1, entry 8) (Fig. 2).

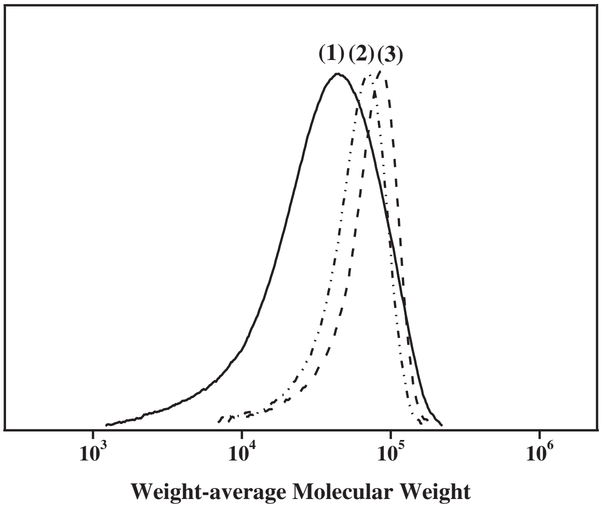


Fig. 1. GPC profiles of ethylene/DCPD/1-hexene terpolymers produced by catalysts **1a** and **1b**: (1) M_w = 49.0 kg/mol, PDI = 2.19 (Table 1, entry 12) (2) M_w = 62.5 kg/mol, PDI = 1.28 (Table 1, entry 5); (3) M_w = 74.9 kg/mol, PDI = 1.27 (Table 2, entry 2).

The microstructure of the ethylene/DCPD/1-hexene terpolymer is established by ^{13}C NMR spectra and all chemical shifts observed can be assigned clearly according to previous literatures [6,8,44]. As shown in Fig. 2, the peaks at 14.2, 23.5, 29.8, 34.4, 34.9 and 38.5 ppm are attributed to characteristic chemistry shifts of 1-hexene unit. In addition, the peaks at 132.8 and 130.6 ppm are attributed to retain double bond of DCPD unit and the peak at 30.2 ppm is attributed to the ethylene unit. Furthermore, the GPC profile with unimodal distribution indicates the homogeneous composition of obtained polymer. The analysis of ^{13}C NMR spectra together with GPC profiles demonstrates that catalysts **1a**–**b** produce ethylene/1-hexene/DCPD terpolymer. Moreover, the peaks at 132.8 and 130.6 ppm reveal that terpolymer bears cyclopentene units, indicating that the terpolymerization proceeds through the enchainment of norbornene ring [8]. It is noteworthy that the regioselective nature maintains under various reaction conditions. Consequently, the intracyclic double bonds were retained near the main chain and no evidence of cross-linking was detected for all the terpolymers. In addition, homogeneous solution was observed during polymerization reaction and the terpolymer with high monomer content exhibited excellent dissolvability in THF or $CHCl_3$, which further confirmed that the cross-linking was negligible.

The thermal transition temperature of ethylene/1-hexene/DCPD terpolymer was examined by Differential Scanning Calorimetry (DSC) analysis. Fig. 3 shows the second heating scans of DSC curves for typical terpolymers at the rate of 10 °C/min. As observed, melting temperature (T_m) and glass transition temperature (T_g) are very sensitive to terpolymer composition and the morphology can be easily tuned from semicrystalline state to amorphous state. As

