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Precision Vinyl Acetate/Ethylene (VAE) Copolymers by ROMP of Acetoxy-Substituted Cyclic Alkenes

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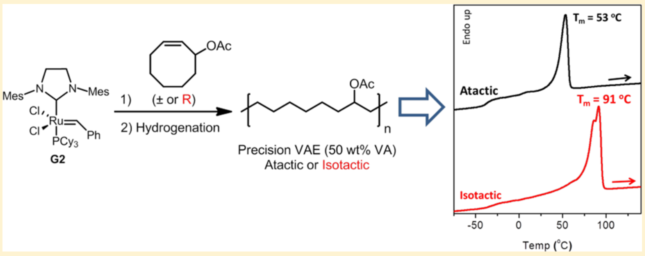
Ⓢ *Supporting Information*



ABSTRACT: Precision linear vinyl acetate/ethylene (VAE) copolymers containing acetoxy groups on precisely every eighth backbone carbon were synthesized by ring-opening metathesis polymerization (ROMP) of racemic 3-acetoxy cyclooctene (3AcCOE) followed by hydrogenation. The use of enantiomerically pure 3AcCOE resulted in an optically active polyalkenamer that afforded isotactic precision VAE materials after hydrogenation. Both of these VAE polymers are semicrystalline (by differential scanning calorimetry and wide-angle X-ray scattering) due to their high degrees of regioregularity and the isotactic VAE samples exhibited a higher apparent degree of crystallinity and melting point compared to the atactic version. In contrast, analogous linear VAE copolymers derived from ROMP−hydrogenation of racemic 4- or 5-acetoxy cyclooctenes were regio-irregular and completely amorphous. The ROMP−hydrogenation of 3-acetoxy cycloheptene also affords precision linear VAE copolymers with acetoxy groups on every seventh carbon, but this polymer was noncrystalline. Mechanical characterization showed that the precision 3AcCOE-derived VAE samples possess improved mechanical properties compared to the compositionally similar commercial VAE copolymers produced by radical copolymerization.

Precision control of polymer structure is important for both tailoring ultimate properties and gaining a complete understanding the structure−property relationships. Biomacromolecules often possess high degrees of specificity and structural complexity not commonly found in synthetic polymers. In synthetic polymers the control of size (molar mass) and architecture has been demonstrated in various approaches during the past several decades.[1] Polymer microstructures (i.e., comonomer sequence and stereochemistry), on the other hand, are more challenging to regulate.[2] The control over repeating unit sequence has been achieved mainly through polymerization of prestructured monomers with built-in sequence,[3] coupling of sequence-specific short oligomers,[4] and particular copolymerization processes in which monomers exhibit different reactivity[5] or where external templates are applied.[6] One of the notable examples of the first approach is the preparation of precision polyethylene by acyclic diene metathesis (ADMET) polymerization[7] of symmetrically substituted *α*,*ω*-dienes.[3g−i] Alternating copolymerization of 1,3-butadiene with other vinyl monomer (e.g., methyl methacrylate) and polymerization of substituted 1,3-butadiene were reported to eventually result in periodic ethylene copolymers.[3c] Use of stereoselective catalysts is by far the most popular strategy to control backbone stereochemistry which includes *E*−*Z* isomerism and tacticity.[8] However, the complete control over both the sequence and stereochemistry has only been realized in limited cases.[9]

Recently, we discovered that ring-opening metathesis polymerization (ROMP)[10] of *cis*-cyclooctene (COE) substituted with hydrocarbon groups at the 3-position (3RCOE) using the well-defined Grubbs second (G2) or third (G3) generation catalyst leads to highly regio- and stereoregular polyalkylenamers.[11] The polymers possess high levels (>95%) of head-to-tail (HT) repeating unit connectivity and *E* double bond configurations. Hydrogenation of these polyalkylenamers afforded model linear low density polyethylene (LLDPE) with precisely positioned branches. In a recent computational study,[12] we proposed that the rate-limiting step for the polymerization of COE and its derivatives by Grubbs type catalysts is determined by the barrier for breakdown of the metallacyclobutane intermediate formed between the catalyst and the monomer. Consequently, the regio- and stereochemistry seen in the ROMP of 3RCOEs is mainly due to significant repulsive interaction between the substituent and the *N*-heterocyclic carbene (NHC) mesityl ligand.

