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Synthesis of Sequence-Specific Vinyl Copolymers by Regioselective ROMP of Multiply Substituted Cyclooctenes

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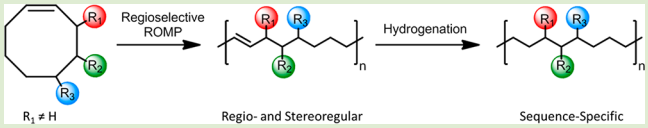
Supporting Information

ABSTRACT: A variety of multisubstituted cyclooctenes were prepared and employed as monomers for ring-opening metathesis polymerization using the Grubbs second or third generation catalysts. The resulting polymers were characterized by NMR spectroscopy, size exclusion chromatography, and differential scanning calorimetry. Monomers possessing a substituent at the 3-position afforded highly regio- and stereoregular polyalkenamers, from which the corresponding sequence-specific vinyl quaterpolymers were obtained upon hydrogenation. Simultaneous control of tacticity was also demonstrated by employing monomers with defined stereochemistry.



Polymer properties are intimately related to their primary structures and, thus, precise control of polymer structure is an important pursuit. Control of polymer architecture has been extensively studied,[1] however, precise control of the backbone microstructure (i.e., sequence and tacticity) of synthetic polymers is a formidable challenge.[2] For biological macromolecules that string together diverse monomeric units, the secondary/tertiary structures, catalytic activities, and biological function are critically dependent on the distribution of monomeric units along the backbone. This exquisite level of precision found in naturally occurring materials has not been achieved for synthetic polymers prepared by typical polymerization mechanisms. In the case of vinyl chain polymerizations of more than two monomers, such control of sequence along the backbone is a tall order.

Most of the efforts to generate sequence-controlled polymers have focused on the introduction of the sequence specificity during the polymerization process, which relies on development of polymerization techniques,[3] catalysts,[4] different comonomer reactivities,[5] and the use of templates.[6] These strategies, however, have difficulty generating perfectly sequence-specific polymers. Another approach is through careful monomer design such as in the acyclic diene metathesis (ADMET) polymerization[7] of symmetric α,ω-dienes and appropriately designed cyclic monomers in ring-opening polymerizations.[8] In these cases, the sequence and composition of the polymer are determined by monomer structure that can be accurately manipulated through powerful organic synthesis methods. For example, Cho and co-workers[9] synthesized vinyl copolymers of butadiene with ethylene, propylene, and styrene by ring-opening metathesis polymerization (ROMP) of disubstituted cyclooctenes that have methyl and phenyl groups at the 4- and 6-positions. However, because the polymerization was not regioselective, the resulting polymers were not truly sequence-specific.

We recently discovered that ROMP of 3-substituted cyclooctenes (COE) catalyzed by Grubbs second (G2) or third (G3) generation catalysts proceeds in a regio- and stereoselective fashion, resulting in highly head-to-tail (HT) and *E*-selective products.[10] This finding immediately suggests a way forward to sequence-specific vinyl ter- and quaterpolymers. We posited that G2- or G3-catalyzed ROMP of multisubstituted COEs would be highly regioselective provided that one of the pendant groups is present at the 3-position. Subsequent hydrogenation of these regioregular polymers would give sequence-specific vinyl terpolymers (e.g., $R_1 = R_2 \neq R_3 \neq R_4$) or quarterpolymers ($R_1 \neq R_2 \neq R_3 \neq R_4$), as shown schematically in Figure 1. One can further envision that the control of stereochemistry in these monomers would provide regulation of the tacticity of the resulting polymers. Such sequence-specific and tacticity-controlled polymers will facilitate the detailed understanding of structure−property relationship in such materials and open the door to control of secondary and tertiary structure in synthetic macromolecules.

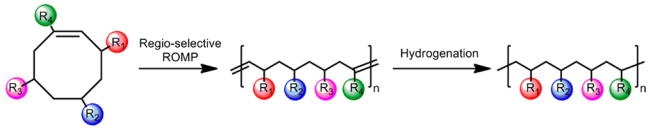


Figure 1. Proposed synthesis of sequence-specific polymers by regioselective ROMP of a multisubstituted cyclooctene ($R_1 \neq H$). Note that the substituents (except R_1) could also be on other ring carbons and are not limited to the positions shown here.