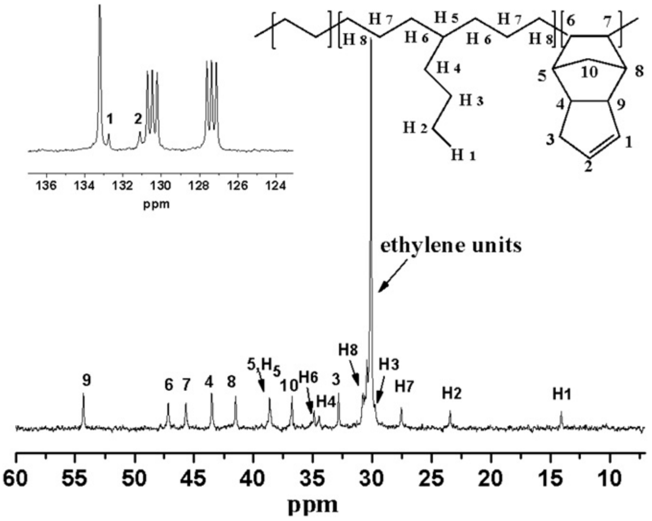


Fig. 2. ^{13}C NMR spectrum of ethylene/DCPD/1-hexene terpolymers (DCPD incorporation = 10.0 mol%, 1-hexene incorporation = 5.1 mol%) obtained by catalyst **1a** in o-$C_6D_4Cl_2$ at 125 °C.

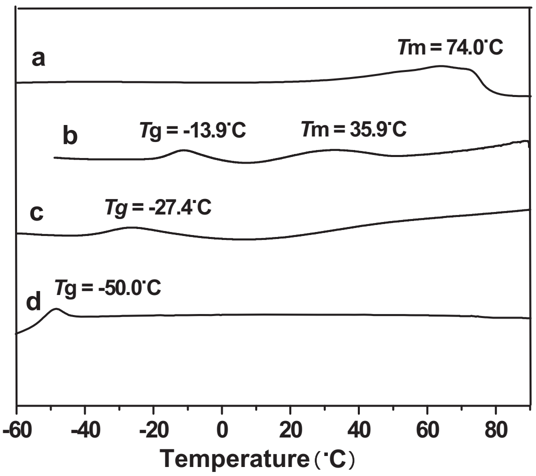


Fig. 3. DSC curves of ethylene/DCPD/1-hexene terpolymers (Table 1): (a) entry 9; (b) entry 3; (c) entry 6; (d) entry 13.

Table 2
A summary of polycaprolactone graft functionalization of terpolymer and reaction conditions.[a]

Entry	ε-CL (g)	Time (h)	THF Soluble (mg)	THF Insoluble (mg)	ε-CL mol% [b]	M_w [c] kg/mol	M_w/M_n [c]	T_m [d] (°C)
1	1.0	15	10	270	15.3	146.8	1.79	54.3, 75.2
2	1.0	24	14	350	27.0	228.8	2.08	54.9, 77.6
3	1.0	32	20	580	55.6	280.7	1.91	56.1, 78.5
4	2.0	24	20	420	36.2	250.0	2.14	55.4, 78.3

[a] Conditions: 200 mg hydroxyl terpolymers (Table 1 entry 2), $T = 25$ °C, $V_{total} = 15$ mL.

[b] Determined by ^{1}H NMR spectra.

[c] Weight-average molecular weights and polydispersity indices determined by GPC equipped by the light scattering detector at 150 °C in 1,2,4-$C_6Cl_3H_3$ *vs* narrow polystyrene standards.

[d] Melt temperatures were measured by DSC.

shown in Fig. 3c, the T_m disappeared completely when total content of 1-hexene and DCPD is more than 19 mol% (Table 1, entry 6). In contrast, nearly equal molar ratio of ethylene/propylene (55/45 mol ratio) was required to form amorphous structure in traditional EPDM terpolymers produced by Ziegler–Natta catalysts [5]. Apparently, these results clearly indicated that 1-hexene relative to propylene effectively prevents the crystallization of small consecutive ethylene units, which is consistent with previous reports [4,5]. In addition, the terpolymer with amorphous structure also exhibits a DSC curve with sharp T_g corresponding to its composition. The terpolymer with more DCPD or less 1-hexene exhibited higher glass transition temperature (Table 1, entry 4 *vs* 5 and entry 5 *vs* 6). As shown in Fig. 3d, with ethylene/1-hexene/DCPD molar ratio about 67/28/5, the T_g as low as −50.0 °C without any detectable T_m is achieved (Table 1, entry 13) and this terpolymer has a great potential to serve as elastomer. The detailed studies on the elasticity of terpolymer are currently in progress.

