

SYNTHESIS OF FUNCTIONAL POLYETHYLENE *via* COPOLYMERIZATION OF ETHYLENE AND SUBSTITUTED ALLENE USING BIS(β -ENAMINOKETONATO)TITANIUM CATALYSTS*

Miao Hong^{a,b}, Bai-xiang Li^a and Yue-sheng Li^{a**}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b Graduate School of the Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China

Abstract Novel copolymerization of ethylene with substituted allenes ($\text{CH}_2=\text{C}=\text{CH}-\text{R}$, **1**: $\text{R} = n$ -butyl, **2**: $\text{R} = n$ -octyl) using bis(β -aminoketonato)titanium catalysts $[\text{PhN}=\text{C}(\text{R}_2)\text{CHC}(\text{R}_1)\text{O}]_2\text{TiCl}_2$ (**1a**: $\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{CH}_3$; **1b**: $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{CF}_3$) has been investigated. In the presence of modified methylaluminoxane, these catalysts can copolymerize ethylene with substituted allenes, affording copolymers with unimodal molecular weight distributions and homogeneous compositions. By varying the reaction conditions, the comonomer incorporation can be tuned in the range of 0–3.6 mol%. ^1H -NMR spectra reveal that the copolymerization proceeds through 1,2-insertion fashion of allene comonomer exclusively, and the regioselective nature maintains under various reaction conditions. The retained intra-chain double bond can be converted into the epoxy group under mild conditions.

Keywords: Ziegler-Natta polymerization; Functional polyethylene; Allene.

INTRODUCTION

Despite commercial importance of polyolefin, the lack of functional groups in polyolefins has significantly limited many end uses, particularly those in which adhesion, dyeability, paintability, printability and compatibility with other polymers are paramount^[1–3]. It has been a long scientific challenge in exploring the routes to functionalize polyolefins. In recent years, the precise and efficient synthesis of polyethylene bearing double bonds *via* copolymerization of ethylene with dienes has attracted wide attention because the retained double bonds can be converted into functional groups. Aromatic dienes^[4], linear dienes^[5] and cyclic dienes^[6] are the common dienes and the copolymerization behaviors of ethylene with these dienes have been widely investigated. Compared with these diene, allene derivative is a very promising and attractive monomer with cumulative double bonds, which exist in many natural products with interesting biological activities^[7, 8]. During the last 8–10 years, allene derivatives have been shown to demonstrate nice reactivities as well as selectivities, and widely used as starting materials to synthesize various organic compounds and polymeric materials. Our interest has been focused on the utilization of allene derivatives as the comonomer in copolymerization with ethylene. If one of the cumulative double bonds selectively participates in copolymerization, the remaining double bonds in copolymers can be utilized in preparation of functional polyethylene. However, to date, the copolymerization of ethylene with allene derivatives has not been reported yet and the investigation of allene

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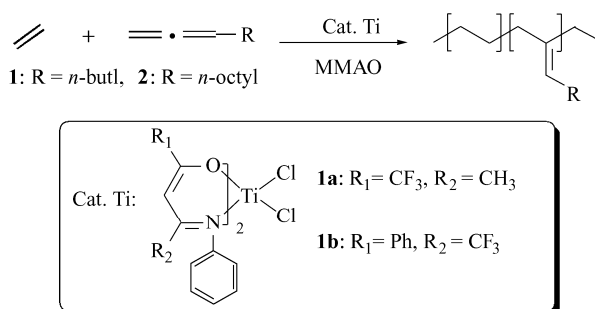
** Corresponding author: Yue-sheng Li (李悦生), E-mail: ysli@ciac.jl.cn