To test this strategy, we prepared an array of multisubstituted COEs with one substituent (not H) at the 3-position. The monomers must be single regio-isomers to ensure perfect sequence control. Our first successful approach was the utilization of the conjugate addition of nucleophiles to α,β-unsaturated ketones (Scheme 1A). Cycloocta-2,7-dienone (**1**)

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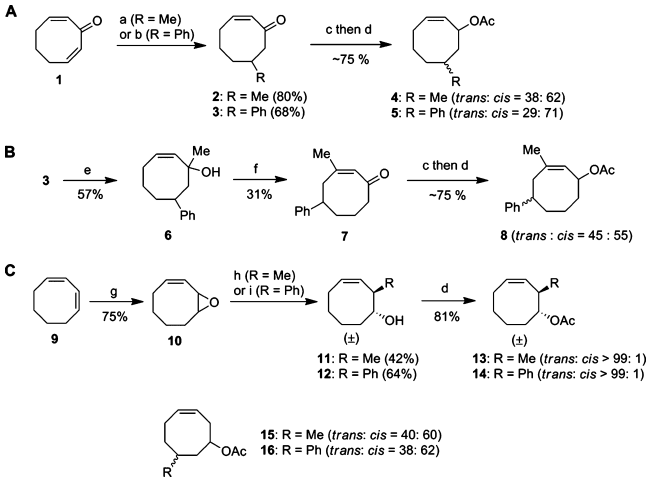
Scheme 1. Synthesis of Di- and Trisubstituted Cyclooctenes[a]



[a]Reagents and conditions: (a) MeLi, CuI (stoichiometric), THF/Et_2O, −20 °C, 15 min; (b) PhMgCl, CuI (catalytic), THF, −40 °C, 1 h; (c) $LiAlH_4$, THF, reflux, 1 h; (d) acetyl chloride, pyridine, CH_2Cl_2, 0 °C → RT, 2 h; (e) MeLi, THF, −78 °C → RT, 2 h; (f) PCC, CH_2Cl_2, RT, 2 h; (g) mCPBA, $CHCl_3$, 0 °C → RT, 18 h; (h) MeLi, $BF_3{\cdot}Et_2O$, Et_2O, −75 °C, 30 min; (i) PhLi, $BF_3{\cdot}Et_2O$, Et_2O, −75 °C, 30 min.

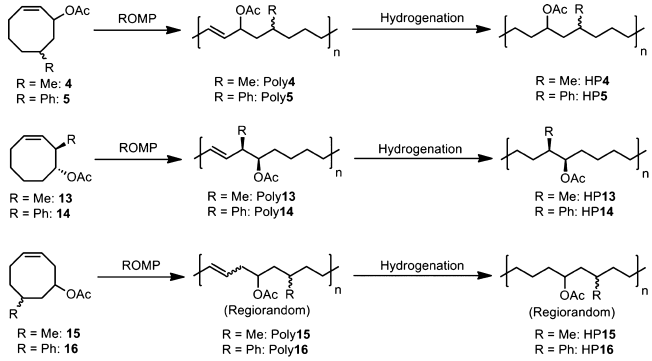
prepared from cyclooctanone according to literature procedures,[11] was treated with methyllithium (MeLi) or phenylmagnesium chloride (PhMgCl) in the presence of copper(I) iodide (CuI) followed by an acidic workup to give the methyl (**2**) or phenyl (**3**) substituted cyclooct-2-enone, respectively.[12] With CuI, the reaction proceeds with 1,4-addition only. Compounds **2** and **3** were reduced with lithium aluminum hydride ($LiAlH_4$), and the resulting alcohol was acetylated to afford the corresponding 3,5-disubstituted COEs, **4** and **5**. The same synthetic route was found to be applicable to seven-membered rings, rendering 3-acetoxy-5-methyl or 3-acetoxy-5-phenylcycloheptenes, as described in the Supporting Information (compounds **23** and **24**).

