

Regio- and Stereoselective Ring-Opening Metathesis Polymerization of 3-Substituted Cyclooctenes

Shingo Kobayashi, Louis M. Pitet, and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

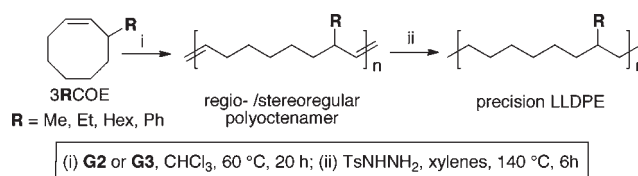
Supporting Information

ABSTRACT: 3-Substituted *cis*-cyclooctenes (3RCOE, R = methyl, ethyl, hexyl, and phenyl) were synthesized and polymerized, and the polymers therefrom were hydrogenated to prepare model linear low density polyethylene (LLDPE) samples. The ring-opening metathesis polymerization (ROMP) of the 3RCOE using Grubbs' catalyst proceeded in a regio- and stereoselective manner to afford polyoctenamers [poly(3RCOE)] exhibiting remarkably high head-to-tail regioregularity and high *trans*-stereoregularity. The overall selectivity increases with the increasing size of the R substituent. Hydrogenation of poly(3RCOE)s afforded precision LLDPEs with R substituents on every eighth backbone carbon.

Precision control of polymer stereo- and regiochemistry is a powerful approach for the manipulation of polymer properties. This is particularly true in the case of polyolefins where tacticity and regiochemistry can have a dramatic influence on the thermal, rheological, and crystallization properties. While Zeigler/Natta, metallocene, and other single-site catalysts have revolutionized the polymerization of acyclic olefins, ring-opening metathesis polymerization (ROMP) of cyclic olefins followed by hydrogenation is an attractive, alternative approach to model polyolefins.^{1–3} The impressive tolerance of ruthenium-based metathesis catalysts to wide-ranging conditions and functionalities^{4,5} has enabled a variety of polyolefin structures using this combination of techniques. The ROMP of *cis*-cyclooctenes (COEs) represents a straightforward route to linear polyolefins due to the availability of suitable starting materials and substantial ring strain of the eight-membered ring. However, simple alkyl substituted cyclooctenes can be tedious to prepare,⁶ and the ROMP of 5-substituted cyclooctenes gives regio- and stereoirregular polymers.^{1,6} Motivated by the desire to efficiently prepare high molar mass linear low-density polyethylene, we explored the ROMP of 3-substituted cyclooctenes (3RCOE) and discovered that regio- and stereochemically pure polyoctenamers [poly(3RCOE)] resulted (Scheme 1). Here we describe these polymers and the saturated derivatives and provide a mechanistic rationale for the high level of selectivity.

There are only a few reports describing the regio- and stereoselective ROMP of the smaller cyclobutenes^{7–10} and only one report with 3-alkylated variants using Mo or W catalyst.⁷ Likewise, only two early reports exist describing the ROMP of 3-alkyl cyclooctenes (3RCOE),^{11,12} both of which employ classical tungsten hexachloride based catalysts. However, these poly(3RCOE)s were

Scheme 1



stereoirregular and no comment was provided with respect to the regiospecificity.^{11,12} Alternatively, the polymerization of the isomerically pure monocyclic hydrocarbon (3*S*)-methylcyclopent-1-ene with a Mo-centered catalyst gave a polymer reported to be regioregular.¹³ The ROMP of the strained cyclic olefin 1-methylbicyclo[2.2.1]-hept-2-ene gave perfectly head-to-tail regioregularity upon polymerization with a Re-based catalyst system.¹⁴ Also, the *cis*,*syndio* selective polymerization of dicarbomethoxynorbornenes has recently been reported using Mo- and W-based catalysts.¹⁵ Ru-based catalysts have to date yielded only a few polymers with microstructural homogeneity.^{8,9}

We prepared four 3RCOE derivatives starting with the simple allylic bromination of (COE) using *N*-bromosuccinimide.¹⁶ Methyl, ethyl, hexyl, and phenyl (Me, Et, Hex, and Ph, respectively) groups were then introduced by CuI-catalyzed nucleophilic substitution using the appropriate Grignard reagent (RMgX). Isolated yields of monomers were consistently high (60–80%) after purification by fractional distillation. The identities of the monomers were established by NMR spectroscopy and high-resolution mass spectrometry (see Supporting Information pp S12–S46).

The 3RCOE were polymerized with the Grubbs second generation catalyst (G2) at a ratio of [3RCOE]₀/[G2]₀ ≈ 4300 and [3RCOE]₀ ≈ 1.8 M in CHCl₃ (Table 1).^{17,18} We also showed that the molecular weight of poly(3RCOE)s can be readily controlled by adding *cis*-4-octene as a chain transfer agent¹⁹ (see Supporting Information pp S4–S5). The 3RCOE polymerization rates were notably lower than that of unsubstituted COE; only 38% of the 3HexCOE was consumed after 20 h using G2 while essentially all of the unsubstituted COE was consumed after several minutes.