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derivatives was limited in homopolymerization^[9–16] and copolymerization with other monomer^[17]. Endo *et al.* developed a living coordination homopolymerization of allene derivatives by $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2/\text{PPh}_3$ system, which generally produced polymer with both 1,2- and 2,3-polymerized units^[11–14]. Shen *et al.* reported homopolymerization of *n*-octylallene by bis[*N,N*-(3,5-di-*tert*-butylsalicylidene) anilinato]titanium dichloride/ $\text{Al}(i\text{-Bu})_3$ system with 100% yield after aging at 80°C for 1 h and polymerizing at 80°C for 16 h^[15]. Very recently, the copolymerization of *n*-octylallene with styrene by using bis[*N,N*-(3,5-di-*tert*-butylsalicylidene) anilinato]titanium dichloride/ $\text{Al}(i\text{-Bu})_3$ system and subsequent functionalization have also been reported by Shen and coworkers^[17]. Therefore, if the allene derivative can successfully copolymerize with ethylene, it will be a new “reactive polyolefin intermediate” to synthesis functional polyethylene.

Herein, we report the novel copolymerization of ethylene with substituted allenes ($\text{CH}_2=\text{C}=\text{CH}-\text{R}$, **1**: R = *n*-butyl, **2**: R = *n*-octyl) 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**: $\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{CH}_3$; **1b**: $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{CF}_3$) (Scheme 1) which exhibited high activity towards ethylene polymerization and displayed excellent ability to copolymerize ethylene with cyclic monomer or α -olefin^[18, 19]. In the presence of modified methylaluminoxane (MMAO), the substituted allene is regioselectively incorporated into polymer chain *via* 1,2-insertion fashion exclusively. By varying the reaction conditions, the comonomer incorporation can be tuned in the range of 0–3.6 mol%. In addition, the research on the epoxidation of ethylene/substituted allene copolymer bearing intra-chain double bond is also discussed in this paper.



Scheme 1 The synthetic route for ethylene/substituted allene copolymer and the structures of catalysts used in this study

EXPERIMENTAL

Materials

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 an MBraun Solvent Purification System. Modified methylaluminoxane (MMAO, 7% Aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc and used without further purification. 1-Octyl bromide, 1-butyl bromide and 3-bromo-1-propyne purchased from Aldrich were dried over molecular sieve for 3 days and vacuum-distilled before use. Magnesium powder was purchased from Aldrich and used without further purification. Catalysts **1a–1b** were synthesized by the method described in the literature^[18].

Characterization

All ^1H - and ^{13}C -NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (399.65 MHz for ^1H , 100.40 MHz for ^{13}C), and all chemical shifts δ were given referenced to Me_4Si . The monomer contents of copolymers were determined by ^1H -NMR spectra and calculated according to the formula $\text{BAE mol\%} = [4I_{\delta=5.26}/(I_{\delta=0.9-1.51} - 3I_{\delta=5.26})] \times 100\%$, $\text{OAE mol\%} = [4I_{\delta=5.26}/(I_{\delta=0.9-1.51} - 11I_{\delta=5.26})] \times 100\%$, where I is the peak area of the corresponding protons (BAE: *n*-butylallene; OAE: *n*-octylallene). 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 with

a 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 FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. 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 20 K/min and cooled down at a rate of 20 K/min.

Synthesis of Substituted Allene

A dry 500 mL three-necked flask was fitted with a dropping funnel, stirrer and condenser. Dried diethyl ether (50 mL), magnesium powder (3 g) and a small amount of iodine were added to the flask quickly under N₂ atmosphere, and the dropping funnel was charged with 1-octyl bromide (18 mL). A small amount of 1-octyl bromide was added to initiate the reaction before vigorous stir. Then the residual 1-octyl bromide was added dropwise slowly, and the reaction mixture was kept to boil gently for about 3 h. During this period, the reaction mixture gradually turned gray-black. After magnesium powder was reacted completely, the reaction mixture was cooled to -50°C and the dropping funnel was charged with 3-bromo-1-propyne (9 mL). When the addition of 3-bromo-1-propyne was complete, the reaction mixture was allowed to warm to room temperature and left stirring overnight. The ice water was slowly added to the reaction mixture and the organic layer is separated. The aqueous layer was extracted with three 50 mL portions of diethyl ether, and the combined diethyl ether solutions were washed with 50 mL of saturated aqueous Na₂CO₃ and NaCl in turn. The diethyl ether solution was dried over with anhydrous magnesium sulfate, filtered and stripped of solvent on a rotary evaporator. Distillation of the residue yielded *n*-octylallene (OAE, 11 g, 75%). By using a similar procedure, *n*-butylallene (BAE) was synthesized with yield of 70%.