These reports suggest that any 3-substituted COE having a sufficiently bulky functional group could also lead to regio- and stereoregular polymers.[13] Furthermore, the use of enantiomerically pure 3-substituted COEs in such polymerization would enable the synthesis of isotactic, all-*E*, and sequence specific polymers. To test this hypothesis we focused on the acetoxy-substituted system[14] (Figure 1) because of the convenient accessibility of the monomers, the introduction of a functional group and the practical value of the final polymers, as they are

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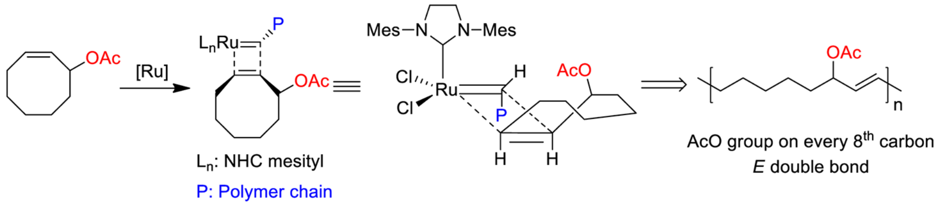


Figure 1. Proposed synthesis of regio- and stereoregular polymer by ROMP of 3AcCOE catalyzed by G2 or G3.

comparable to copolymers of vinyl acetate (VA) and ethylene prepared by radical copolymerization.

Copolymers of VA and ethylene (EVA when ethylene >50 wt % or VAE when vinyl acetate >50 wt %) and their hydrolysis products are widely used as adhesives, coatings and foams.[15] Industrial production of EVA/VAE involves high-pressure free radical conditions similar to those used in the production of low density polyethylene; branched polymers with difficult-to-control structures are typically produced. Linear EVA can be synthesized by palladium-catalyzed coordination copolymerization of ethylene and vinyl acetate, but the incorporation of vinyl acetate is limited to ~2 mol %.[16] Poly(ethylene-*alt*-vinyl acetate) (75 wt % VA) was synthesized by Yokota et al[17] through cationic polymerization of 1-trimethylsilyloxy-1,3-butadiene followed by several steps of postpolymerization modification, but significant branching (~15%) was unavoidable during the polymerization.

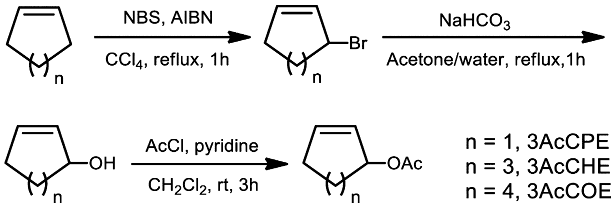
Combination of metathesis polymerization and hydrogenation is an attractive way to generate perfectly linear EVA/VAE copolymers due to the branch-free nature of the polymerization and the tolerance of certain metathesis catalysts to esters. For example, in 1995 the Grubbs group[18] employed ROMP of 5-acextoxycyclooctene (5AcCOE) followed by hydrogenation to synthesize linear VAE with ~50 wt % VA. The work of Wagener and his group[19] demonstrated the ability to tune the composition of EVA by performing ROMP or ADMET polymerization of appropriately functionalized comonomers. However, in these examples the EVA/VAE analogues were regio-irregular and atactic. Using symmetrically substituted monomers in ADMET, Wagener and co-workers[20] also prepared model linear EVA materials with 20–25 wt % VA that have precisely positioned acetoxy groups on the backbone. Precision linear EVA/VAE polymers with >25 wt % VA have rarely been reported, and the above examples involved only symmetrically substituted monomers.[9c,21]