3.2. *Polycaprolactone graft functionalization of terpolymer*

The remaining double bonds of ethylene/1-hexene/DCPD terpolymer not only can be served as the reactive sites for cross-linking, but also can be utilized in subsequent graft reaction that produces functional graft polyethylene with improved performance. Usually, the graft density can be controlled by the concentration of double bonds. However, high graft density will lose the desired properties of polyolefin backbone [19]. Therefore, the terpolymer used in following PCL (PCL: polycaprolactone) graft functionalization is derived from the sample containing 1.6 mol% DCPD and 4.3 mol% 1-hexene which has low crystallinity (Table 1, entry 2).

The terpolymer with this composition has the excellent dissolvability in toluene at 40 °C. After the epoxidation and following ring opening reaction [9], hydroxylated terpolymer could be easily synthesized (^{1}H NMR spectrum see Supporting Information, Fig. S1). The obtained hydroxylated terpolymer reacted with $AlEt_2Cl$ to generate the aluminum alkoxide that initiated the ring opening polymerization of ε-CL. The typical experimental results and reaction conditions are summarized in Table 2. It is interesting that the graft reaction was carried out in the suspension at room temperature, producing the crude polymers separated into THF soluble fraction and THF insoluble fraction, which could be extracted effectively by a Soxhlet apparatus. ^{1}H NMR spectrum (see Supporting Information, Fig. S2) indicates the THF soluble fraction is PCL homopolymer initiated by residual $AlEt_2Cl$, which cannot be completely washed out by the solvent. The microstructure of THF insoluble fraction, which was soluble in *o*-$C_6D_4Cl_2$ at 125 °C, was also established by ^{1}H NMR spectra. As shown in Fig. 4, the peaks at 4.1, 2.3 and 1.6 ppm are attributed to methylene groups in PCL (CH_2O, marked as "1"; $CH_2C{=}O$, marked as "2" and CH_2 marked as "3", respectively). The peaks appeared from 1.5 to 0.8 ppm are attributed to methylene in PCL (marked as "4") and ethylene sequence [39]. Both appearance of ethylene sequence and PCL segment in ^{1}H NMR spectrum indicates THF insoluble fraction is the PEHD-*g*-PCL copolymer (PEHD: poly(ethylene-*ter*-1-hexene-*ter*-dicyclopentadiene)). In addition, it is difficult to distinguish the protons of ethoxy group (marked as "6") from the methenyl connecting to ethoxy group (marked as "7") and methylene connecting to hydroxyl group (marked as "5") because these characteristic peaks overlap together. However, the peak at 3.9 ppm attributed to the proton of methenyl connecting to PCL (marked as "8") suggests the protons of ethoxy group exist in ^{1}H NMR spectra. Moreover, the graft reaction was also monitored by GPC and typical curves are exhibited in Fig. 5. As observed, molecular weight increased with reaction time while unimodal distribution retained without evidently low molecular weight, confirming the homogeneous composition of graft copolymer. The results of GPC in conjunction with the NMR analyses apparently demonstrate that the graft reactions carry out successfully. However, compared with the terpolymer, the molecular weight distribution broadened after graft reaction (from 1.27 to nearly 2.0). It is because the ring opening polymerization of ε-CL cannot be initiated simultaneously

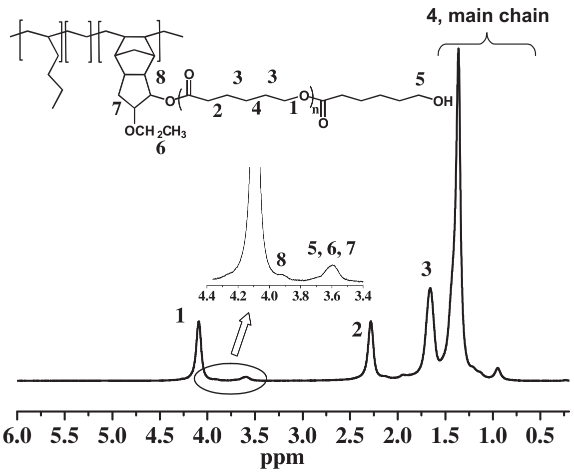


Fig. 4. ^{1}H NMR spectrum of functional graft copolymer containing 27.0 mol% PCL in *o*-$C_6D_4Cl_2$ at 125 °C.