Typical Polymerization Procedure

Polymerizations 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/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.

Epoxidation of Ethylene/Substituted Allene Copolymers

In a 250 mL, three-necked round bottom flask equipped with a magnetic stirrer, an amount of 200 mg of the copolymer was suspended in 40 mL toluene. The flask was heated to 65°C and then a toluene solution (10 mL) of *m*-chloroperbenzoic acid (10 equiv of the epoxy groups) was added dropwise. The reaction mixture was stirred for 6 h at 65°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.

RESULTS AND DISCUSSION

Synthesis of Substituted Allenes

The substituted allenes are synthesized by the reaction of grignard reagent and 3-bromo-1-propyne under -50°C and obtained in good yields (70%–75%). ¹H-NMR spectra of the OAE and BAE are shown in Fig. 1. The characteristic peaks ascribed to the methine and methylene groups in the cumulative double bond are observed at $\delta = 5.09$ and 4.14, respectively. The peaks at $\delta = 2.00$ and 0.9 are attributed to the protons of methylene groups near the cumulative double bond and methyl groups in the chain end, respectively, while the peaks at the range of $\delta = 1.2$ –1.5 are attributed to the methylene groups in the chain. The successful synthesis of allene monomers can also be proved by the IR spectrum (Fig. 2), which displays characteristic absorption at 1964 cm⁻¹ attributed to the stretching vibration of the cumulative double bond.

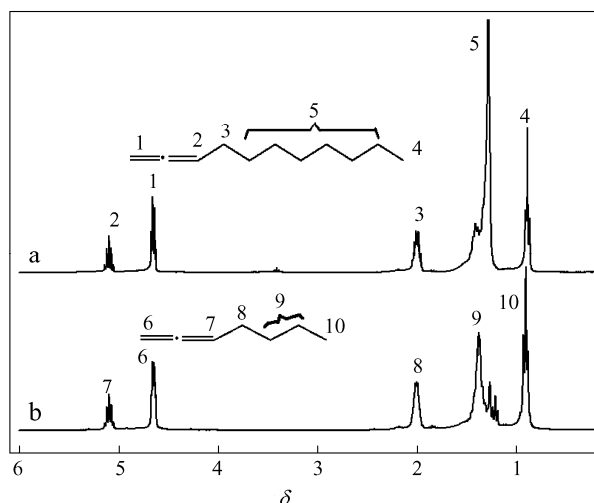


Fig. 1 ^1H -NMR spectra of substituted allenes in CDCl_3 at 25°C : (a) OAE monomer and (b) BAE monomer

