



# Elastomeric properties of ethylene/1-octene random and block copolymers synthesized from living coordination polymerization



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## ABSTRACT

The elastomeric performance of a series of ethylene/1-octene random and block copolymers prepared from living coordination polymerization was studied in this work. All the polymer samples exhibited good toughness. The living random copolymers had better elasticity than commercial metallocene random copolymers. The strain recovery of the living random copolymers was about 90% with an applied strain up to 800%. It was demonstrated that the copolymer elasticity was mainly determined by their block structure, with little influence by their molecular weight. It was also found that either too high or too low content of hard-block content deteriorated the copolymer elastomeric behavior. The diblock copolymer having about 42 wt% hard block content (LBC1) gave the best elasticity among the studied block copolymers and retained the strain recovery about 80% under the applied strain of 600%.

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## 1. Introduction

Ethylene/ $\alpha$ -olefin copolymer with high comonomer incorporation is one of the most widely-used high performance thermoplastic elastomers (TPEs) [1]. Compared with other TPE types, polyolefin-based thermoplastic elastomers have received considerable attention due to their better chemical resistance, lower density, excellent weatherability and lower cost for elasticity formation [2]. For good elastomeric property of low modulus and high recovery from large deformation, crystallinity must be lower than 20 wt% [3], which is usually realized by incorporating  $\alpha$ -olefins, such as propylene, 1-butene, 1-hexene and 1-octene into polyethylene main chain to disrupt crystallization of the methylene sequences. Thermal and mechanical properties of the ethylene/ $\alpha$ -olefin random copolymer elastomers (POE) have been well studied since their commercialization by DOW and ExxonMobil [4–7]. Most of these commercially available POE products are made from metallocene catalysts and were usually compared with those copolymers from Z-N catalysts. It has been demonstrated that metallocene-catalyzed ethylene/ $\alpha$ -olefin copolymers have

narrower molecular weight and composition distributions than Z-N's, and thus have better mechanical properties [4]. However, little work reported on the comparison of mechanical properties between the metallocene-catalyzed copolymers and those from living coordination copolymerization with post-metallocene catalysts.

In 2006, a novel type of ethylene/1-octene olefin block copolymer (OBC) was commercialized by DOW through a chain shuttling polymerization (CSP) mechanism [8,9]. In CSP, two post-metallocene catalysts are employed, with one catalyst good at ethylene/ $\alpha$ -olefin copolymerization that generates soft amorphous copolymer segments and the other catalyst poor in the copolymerization that produces hard semi-crystalline segments. The hard and soft segments are shuttled between the two metallic active centers through an appropriate chain shuttling agent. The multi-block copolymers (hard-soft-hard ...) are thus formed. It was found that OBC exhibited better elasticity at high temperature than POE [10]. Although great attention has been paid to OBC mechanical properties and melt phase behaviors [11–17], their structure/property relationships are still lacking. In OBC, the soft and hard segments are statistical numbers and lengths. The comonomer incorporation in the hard and soft segments is not clear. There is usually certain amount of random copolymer impurities in the commercial OBC products [18,19]. In researching OBC performance, it is difficult to focus on a single factor in establishing a clear relationship between chain microstructure and property. In contrast,

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living olefin copolymerization can provide well defined and controlled polyolefin chain microstructures. Polyolefins with an explicit chain microstructure can be obtained from living coordination polymerization.

In the recent years, numerous ethylene/ $\alpha$ -olefin block copolymers were synthesized through living olefin polymerization [20–22]. For example, PE-b-PEP-b-SPP and PE-b-PEP-b-PE triblock copolymers were first synthesized by Fujita group using a fluorinated FI-Ti catalyst, which is a well-known living coordination polymerization catalyst system [23]. PE-b-Poly(ethylene-co-1-hexene) diblock copolymers were also synthesized by Fujita group [24]. Coates group reported the synthesis of iPP-b-PEP-b-iPP triblock copolymers, iPP-b-PEP-b-iPP-b-PEP-b-iPP pentablock copolymers, and iPP-b-PEP-b-iPP-b-PEP-b-iPP-b-PEP-b-iPP heptablock copolymers using another fluorinated FI-Ti catalyst [25]. The advent of living olefin polymerization technique allows precise design of the polyolefin chain microstructure, so as to tailor-make polyolefin materials [22]. Some authors noted that ethylene/ $\alpha$ -olefin block copolymers synthesized from living polymerization technique exhibited good elastomeric behavior and excellent toughness [26]. However, detailed mechanical studies on the living block copolymers were very scattered.

In our previous work, we synthesized a series of ethylene/1-octene random and block copolymers by living coordination polymerization [27–29] and demonstrated that the copolymer samples possessed narrower intra-chain composition distributions than those prepared from conventional metallocene catalysts [19]. The objective of this work is to investigate their elastomeric behaviors.

## 2. Materials and methods

The ethylene/1-octene copolymer samples used in this work were synthesized from bis[N-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium(IV) dichloride/dMAO [30]. The synthesis procedures for copolymer samples and the characterization of molecular weight, composition and DSC properties have been described in our previous papers [27–29]. The characteristics of the random copolymer samples are listed in Table 1 and those of the block copolymers are in Table 2. LRC1 and LRC2 in Table 1 are living random copolymers made from the living coordination polymerization. MRC is a commercial ethylene/1-octene random copolymer sample (Engage 8150) produced from CGC catalyst by DOW Chemical Company. LBC in Table 2 is living block copolymers from the living coordination polymerization.