The synthesis of a trisubstituted COE is shown in Scheme 1B. Compound **3** was reacted with MeLi to give a tertiary allylic alcohol **6** that was then oxidized to generate a methyl, phenyl-substituted cyclooctenone (**7**).[13] Similar reduction and acetoxylation of **7** gave an acetoxy, methyl, phenyl trisubstituted COE (**8**). We recently demonstrated that the ROMP of 3-acetoxy COE generated regioregular polymers.[14]

Compounds **4**, **5**, and **8** exist as a mixture of diastereomers, with the acetoxy and alkyl(aryl) groups in either *trans* or *cis* configuration. Thus, the polymers derived from these monomers would be atactic. To further increase the precision of polymer structures and investigate the impact of tacticity, we synthesized monomers **13** and **14** through the synthetic routes shown in Scheme 1C. The ring-opening of epoxide **10** by organolithium reagents in the presence of boron trifluoride etherate is stereospecific;[15] and compounds **11** and **12** were obtained in high diastereomeric purity. Acetoxylation of **11** and **12** afforded corresponding racemic monomers **13** and **14** as only *trans* isomers. Finally, for comparative purposes, we synthesized two disubstituted COEs, **15** and **16**, that are regioisomeric to monomers **4**, **5**, **13**, and **14** using similar strategies. However, in **15** and **16**, there is no substituent at the 3-position.

The ROMP products of **4**, **13**, and **15** (or **5**, **14**, and **16**) are compositionally identical (Scheme 2). These polymers are

Scheme 2. ROMP and Hydrogenation of Disubstituted Cyclooctenes



equivalent to, in terms of chemical composition, a linear terpolymer of vinyl acetate (33 mol %), butadiene (33 mol %), and propylene (or styrene; 33 mol %) in the unsaturated form, or a linear terpolymer of vinyl acetate (25 mol %), propylene (or styrene; 25 mol %), and ethylene (50 mol %)[16] after saturation of the backbone double bonds. ROMP of the 3-substituted COE monomers **4**, **5**, **13** or **14** is expected to yield regio- (and stereo-) selective polymers as we have demonstrated for 3-monosubstituted COE, such that the repeating units are joined in a head-to-tail (HT) fashion. Furthermore, the two side chain groups are in 1,2-*syn* configuration in polymers of **13** or **14**, while a mixture of 1,3-*syn* and 1,3-*anti* configurations are present in polymers of **4**, **5**, **15**, or **16**.

The disubstituted COE derivatives were subject to ROMP using 0.025 mol % G2 and 1 mol % *cis*-4-octene as a chain transfer agent (CTA; Table 1). The polymerizations gave complete conversion in 24 h in most cases. Chemical hydrogenation using *p*-toluenesulfonyl hydrazide at 150 °C[17] was found to be effective in all cases. The olefinic bonds in the polymer backbone were saturated quantitatively, while the pendant phenyl and acetoxy groups were retained, as indicated by ^{1}H NMR spectroscopy.

The microstructures of these polymers were characterized by NMR spectroscopy. As an example, the ^{1}H and ^{13}C NMR spectra of the unsaturated polymer poly**14** (top) and the hydrogenated polymer HP**14** (bottom) are shown in Figure 2A and B, respectively. Only one major resonance was observed for the methine proton adjacent to the phenyl group (3.38 ppm) and the one adjacent to the acetoxy group (5.12 ppm), indicating high 1,2-*syn* content. The ^{13}C NMR spectrum of poly**14** displays 14 peaks that correspond to the 14 chemically different carbons in the repeating unit, which suggests a high degree of regioregularity and a single double bond configuration. Detailed two-dimensional NMR analysis of poly**14** (see Supporting Information, Figure S1-1) revealed that this polymer has predominately (>99%) a HT structure with *E*-double bonds, identical to the trend observed with the monosubstituted 3-phenyl COEs.[10] Both the ^{1}H and ^{13}C NMR spectra of HP**14** show complete disappearance of the olefinic signals, consistent with quantitative hydrogenation. The simplicity of these spectra unambiguously corroborates the well-defined microstructure of HP**14**, which can be considered as a sequence-specific and tacticity-controlled model of a vinyl acetate/styrene/ethylene terpolymer. Due to the fact that **14** is