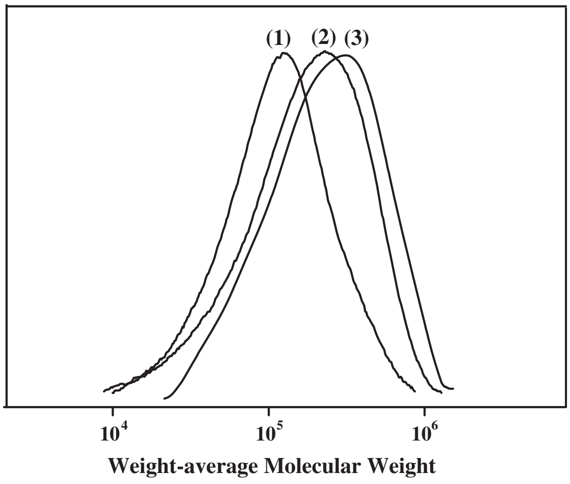


Fig. 5. GPC profiles of graft copolymers containing: (1) 15.3 mol% PCL (Table 2, entry 1); (2) 27.0 mol% PCL (Table 2, entry 2); (3) 55.6 mol% (Table 2, entry 3).

due to the enwrappment of anionic active species by suspended polymer under the heterogeneous reaction conditions [45–48]. Additionally, further evidence of successful graft reaction was also provided by DSC characterization. As shown in Fig. 6, it is clear that the high melting peak in graft copolymer at about 78 °C is attributed to polyethylene segments in the backbone and the low temperature one at about 55 °C is attributed to PCL segments in the side chain. Two melting temperatures also indicated that both phases corresponding to the terpolymer backbone and PCL side chain are evidently separated.

The composition of graft copolymer can be controlled by reaction conditions. PCL content of resulting graft copolymer was enhanced by extending the reaction time or increasing ε-CL concentration in feed. However, the amount of PCL homopolymer also increased with ε-CL concentration (Table 2, entry 3 *vs* 4). Nonetheless, the weight percent of homopolymer was always confined less than 5 wt%. Additionally, in order to enhance the solubility of "reactive intermediate polyolefin", ring opening polymerization of ε-CL was usually carried out at high temperature (80–100 °C) [39,40]. In this work, high concentration of PCL can be incorporated into the side chain despite that reaction was carried out at room temperature. After conducting for 36 h, graft copolymer with 55.6 mol% PCL was obtained (Table 2, entry 3). The high efficiency of graft reaction could be attributed to low crystallinity of terpolymer, which was swelled well in toluene.

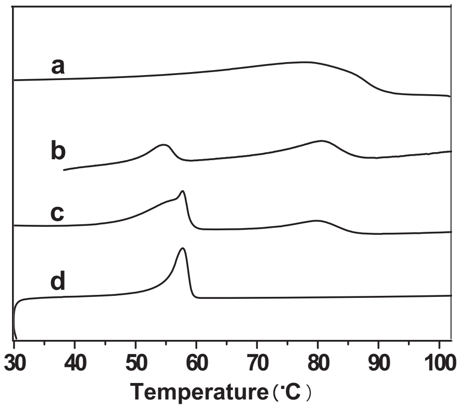


Fig. 6. DSC curves of (a) the ethylene/1-hexene/DCPD terpolymers (Table 1, entry 2); (b) graft copolymer containing 27.0 mol% PCL; (c) graft copolymer containing 55.6 mol % PCL; (d) PCL homopolymer.