All the poly(3RCOE) samples (R ≠ H) exhibit eight backbone signals in the ¹³C NMR spectra, unambiguously revealing a high degree of regio- and stereospecificity. The polymers all exhibit only two predominant olefinic signals (Figure 1) and one predominant allylic signal, indicating a single stereochemistry about the double bond and suggesting one of two possible regioregular scenarios,

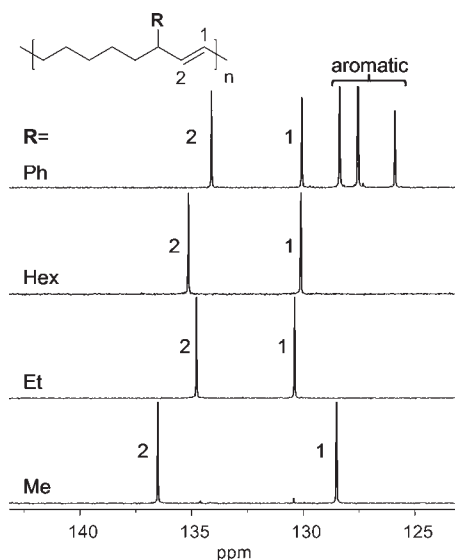
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Table 1. Characteristics of Poly(3RCOE)s from ROMP Using G2^a

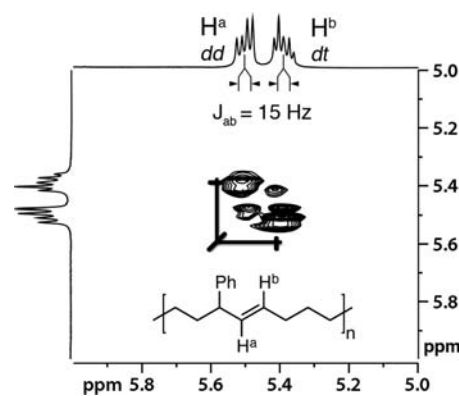
R ^b	conversion ^c %	M _n (kg mol ⁻¹)			trans ^c %	HT ^{c,f} %
		calcd ^d	obsd ^e	M _w /M _n ^e		
H	>99	467	294	1.40	73.4	
Me	93	491	341	1.64	96.8	93.5
Et	56	329	220	1.40	98.5	96.8
Hex	38	313	162	1.52	98.8	98.0
Ph	84	664	468	1.32	98.4	99.9

^a Polymerization performed in CHCl₃ at 60 °C for 20 h; [3RCOE]₀/[G2]₀ ≈ 4300; [3RCOE]₀ ≈ 1.8 M. ^b 3-Position substituent identity. ^c Determined by ¹H NMR spectroscopy. ^d M_{n,calcd} = (MW of 3RCOE) × [3RCOE]₀/[G2]₀ × fractional conversion. ^e Determined by SEC with a MALLS detector using THF as an eluent at 30 °C. ^f Head-to-tail content.

**Figure 1.** Olefinic and aromatic region of ¹³C NMR spectra for poly(3RCOE)s prepared with G2.

namely perfectly head-to-tail (HT) or alternating head-to-head (HH) and tail-to-tail (TT) addition. Regio- and stereorandom polymerization of these asymmetric monomers would consequently lead to eight olefinic signals in the ¹³C NMR spectra.¹ Poly(3MeCOE) showed minor impurities in the ¹³C spectrum, which are attributed to stereo- and regiochemical irregularities (see Supporting Information pp S47, S50).

¹H NMR and IR spectroscopies were used to distinguish between the two stereochemical possibilities (i.e., *cis* or *trans*) and between the two possible regular regioisomers (i.e., HT or HH-*alt*-TT). As an example, the magnitude of the coupling constant for the two distinct olefinic signals in the ¹H NMR spectrum of poly(3PhCOE) (*J*_{ab} = 15.3 Hz) is consistent with a *trans* configuration about the double bond (Figure 2). In poly(3MeCOE), the small amount of the *cis* stereoisomer gives an olefinic coupling constant of 11.0 Hz compared to 15.3 Hz for the *trans* isomer. The preferred *trans* selectivity during conventional cross-metathesis and ROMP under Ru-catalyzed conditions has been established and is amplified in this system by the sterically cumbersome substituent in the 3-position.

**Figure 2.** Olefinic region of ¹H NMR spectra and ¹H–¹H correlated spectra of poly(3PhCOE) polymer prepared with G2.

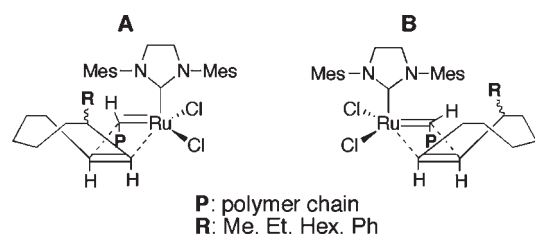
IR spectra of all polymers displayed strong absorptions at 960 cm⁻¹ (e.g., see p S54), also indicating the predominance of *trans* stereochemistry.