In this study, we describe the use of tandem ROMP–hydrogenation of 3-acetoxycyclooctene (3AcCOE) and its enantiomerically pure version to synthesize "precision" model polymers that are equivalent to linear VAE materials (50 wt % VA). We also studied the effect of structural variations including tacticity, substituent position on COE and ring-size of 3-acetoxy cyclic alkenes on the regio- and stereoselectivity of the polymerization as well as on the properties of the final VAE copolymers.

■ RESULTS AND DISCUSSION

Synthesis and ROMP of 3AcCOE. We attempted the direct allylic transition metal catalyzed acetoxylation of *cis*-cyclooctene, which has been reported in literature with various cyclic alkenes.[22] However, approximately 5% the homoallylic product (4-acetoxy cyclooctene) was inevitably generated and proved to be very difficult to separate from the desired allylic product. Although a convenient synthetic method, such impurities complicate the analysis of the structure regularities of the resulting polymers. Therefore, we employed a three-step sequence consisting of α-bromination, hydrolysis, and acetoxylation from COE to synthesize 3AcCOE[23] (Scheme 1). Pure 3AcCOE could be obtained on multigram scale and in overall yields of ~60%.

Scheme 1. Synthesis of 3-Acetoxy-Substituted Cyclic Alkenes



The solution polymerization of 3AcCOE using G2 proceeded smoothly in dry $CHCl_3$; and the monomer conversion is quantitative within hours at room temperature. Polymer molar mass can be efficiently controlled by using *cis*-4-octene as a chain transfer agent (CTA),[24] and the dispersity values ($Đ$ ~ 1.7) are similar to that obtained for poly(COE) by the ROMP of the unsubstituted variant (Figure 2).

The microstructure of poly(3AcCOE) was carefully characterized by ^1H and ^{13}C NMR (Figure 3) and by FT-IR spectroscopies. In the ^{13}C NMR spectrum, the polymer shows two major olefinic signals (128.51 and 134.35 ppm) as opposed

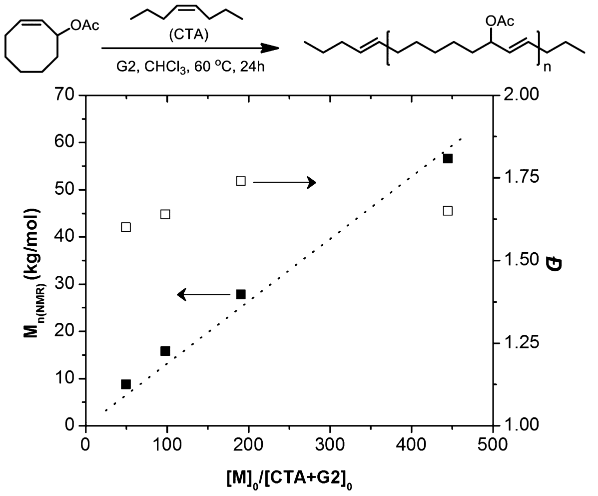


Figure 2. Molar mass and dispersity of poly(3AcCOE) as a function of monomer to CTA ratio. Conditions: $[M]_0 \approx 1.5$ M, $[M]_0/[G2]_0$ = 4000. Monomer conversion was quantitative in all cases. The molar mass was determined by end group analysis using ^1H NMR spectroscopy assuming two end groups from the CTA per chain. The dispersity was determined by SEC using polystyrene standards in $CHCl_3$.