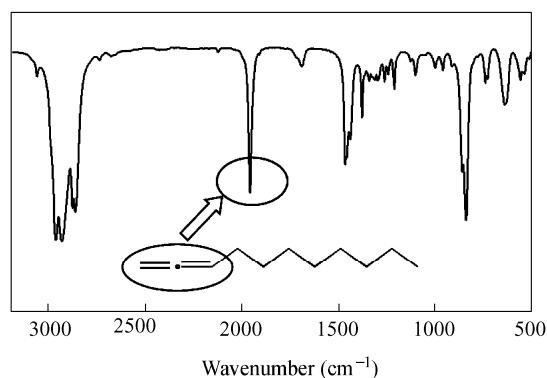


Fig. 2 FTIR spectrum of OAE monomer

Copolymerization of Ethylene/Substituted Allene

The copolymerization of ethylene with substituted allene catalyzed by complexes **1a–1b** in the presence of MMAO is explored under different experimental conditions. Note that catalysts **1a–1b** can copolymerize ethylene with substituted allene, and the typical results are summarized in Table 1. As observed, the catalytic performances are strongly influenced by the reaction conditions. The comonomer incorporation was enhanced by elevating the reaction temperature (Table 1, entries 10, 11 and 14) or increasing comonomer concentration (Table 1, entries 11–14). The high comonomer incorporation up to 3.6 mol% has been achieved by **1b**-catalyzed copolymerization of ethylene and OAE at 40°C (Table 1, entry 13). However, the catalytic activity and comonomer incorporation are not influenced by the variety of comonomers and catalyst structures. We tried to carry out the homopolymerization of substituted allene catalyzed by the present catalyst system under the same conditions used for copolymerization. However, no activity was observed.

Typical GPC profiles of ethylene/substituted allene copolymers are presented in Fig. 3. The curves are all unimodal with relatively narrow molecular weight distributions, which is consistent with the predominance of single homogeneous catalytic species. In addition, the high molecular weight shoulders are not detected in the GPC elution traces, suggesting that the copolymerization proceeds without cross-linking. The thermal transition temperature of ethylene/substituted allene copolymers was examined by DSC analysis. Figure 4 shows the DSC curves of second heating scans for typical copolymers at a rate of 20 K/min. As observed, the melting temperature (T_m) decreased from 124°C to 108°C with increasing the comonomer incorporation. The DSC

curves a and b are unimodal indicating the obtained copolymer possesses the homogeneous composition. Interestingly, the bimodal distribution was observed for an ethylene/OAE copolymer at higher OAE incorporation (3.6 mol%) (curve c), which may be attributed to the different crystalline forms after copolymerizing the long chain substituted allene (OAE) because the copolymer with this incorporation has the unimodal molecular weight distribution.

Table 1. Copolymerization of ethylene with substituted allenes by bis(β -enaminoketonato)titanium/MMAO catalytic systems^a

Entry	Cat. (μ mol)	Comon.	Conc. ^b	Temp. (°C)	Activity ^c	Incorp. ^d (mol%)	$M_w^e \times 10^{-3}$	M_w/M_n^e	T_m^f (°C)
1	1a (8)	BAE	0.0625	25	360	0.54	108	1.91	124.2
2	1a (8)	BAE	0.0625	40	250	0.59	103	2.07	122.9
3	1a (16)	BAE	0.2000	40	48	2.50	80	2.18	116.0
4	1b (8)	BAE	0.0625	25	350	0.45	40	1.80	126.3
5	1b (8)	BAE	0.0625	40	330	0.48	30	1.91	124.3
6	1b (16)	BAE	0.2000	40	50	2.30	16	2.12	115.5
7	1a (8)	OAE	0.0625	25	300	0.42	110	1.75	125.0
8	1a (8)	OAE	0.0625	40	220	0.55	104	1.96	124.7
9	1a (16)	OAE	0.2000	40	48	1.93	92	2.20	118.6
10	1b (8)	OAE	0.0625	25	320	0.40	52	2.18	126.9
11	1b (8)	OAE	0.0625	40	300	0.56	32	1.93	126.0
12	1b (16)	OAE	0.2000	40	45	1.90	24	2.08	119.2
13	1b (16)	OAE	0.2500	40	27	3.60	13	1.81	108.0
14	1b (8)	OAE	0.0625	60	240	0.72	14	1.74	124.0

^a Conditions: ethylene 0.1 MPa, Al/Ti (molar ratio) = 2000, $V_{\text{total}} = 50$ mL, reaction for 10 min;

^b Comonomer concentration charged (mol/L);