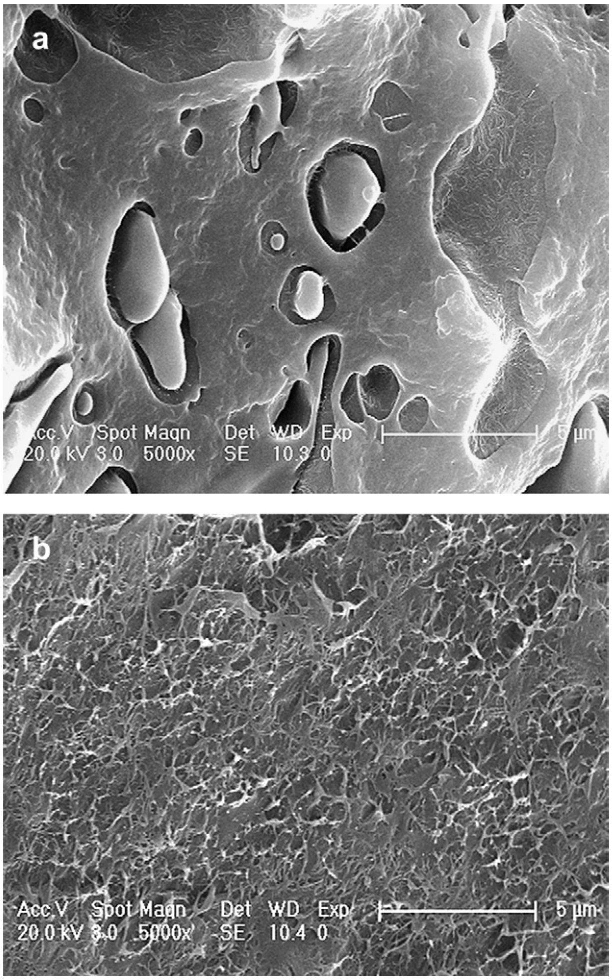


Fig. 7. SEM micrographs of (a) two homopolymer blend with PE/PCL = 70/30 (wt/wt) (5000×); (b) PE/PCL/PEHD-*g*-PCL = 70/30/10 (wt/wt/wt) (5000×), PEHD-*g*-PCL containing 55.6 mol% PCL.

3.3. Application of PCL graft copolymer as a phase compatibilizer

The ability of PEHD-*g*-PCL copolymer to act as a phase compatibilizer for immiscible polyethylene/polar polymer blends was investigated by microscopy studies. Generally, excellent compatibility for polyethylene/polar polymer blends was usually exhibited by the functional graft polyethylene with highly crystallized backbone [31–33]. However, in this work, PEHD-*g*-PCL copolymer with low crystallized backbone proved to be an effective compatibilizer not only for PE/PCL blend but also for PE/PMMA blend.

In PE/PCL blend case, SEM operating with secondary electron imaging was used to observe the surface topography of cold fractured film edges. As shown in Fig. 7a, the PE/PCL homopolymer blend with 70/30 composing was grossly phase separated as could be seen by the minor component PCL which exhibited nonuniform voids dispersed at the fracture surface. This topography was indicative of poor interfacial adhesion between PE and PCL domains. Correspondingly, the film of two homopolymer blend formed in the melt press was very brittle. Upon blending PE and PCL with graft copolymer, a drastic change in the morphology occurred. As showed in Fig. 7b, the compatibilized blend displayed a much flatter fracture surface without obviously nonuniform voids, suggesting the blend was actually miscible without phase separation. As a result, the film of compatibilized blend became evidently ductile. The transformation of mechanical property was

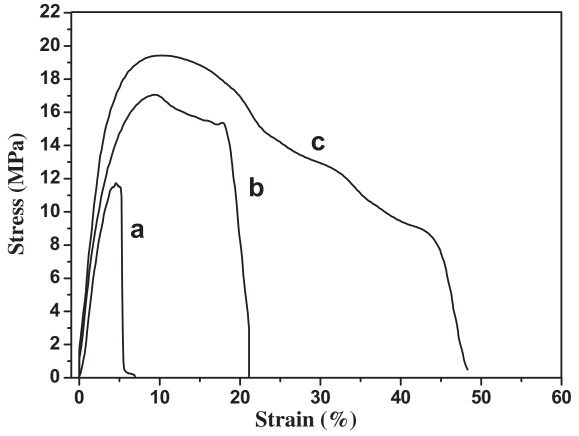


Fig. 8. Tensile stress–strain curves of the different blends: (a) PE/PCL = 70/30 (wt/wt); (b) PE/PCL/PEHD-*g*-PCL = 70/30/10 (wt/wt/wt), PEHD-*g*-PCL containing 27.0 mol% PCL; (c) PE/PCL/PEHD-*g*-PCL = 70/30/10 (wt/wt/wt), PEHD-*g*-PCL containing 55.6 mol% PCL.