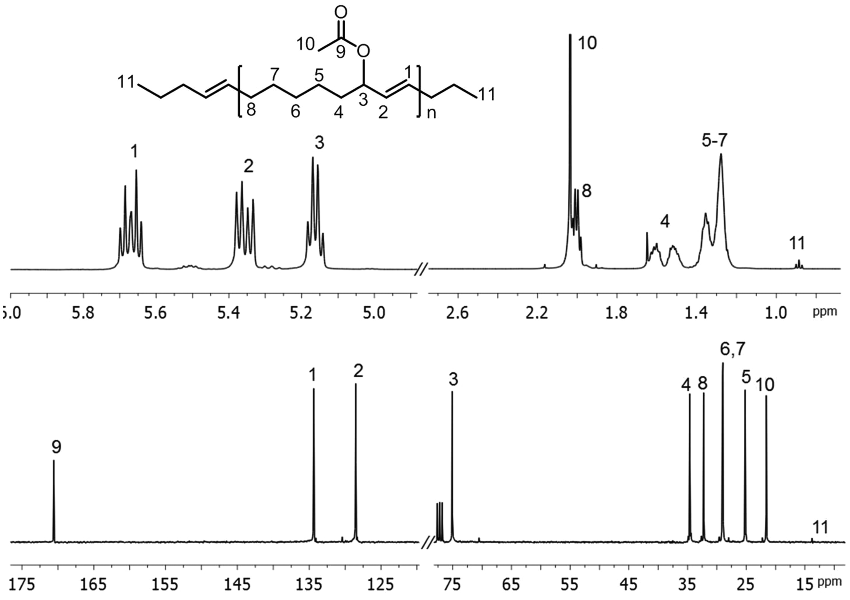


Figure 3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of poly(3AcCOE). Run 1 in Table 1.

Table 1. ROMP of 3AcCOE in Different Solvents at Different Temperatures[a]

run	solvent	temp (°C)	convn (%)[c]	M_n (kg/mol)[b]	$Đ$[b]	E (%)[c]	HT (%)[c]
1	$CHCl_3$	20	>99	29.5	1.60	95.9	99.7
2	cyclohexane	20	>99	33.3	1.71	90.1	97.7
3	toluene	20	>99	35.1	1.64	93.8	99.0
4	toluene	40	>99	34.2	1.68	90.2	98.2
5	toluene	60	>99	35.6	1.67	89.4	97.6
6	toluene	90	>99	33.7	1.74	88.7	97.3

[a]Conditions: $[M]_0 \approx 1.5$ M, $[M]_0/[G2]_0 = 4000$, $[M]_0/[CTA]_0 = 100$, 24 h. [b]Determined by SEC using polystyrene standards in $CHCl_3$. [c]Determined by ^{1}H NMR spectroscopy of the reaction mixture.

to eight signals from the six possible regio- and stereoisomeric structures, and one major signal for the carbon adjacent to the acetoxy group (75.11 ppm).[18] This is strong evidence for high regio- and stereo(E/Z)-regularity of the polymer. Further analysis of the NMR (Figures S7–S11, Supporting Information) and FT-IR spectra (Figure S62, Supporting Information) supports a polymer with a HT structure and E configuration of the double bonds, the same selectivity as shown previously for other 3RCOE samples.[11] The stereoselectivity was slightly lower than those of the 3RCOE polymers obtained under the same conditions. This result might be explained by the differences in sterics and polarity between acetoxy group and the alkyl/aryl group, which may result in a slightly higher fraction of Z product of poly(3AcCOE). Very low levels of the regio- and stereochemical impurities were observed by NMR spectroscopy as mostly the Z-HT units.

The regio- and stereoselectivity of the polymerization was affected by both the polymerization solvent and temperature. As shown in Table 1, polymerization in $CHCl_3$ gave the highest regio- and stereoselectivity. Performing the polymerization in less polar solvent (e.g., toluene or cyclohexane) tends to lead to slight decrease of the regio- and stereoselectivity. This result suggests the transition state for the rate-determining step (break down of the metallocycle) that results in the HT and E product is more polar than the ones leading to other products and is thus stabilized to a greater extent in solvents with higher dielectric constants.[12] Furthermore, in toluene the stereoselectivity of the polymer decreases as the polymerization temperature increases, and a concomitant decrease of the HT selectivity was also observed at elevated temperatures. Nevertheless, it can be concluded that poly(3AcCOE) is highly regio- and stereoregular regardless the polymerization conditions explored here (Table 1).