A correlation between the two olefinic signals in monomeric 3PhCOE is expected (p S44), and the correlation between the olefinic signals H^a and H^b in the poly(3PhCOE) (Figure 2) is strongly supportive of perfectly HT regioregularity. Additionally, the doublet of doublet and doublet of triplet multiplicities for H^a and H^b, respectively, are consistent with HT specificity. The alternate regioregular isomer HH-*alt*-TT would give two distinct olefinic signals exhibiting doublet (d) and triplet (t) multiplicities in the ¹H NMR spectrum, and the signals would not be correlated due to the relatively distant spatial proximity. ¹H NMR spectroscopic analysis of model compounds (i.e., allyl phenyl substituted hydrocarbons) gives identical chemical shifts for the olefinic hydrogens and coupling constants for the all-*trans* configuration. The other poly(3RCOE)s give similar results with respect to regio- and stereoregularities (see Supporting Information, pp S6–S7, S47–S75).²⁶

The circumstances under which the regio- and stereospecificity arise can be attributed to the orientation of the catalyst–monomer pair during coordination. We propose a mechanism that accounts for these selectivities during ROMP (Scheme 2). The 3RCOE monomers can approach the propagating catalyst in two possible orientations assuming *trans* stereochemistry (as confirmed for this system). The two possibilities include one in which the R substituent is positioned either β to the ruthenium (Scheme 2, A) or γ to the ruthenium (Scheme 2, B).

To distinguish between these two possibilities, we examined the reaction product from a stoichiometric mixture of G2 and the 3RCOE monomers by ¹H NMR spectroscopy (Figure S3, p S8). Ring-opening *cis*-cyclooctene with G2 gives an unsubstituted benzyldene terminus [Ph–CH=CH–CH₂–...] with olefinic signals at 6.37 and 6.22 ppm having doublet and doublet of triplet multiplicity, respectively. The intensity of this hallmark signal decreased dramatically in samples of ring-opened 3RCOE in the stoichiometric reaction. Instead, olefinic signals corresponding to the R substituted benzyldene terminus [Ph–CH=CH–CHR–...] were observed with doublet and doublet of doublet multiplicities. This result strongly supports our hypothesis that the monomer insertion consistently proceeds with essentially perfect specificity. This analysis of the reaction product demonstrates in each case that the intermediate with R positioned γ to the ruthenium predominates (intermediate B in Scheme 2; see Supporting Information).^{7,8} The resultant high regio- and stereoselectivity presumably originates

Scheme 2. Orientation during Metathesis between 3RCOE Monomers and G2

Table 2. Thermal Properties of Poly(3RCOE)s and the Hydrogenated Derivatives^a

R ^b	unsaturated		saturated	
	T _g (°C)	T _g (°C)	T _g (°C)	T _m (°C)
Me	-67	-59 ^c		1.7 ^c
Et	-57	-73		
Hex	-71	-74		
Ph	-21	-15		

^aDSC measurements were performed with a rate of 10 °C/min.^bSubstituent identity. ^cMeasured with a rate of 2 °C/min.

from the steric repulsion between the substituent at the 3-position of COE derivatives (and the propagating chain) and the *N*-heterocyclic carbene (NHC) ligand on the ruthenium center.⁷ Chain transfer to the polymer would also be expected to occur regioselectively based on similar arguments.

Chemical hydrogenation of poly(3RCOE)s using *p*-toluenesulfonylhydrazide was successfully accomplished (see ¹H and ¹³C NMR spectra in the Supporting Information, pp S76–S103).²¹ The olefinic signals were absent in ¹H and ¹³C NMR spectra, and the ¹³C NMR spectra of the polymers contain precisely 6, 7, 11, and 9 signals respectively for the Me, Et, Hex, and Ph substituted analogs. These observations further provide strong evidence for regioregularity in the unsaturated precursors. The saturated polymers represent a series of precision LLDPE which have branch points located precisely on every eighth backbone carbon.²² Notably, our observations provide a structurally unique contribution to the existing library of precision LLDPEs prepared by ADMET; precision LLDPEs with branch points positioned on evenly numbered backbone carbons are presumably inaccessible using ADMET. In addition, the ROMP method allows ready access to high-molecular-weight materials (see Table 1 and Supporting Information Tables S2 and S3 on pp S4–S5).

Differential scanning calorimetry (DSC) analysis of the unsaturated and saturated polymers show clearly defined glass transition temperatures (T_g) (Table 2; Supporting Information p S9).²³ Furthermore, the saturated version of the Me substituted polymer showed not only a T_g at -59 °C but also melting and crystallization transitions at 1.7 and -13 °C, respectively. This is strikingly similar to values reported by Wagener and co-workers for the precision LLDPE having methyl groups on every ninth backbone carbon (Supporting Information, p S10).^{22,24}

ROMP of 3-substituted cyclooctenes using different derivatives of the Grubbs catalysts proceeded to afford polymers having essentially pure head-to-tail regioregularity and *trans*-stereoregularity. The poly(cyclooctene)s were hydrogenated to afford

precision LLDPEs having side-chain branches on every eighth backbone carbon. This methodology allows for the preparation of high molecular weight model LLDPEs from monomers synthesized from readily accessible starting materials in two reaction steps.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details and detailed characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

hillmyer@umn.edu

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