^c Catalytic activity: kg/(mmol_{Ti}·h);

^d Comonomer incorporation (mol%) established by ¹H-NMR spectra;

^e Weight-average molecular weights and polydispersity indices determined by high temperature GPC at 150°C in 1,2,4- $\text{C}_6\text{Cl}_3\text{H}_3$ versus narrow polystyrene standards;

^f Melting temperatures determined by DSC

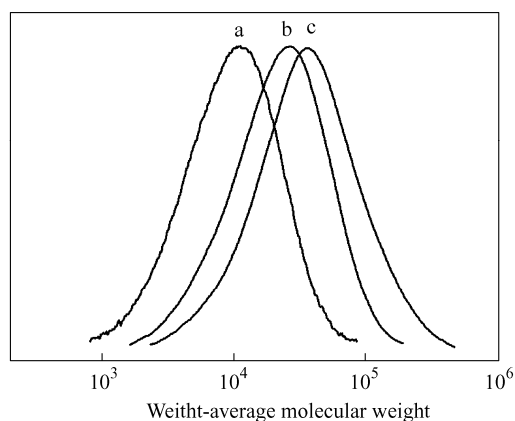


Fig. 3 GPC curves of ethylene/allene copolymer: (a) ethylene/OAE copolymer: $M_n = 13 \times 10^3$, PDI = 1.81 (Table 1, entry 13), (b) ethylene/BAE copolymer: $M_n = 30 \times 10^3$, PDI = 1.91 (Table 1, entry 5), (c) ethylene/OAE copolymer: $M_n = 52 \times 10^3$, PDI = 2.18 (Table 1, entry 10)

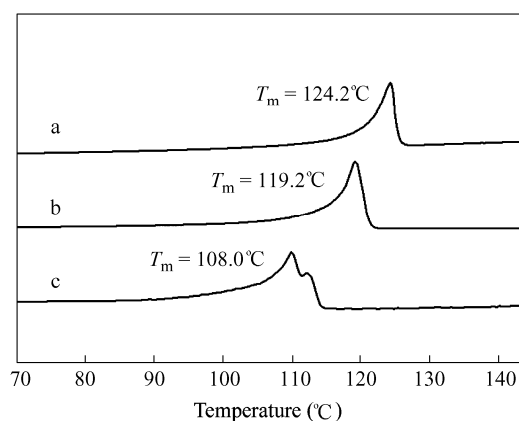


Fig. 4 DSC curves of ethylene/allene copolymer: (a) ethylene/BAE copolymer (0.54 mol%) (entry 1), (b) ethylene/OAE copolymer (1.90 mol%) (entry 12), (c) ethylene/OAE copolymer (3.60 mol%) (entry 13)

The microstructures of the ethylene/substituted allene copolymers produced by catalysts **1a–1b** have been established by ¹H-NMR and ¹³C-NMR spectra. The typical ¹³C-NMR spectrum is provided in Fig. 5. The peaks at $\delta = 140.2$ and 125.6 are attributed to quaternary carbons and tertiary carbons in the intra-chain double bond

(marked as 1 and 2 in Fig. 5) generated from 1,2-insertion fashion of OAE, while the peaks ascribed to 2,3-insertion fashion are not observed (about $\delta = 155.0$ and 109.1). It is noteworthy that the OAE is regioselectively incorporated into the polymer chain *via* 1,2-insertion fashion exclusively. The peak at $\delta = 37.6$ is ascribed to the methylene groups near double bond (marked as 3). Additionally, the peaks at $\delta = 14.2$, 23.0 and 32.4 are attributed to the chain end of OAE (marked as 11–13) and those peaks in the region of $\delta = 31.1$ – 28.4 are assigned to methylene groups in OAE (marked as 5–10) and ethylene units. The typical ^1H -NMR spectrum of ethylene/OAE copolymer is shown in Fig. 6. The peaks at $\delta = 5.26$ and 2.14 are attributed to the protons in intra-chain double bond and methylene groups near double bond, respectively (marked as 1 and 2 respectively).