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Table 1. Characterization Data for Unsaturated and Hydrogenated Polymers[a]

	unsaturated polymer							hydrogenated polymer			
monomer	conv.[b] (%)	yield[c] (%)	$M_{n\ (calc)}$[d] ($\times 10^3$)	$M_{n\ (SEC)}$[e] ($\times 10^3$)	$M_{n\ (NMR)}$[f] ($\times 10^3$)	$Đ$[e]	T_g[g] (°C)	yield[c] (%)	$M_{n\ (SEC)}$[e] ($\times 10^3$)	$Đ$[e]	T_g[g] (°C)
4	>99	65	17.8	26.4	[h]	1.71	−21	43	29.8	1.62	−29
5	>99	85	23.8	25.8	18.8	1.84	10	73	37.7	1.61	13
13	95	52	16.9	27.9	[h]	1.66	−22	60	32.3	1.45	−31
14	98	67	23.8	27.7	17.3	1.71	25	81	33.1	1.59	16
15	>99	63	17.8	26.9	[h]	1.83	−26	88	31.0	1.57	−32
16	>99	83	23.8	31.8	24.2	1.96	6	82	44.4	1.75	14

[a] $[M]_0 \approx 2$ M, $[M]_0/[G2] = 4000$, $[M]_0/[CTA] = 100$, $CHCl_3$, 60 °C, 24 h, CTA = *cis*-4-octene. [b] Determined by ^1H NMR of the reaction mixture. [c] Isolated yield. [d] $M_{n\ (cal)}$ = MW (monomer) × conv. × $[M]_0/([G2] + [CTA])$. [e] Determined by SEC in $CHCl_3$ with polystyrene standards. [f] Determined by end group analysis using ^1H NMR assuming two CTA end groups per chain. [g] Determined by DSC (2nd heating cycle) at 10 °C min^{-1}. [h] Unavailable due to overlapping resonances.

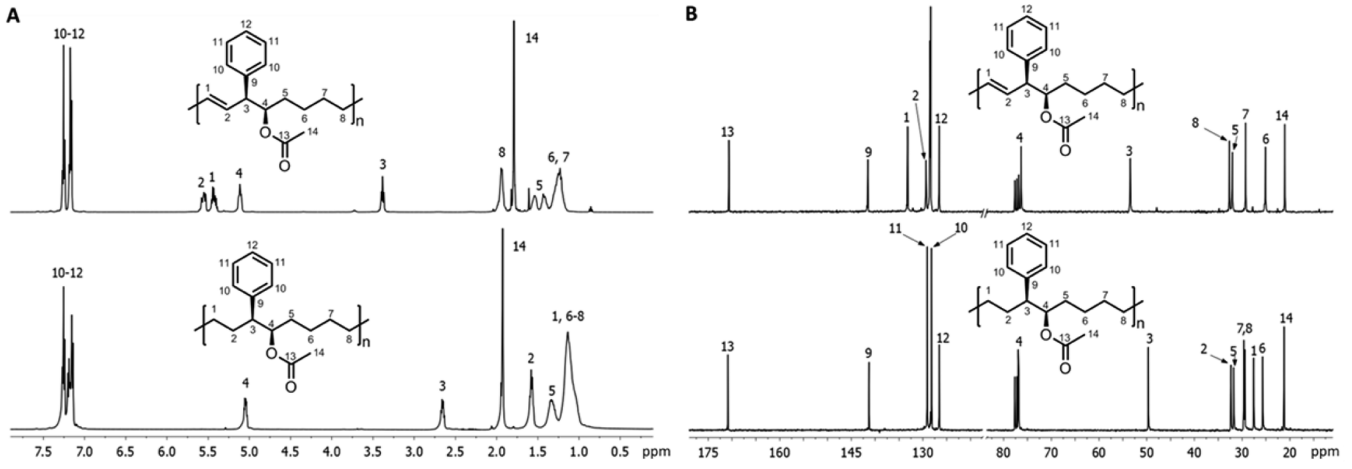

Figure 2. ^1H (A) and ^{13}C (B) NMR spectra of poly**14** (top) and HP**14** (bottom) in $CDCl_3$.

a racemic compound, poly**14** and HP **14** are not isotactic. However, the relative orientation of the adjacent acetoxy and phenyl groups is fixed within a given repeating unit, which is in contrast to the cases of the analogous polymers poly**5**, poly**19**, HP**5**, and HP**16**. This difference influences the thermal properties of these materials, as discussed below.