also confirmed by the tensile tests and the typical stress–strain curves are presented in Fig. 8. As observed, the blend of two homopolymers displayed no yield point and its elongation at break was only about 4.9% (Fig. 8a). On the contrary, the compatibilized blend showed distinct yielding and neck growth (Fig. 8b,c). It is interesting to note that not only the elongation at break but also the tensile strength enhanced remarkably after the addition of graft copolymer. Take the blend containing graft copolymer with 55.6 mol% PCL as an example (Fig. 8c), the elongation at break reached 48% which increased by 10 times over that of two homopolymer blend, while the tensile strength was 17.0 MPa which was also higher than that of two homopolymer blend (11.7 MPa). These results indicated that fracture behavior of the specimen displayed a transition from brittle fracture to ductile fracture after the addition of graft copolymer. The transformation of mechanical property may be explained by increasing interfacial adhesion between the separated phases, which were tied by the graft copolymer with the covalent bond.

A similar compatibilized study for PE/PMMA blend was also carried out by polarized optical microscope. Fig. S3a (see Supporting Information) represented the micrograph of PE/PMMA blend with 70/30 composing. Obvious phase separation of large spherulitic PE and amorphous PMMA was observed. After adding graft copolymer with 55.6 mol% PCL, as shown in Fig. S3b, it is noticeable that the morphology of blend became more homogeneous with PMMA finer dispersed in the PE matrix and only small distorted spherulites were observed. It certainly suggested the excellent compatibility of graft copolymer for PE/PMMA blend. It is interesting to note that the films of compatibilized blend formed by the melt press became evidently translucent, which is very different from the film containing the two homopolymers that were opaque. This transformation may be caused by the lack of large spherulites in the compatibilized blend, which minimizes the light scattering.

4. Conclusions

Bis(β-enaminoketonato) titanium complexes **1a**–**b** in the presence of MMAO can effectively terpolymerize ethylene with 1-hexene and DCPD, affording terpolymers with a broad range of monomer compositions and unimodal molecular weight distributions. ^{13}C NMR spectra reveal the regioselective nature of DCPD maintains under various reaction conditions and cross-linking was never detected. 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 has the glass transition temperature low as −50.0 °C and possesses a great potential to serve as polyolefin elastomer. Additionally, the terpolymer with low crystallinity was served as the “reactive intermediate polyolefin” for PCL graft reaction. High graft efficiency was observed with controllable copolymer compositions. Despite of low crystallized backbone, PEHD-*g*-PCL proved to be an effective compatibilizer for polyethylene/polar polymer by improving the interfacial adhesion between separated phases, which was confirmed by microscopy studies together with the tensile tests.

Acknowledgments

The authors are grateful for subsidy provided by the National Natural Science Foundation of China (Nos. 50703040, 20734002), and by the Special Funds for Major State Basis Research Projects (No. 2005CB623800) from the Ministry of Science and Technology of China.