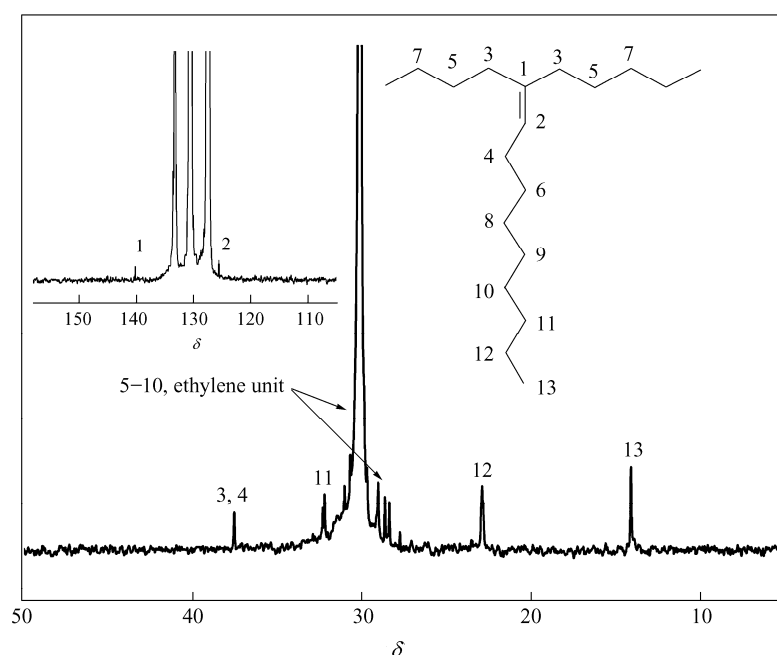


Fig. 5 ^{13}C -NMR spectra of ethylene/OAE copolymer in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 125°C (OAE% = 3.6 mol%)

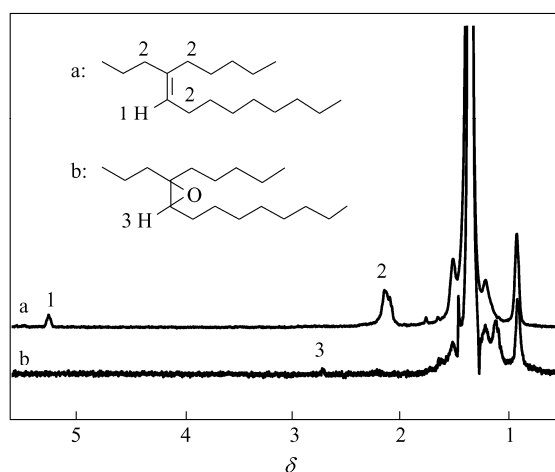


Fig. 6 ^1H -NMR spectra of ethylene/OAE copolymer before and after epoxidation in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 125°C : (a) ethylene/OAE copolymer (OAE% = 3.6 mol%), (b) ethylene/OAE copolymer after epoxidation

The peaks appeared from $\delta = 1.5$ to 1.2 are attributed to methylene groups in OAE and ethylene units while the peak at $\delta = 0.9$ is attributed to methyl groups in polymer chain and OAE. The peak at $\delta = 5.26$ further confirms the regioselective incorporation of OAE, because the peak ascribed to 2,3-insertion fashion is not observed (around $\delta = 4.6$)^[12]. Remarkably, the regioselective nature maintains even at higher reaction temperature (60°C , Table 1, entry 14). Consequently, the intra-chain double bonds were retained near the main chain and no evidence of cross-linking was detected. For ethylene/BAE copolymer, the ^{13}C - and ^1H -NMR spectra are similar to ethylene/OAE copolymer, also suggesting the regioselective copolymerization.