Polymers from **13** exhibit slightly lower degrees of regioregularity relative to polymers from **14**, consistent with the differences we previously observed between the polymerization of 3-methyl COE and 3-phenyl COE.[10] As a result of the presence of both 1,3-syn and 1,3-anti configurations, most protons and carbons in the polymers of **4** and **5** are split into two signals with integral ratios equal to the ratios of the *trans* and *cis* diastereomeric ratios in the respective monomers (Figures S2-46−55 and -81−90). Nevertheless, these polymers were also highly regioregular (>95% HT). In contrast, the ^{13}C NMR spectra exhibited a number of peaks for the olefinic carbons of poly**15** and poly**16** (Figures S2-67 and -72, respectively) and for the methine carbon adjacent to the acetoxy group of HP**15** and HP**16** (Figures S2-102 and -107, respectively). These results indicate that polymers of **15** or **16** contain a mixture of HT, HH, and TT regioisomers, as opposed to the regioregularity found in the other polymers. Moreover, the backbone double bonds in poly**15** and poly**16** consist of both *E* and *Z* configurations. The lack of regio- and stereoregularity in poly**15** and poly**16** is consistent with the observations in other reports about monosubstituted COE without a substituent at the 3-position.[14,18]

Thermal properties of all unsaturated and saturated polymers were characterized by differential scanning calorimetry (DSC). All polymers were amorphous as only glass transitions were observed (Table 1 and Figures S2-117−130) between −85 and 150 °C. The measured T_g of the hydrogenated polymers are very close to what is predicted by the Fox equation[19] in which the impact of microstructure is neglected: −27 °C for the equivalent terpolymer of vinyl acetate, propylene, and ethylene (HP**4**, HP**13**, and HP**15**), and 11 °C for the equivalent terpolymer of vinyl acetate, styrene, and ethylene (HP**5**, HP**14**, and HP**16**). This observation is in contrast to other equimolar copolymer systems where the statistical and the alternating copolymers exhibit different T_g values.[20]

Despite identical chemical composition and comparable molar masses, the sequence-specific poly**14** and poly**5** display T_g values of 25 and 10 °C, respectively. These are 19 and 4 °C higher than that of the regiorandom poly**19**, respectively. The effect of regulated tacticity manifests itself as a 15 °C decrease in T_g from the tacticity-controlled poly**14** to the atactic poly**5**. This difference is less pronounced in the methyl/acetoxy series, where the T_g values for poly**4** and poly**13** are very close and only a few degrees higher than the T_g of poly**15**. The T_g differences among the same series of polymers is diminished post-hydrogenation.

The contrast in thermal behaviors between the unsaturated polymers and the hydrogenated polymers suggests that the stereochemistry about the backbone double bond (i.e., *E* and *Z*) plays a more important role than other microstructural variables in terms of solid state structure. Previous studies[20a,21]

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on vinyl copolymers indicated that T_g of copolymers is affected not only by the fraction of each monomer unit, but also by the fractions of different diad sequences in the copolymer chain. For the unsaturated polymers, the presence of different double bond stereochemistry (mostly *E* for poly**4**, poly**5**, poly**13**, and poly**14**, and both *E* and *Z* for poly**15** and poly**16**) as well as their different positions relative to the side chain groups in each polymer results in different T_g values. On the other hand, the hydrogenated polymers derived from substituted COEs have similar diad sequences within one repeating unit (4 diads). Thus, the hydrogenated polymers from the same series show similar T_g values, even in HP**15** or HP **16** that are not sequence-specific. Furthermore, specific sequence and more defined tacticity may influence the specific packing, but the effect only becomes prominent when the substituent is bulky enough, which is supported by the differences between the unsaturated polymers of the phenyl/acetoxy series and the methyl/acetoxy series.

Although Grubbs and co-workers showed that 1,5-dimethyl-1,5-cyclooctadiene can be polymerized by G2 and G3,[22] several attempts at the ROMP of **8** were unsuccessful, In addition, the ROMP of the disubstituted 7-membered ring monomers (**23** and **24**) required more demanding conditions than those reported in Table 1 (see Table S1). We attribute this to lower ring strain in the cycloheptene-based monomers.[23] The resulting polymers exhibit reduced regio- and stereoregularity compared to the cyclooctene derivatives, which agrees with our observation of another 3-substituted cycloheptenes.[14] These results suggest the preferred strategy to sequence specific quarterpolymers would be through the ROMP of COEs with $R_1 \neq R_2 \neq R_3 \neq H$ and $R_1 = H$. While challenging to synthesize, the ROMP of such monomers with various functional groups[24] would open exciting new vistas in the preparation of sequence specific macromolecules.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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