Appendix. Supplementary material

The supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.polymer.2010.06.006

References

[1] Baldwin FP, Ver Strate G. Rubber Chem Technol 1972;45(3):709.
[2] Cozewith C, Ver Strate G. Macromolecules 1971;4:482.
[3] Cheng HN. J Appl Polym Sci Appl Polym Symp 1988;43:129.
[4] Dong JY, Hong H, Chung TC. Macromolecules 2003;36:6000–9.
[5] Lu HL, Hong S, Chung TC. Macromolecules 1998;31:2028–34.
[6] Li XF, Hou ZM. Macromolecules 2005;38:6767–9.
[7] Li XF, Hou ZM. Chem Commun 2007:4137–9.
[8] Pan L, Hong M, Li YS. Macromolecules 2009;42:4391–3.
[9] Hong M, Pan L, Li YS. J Polym Sci Part A Polym Chem 2010;48:1764–72.
[10] Suzuki J, Shiono T. J Appl Polym Sci 1999;72:103–8.
[11] Simanke AG, Galland GB. J Polym Sci Part A Polym Chem 2002;40:471–85.
[12] Naga N. Polymer 2006;47:520–6.
[13] Shiono T. J Polym Sci Part A Polym Chem 2007;45:4581–7.
[14] Heiser DE, Mülhaupt R. Macromol Chem Phys 2005;206:195–202.
[15] Nishii K, Shiono T. Chem Lett 2008;37:590–1.
[16] Naga N. J Polym Sci Part A Polym Chem 2005;43:1285–91.
[17] Chung TC. Functionalization of polyolefins. San Diego, CA: Academic Press; 2002.
[18] Chung TC. Prog Polym Sci 2002;27:39–85.
[19] Dong JY, Hu YL. Coord Chem Rev 2006;250:47–65.
[20] Pan L, Liu JY, Ye WP, Hong M, Li YS. Macromolecules 2008;41:2981–3.
[21] Dong JY, Chung TC. Macromolecules 2002;35:2868–70.
[22] Proto A, Avagliano A, Saviello D, Capacchione C. Macromolecules 2009;42:6981–5.
[23] Nomura K, Itagaki K. Macromolecules 2009;42:5097–103.
[24] Ishihara T, Ban HT, Hagihara H, Shiono T. J Polym Sci Part A Polym Chem 2007;45:5731–40.
[25] Chung TC, Janvikul W, Bernard R, Jiang GJ. Macromolecules 1994;27:26–31.
[26] Ho CH, Wang CH, Lin CI, Lee YD. Polymer 2008;49:3902–10.
[27] Robin JJ, Boyer C, Boutevin B, Loubat C. Polymer 2008;49:4519–28.
[28] Coltelli MB, Passaglia E, Ciardelli F. Polymer 2006;47:85–97.
[29] Toyotaa A, Mizunob A, Tsutsuic T, Kanekod H, Kashiwa N. Polymer 2002;43:6351–5.
[30] Tselios Ch, Bikiaris D, Maslis V, Panayiotou C. Polymer 1998;39:6807–17.
[31] Chung TC, Lu HL, Ding RD. Macromolecules 1997;30:1272–8.
[32] Kashiwa N, Matsugi T, Kojoh SI, Kaneko H, Kawahara N. J Polym Sci Part A Polym Chem 2003;41:3657–66.
[33] Zheng Y, Li YG, Pan L, Li YS. Polymer 2007;48:2496–502.
[34] Chiu FC, Fu SW, Chuang WT, Sheu HS. Polymer 2008;49:1015–26.
[35] Deng KQ, Winnik MA, Yan N, Jiang ZH, Yaneff PV, Ryntz RA. Polymer 2009;50:3225–33.
[36] Park CE, Kim S, Kin JK. Polymer 1997;38:1809–15.
[37] Tang LM, Hu T, Pan L, Li YS. J Polym Sci Part A Polym Chem 2005;43:6323–30.
[38] Chung TC, Rhubright D. Macromolecules 1994;27:1313–9.
[39] Lu YY, Hu YL, Chung TC. Polymer 2005;46:10585–91.
[40] Nomura K, Liu JY, Fujiki M, Takemoto A. J Am Chem Soc 2007;129:14170–1.
[41] Alfrey T, Goldfinger G. J Chem Phys 1944;12:205.

[42] Srivastava AK, Kamal M, Kaur M, Pandey S, Daniel N, Chaurasia AK, et al. J Polym Res 2002;9:213–20.

[43] Alfrey T, Goldfinger G. J Chem Phys 1946;14:115–6.

[44] Sun WH, Liu SF, Zhang WJ, Zeng YN, Wang D, Liang TL. Organometallics 2010;29:732–41.

[45] Chung TC, Janvikul W, Lu HL. J Am Chem Soc 1996;118:705–6.

[46] Hong H, Chung TC. Macromolecules 2004;37:6260–3.

[47] Fujita T, Mitani M, Mohri J, Yoshida Y, Saito J, Ishii S, et al. J Am Chem Soc 2002;124:3327–36.

[48] Li XF, Dai K, Ye WP, Pan L, Li YS. Organometallics 2004;23:1223–30.