Epoxidation of Ethylene/Substituted Allene Copolymers

The ethylene/substituted allene copolymers bearing intra-chain double bonds are the promising candidates for preparation of functional polyethylene with improved adhesion, dyeability and paintability. Like the terminal double bond^[5], the epoxidation of intra-chain double bond is not inhibited by the insolubility of the copolymers and can be completely converted into the epoxy groups using *m*-chloroperbenzoic acid as the oxidant in toluene at 65°C for 6 h. As shown in the ^1H -NMR spectrum (Fig. 6), after epoxidation, the characteristic peak of intra-chain double bond in OAE at $\delta = 5.26$ disappears completely while the peak at $\delta = 2.72$ corresponding to the epoxy group appears, indicating the epoxidation has been achieved.

CONCLUSIONS

Bis(β -enaminoketonato) titanium complexes **1a–1b** in the presence of MMAO can copolymerize ethylene with substituted allenes, affording copolymers with unimodal molecular weight distributions and homogeneous composition. The catalytic performances under different reaction conditions have been fully investigated. By varying the reaction conditions, the comonomer incorporation can be tuned in the range of 0–3.6 mol%. ^1H -NMR spectra reveal the substituted allene is regioselectively incorporated into polymer chain *via* 1,2-insertion fashion exclusively and the regioselective nature maintains under various reaction conditions. The retained intra-chain double bond can be converted into the epoxy group under mild conditions.

REFERENCES

- 1 Dong, J.Y. and Hu, Y.L., *Coord. Chem. Rev.*, 2006, 250: 47
- 2 Chung, T.C., *Prog. Polym. Sci.*, 2002, 27: 39
- 3 Younkin, T.R., Connor, E.F., Henderson, J.I., Frendrich, S.K., Grubbs, R.H. and Bansleben, D.A., *Science*, 2000, 287: 460
- 4 Dong, J.Y. and Chung, T.C., *Macromolecules*, 2002, 35: 2868
- 5 Nomura, K., Liu, J.Y., Fujiki, M. and Takemoto, A., *J. Am. Chem. Soc.*, 2007, 129: 14170
- 6 Pan, L., Hong, M., Ye, W.P. and Li, Y.S., *Macromolecules*, 2009, 42: 4391
- 7 Endo, T. and Tomita, I., *Prog. Polym. Sci.*, 1997, 22: 565
- 8 Ma, S.M., *Chem. Rev.*, 2005, 105: 2829
- 9 Legand, J., Boucher, J. and Anderson, K., *J. Polym. Sci., Polym. Chem. Ed.*, 1977, 15: 2785
- 10 Takahashi, T., Yokozawa, T. and Endo, T., *J. Polym. Sci., Polym. Chem. Ed.*, 1992, 30: 583
- 11 Takagi, K., Tomita, I. and Endo, T., *Macromolecules*, 1997, 30: 7386
- 12 Endo, T., Takagi, K. and Tomita, I., *Tetrahedron*, 1997, 53: 15187
- 13 Tomita, I., Kondo, Y., Takagi, K. and Endo, T., *Macromolecules*, 1994, 27: 4413
- 14 Mochizuki, K. and Tomita, I., *Macromolecules*, 2006, 39: 6336
- 15 Zhu, W.W., Ni, X.F. and Shen, Z.Q., *Chem. J. Chinese Universities*, 2008, 29: 2554
- 16 Zhang, X.H., Shen, Z., Li, L.T., Lu, G.L., Gu, L.N. and Huang, X.Y., *Polymer*, 2007, 48: 5507
- 17 Ni, X.F., Zhu, W.W. and Shen, Z.Q., *Polymer*, 2010, 51: 2548
- 18 Li, X.F., Dai, K., Ye, W.P., Pan, L. and Li, Y.S., *Organometallics*, 2004, 23: 1223
- 19 Tang, L.M., Duan, Y.Q., Pan, L. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2005, 43: 1681