The samples that submitted to mechanical tests were solution cast into uniform films with thickness between 70 and 100  $\mu\text{m}$ . Xylene was used as the solvent. The film thickness was measured by a digital electron thickness gauge. Dumbbell-shaped tensile specimens for uniaxial elongation tests and hysteresis experiments were cut from the solution cast films. The tensile stress–strain behavior was performed on the universal material tester Zwick/Roell Z020 at

room temperature with the cross-head speed of 800%/min. The test method is GB1040.2-2006. Each test was repeated at least four times. The initial length of the specimens between the clamps was 50 mm, having width of 4 mm. For the elastic strain recovery test, the hysteresis experiments were performed on the MTS tensile instrument (MTS Systems China Co. Ltd) at room temperature. The test method is GB1040.3-2006. The fixed strain of 300% or a gradually increased strain between 50 and 800% was used in the hysteresis experiments. The specimens were cyclically loaded to the targeted strain and unloaded to stress zero with the strain rate of 125%/min. The initial clamp distance was 80 mm, with the width of 6 mm, the force transducer was 2.5 KN. The strain recovery in the hysteresis test was calculated as: Strain Recovery =  $(1 - \epsilon_{\text{plastic}} / \epsilon_{\text{applied}}) \times 100\%$ , where  $\epsilon_{\text{applied}}$  is the applied strain,  $\epsilon_{\text{plastic}}$  is the residual plastic strain, after the stress was unloaded to zero in each cycle.

## 3. Results and discussion

### 3.1. Random copolymers

As shown in Table 1, LRC1 and LRC2 possessed almost the same average 1-octene incorporation, the same molecular weight distribution polydispersity index, the same melting temperature and crystallinity. However, the weight-average molecular weight of LRC2 (608.5 kg/mol) is almost doubled than LRC1 (317.9 kg/mol). The stress–strain curves of these random copolymers are shown in Fig. 1 and the tensile properties are listed in Table 1. All these copolymers possessed very good toughness, as the samples were not broken at the strain of 1200% with the strain speed of 800%/min.

To study elasticity of the elastomer samples, the hysteresis experiments were first performed under the fixed strain of 300%. Fig. 2 shows their hysteresis curves with ten recycles. All the samples suffered prominent deformation after the first load cycle (with about 30% residual strain). The solid state morphology structure obviously changed in the first cycle. However, no further change was observed in the subsequent load cycles, as the hysteresis loop after the second cycle showed little difference. Fig. 3 compares the evolution of the strain recovery with cycle times. The strain recovery of LRC1 and LRC2 were stable over 85%, almost constant as the load cycle times increased. While the strain recovery of MRC showed a slight decrease trend with the load cycle times. The order of the strain recovery of these random copolymers followed: MRC < LRC1  $\approx$  LRC2.

The hysteresis experiment was then performed under the gradually increased strains between 50 and 800%. The results are shown in Fig. 4. All samples gave a typical elastomeric performance. The hysteresis loop enlarged gradually as the applied strain increased. For LRC1 and LRC2, the residual permanent strain (unrecovered plastic deformation) after each cycle remained less than 100%. Fig. 5 compares the strain recoveries. The elasticity of LRC1

**Table 1**  
Characteristics of the ethylene/1-octene random copolymers.

Sample no <sup>a</sup>	$\bar{F}_2^b$ (mol%)	$M_w^c$ ( $10^4$ g/mol)	PDI <sup>c</sup>	$T_g^d$ ( $^{\circ}\text{C}$ )	$T_c^d$ ( $^{\circ}\text{C}$ )	$T_m^d$ ( $^{\circ}\text{C}$ )	$\Delta H_m^d$ (J/g)	$X_{C,DSC}^e$ (wt%)	5% secant modulus (MPa)	Ultimate tensile stress (MPa)	Ultimate elongation (%)
LRC1	14.7	31.79	1.14	−61.2	8.3	37.4	25.4	9	$2.8 \pm 0.2$	>15	>1200
LRC2	14.5	60.85	1.15	−58.0	14.3	36.9	26.5	9	$6.6 \pm 0.3$	>22	>1200
MRC <sup>f</sup>	13.3	12.13	2.22	−55.2	35.2	50.9	40.0	14	$11.3 \pm 0.3$	>7.9	>1200

<sup>a</sup> LRC: living random copolymer (random copolymer made from living coordination polymerization), MRC: metallocene-catalyzed random copolymer.

<sup>b</sup> Average 1-octene molar incorporation in the copolymers, determined by the high temperature  $^{13}\text{C}$  NMR.

<sup>c</sup> Determined by high temperature GPC.

<sup>d</sup> Determined by DSC.

<sup>e</sup> Crystallinity from heat of melting,  $X_{C,DSC} = \Delta H_m / \Delta H_m^0$ ,  $\Delta H_m^0 = 293$  J/g.

<sup>f</sup> Engage 8150, from DOW chemical.

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