To better understand the regioselectivity observed during ROMP of 3AcCOE, we performed quantum chemical calculations for the breakdown of the metallocyclobutane intermediate during the initiation step as we described previously for the aliphatic and aromatic cyclooctenes.[12] Starting from the lowest energy conformers we calculated both distal and proximal approaches in the gas and solution ($CHCl_3$) states (Figure 4). The calculations indicated that the distal approach is thermodynamically more favored by over 12 kcal/mol. Coordination of the acetoxy group with the Ru metal center was not observed in either approach. Free energies and Boltzmann-weighted product distributions are provided in the

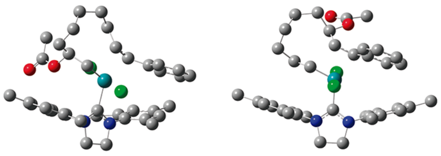
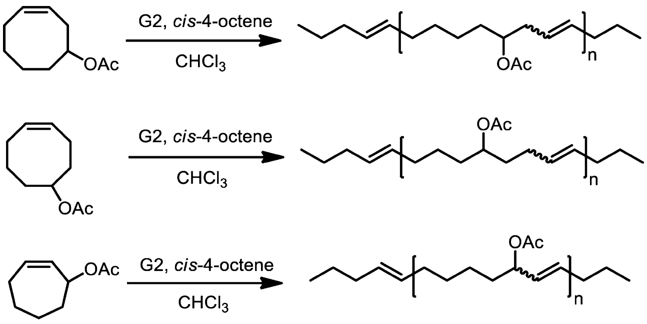

Proximal *Distal*

Figure 4. Optimized M06-L E **TS2** structures for the *proximal* and *distal* reactions of 3AcCOE. Hydrogens were omitted for simplicity.

Supporting Information. We also attempted a 1:1 3AcCOE:Ru experiment in an attempt to verify this result as we did previously.[11] However, the resultant NMR data was inconclusive and we were unable to make definitive determination concerning the approach of 3AcCOE to the Ru center.

ROMP of other Acetoxy-Substituted Cyclic Alkenes. In addition to the ROMP of 3AcCOE, we also (re)examined the polymerization of two regio-isomers of 3AcCOE, namely 4-acetoxy cyclooctene (4AcCOE) and 5-acetoxy cyclooctene (5AcCOE) (Scheme 2). NMR kinetic experiments showed that 3AcCOE and 4AcCOE polymerize more slowly than 5AcCOE (Figure S1, Supporting Information). The reduced reactivity of 3AcCOE and 4AcCOE can be attributed to the steric impact of the acetoxy group being in close proximity to the metathesis reactive double bond.

Scheme 2. ROMP of 4AcCOE, 5AcCOE, and 3AcCHE



NMR studies revealed that both poly(4AcCOE) and poly(5AcCOE) are completely regio-irregular as equal intensities of the resonances corresponding to the HH, HT and TT polymers can be seen in the ^{13}C NMR spectra (Figure 5a and b). The *E*/*Z* ratio of both polymers is approximately 80/20, which is close to the ratio observed in poly(COE) generated using G2.

To explore the impact of ring-size on the selectivity in the ROMP of 3-substituted cyclic olefins, we prepared 3-acetoxycyclopentene (3AcCPE) and 3-acetoxycycloheptene (3AcCHE) using a procedure similar to the synthesis of 3AcCOE (Scheme 1). No polymerization was observed with 3AcCPE, even when the polymerization was conducted at room temperature for a week, which is likely due to its low ring strain.[21] As for 3AcCHE, the reactivity was significantly lower than 3AcCOE, so higher concentration, lower temperature and longer reaction times were required to obtain high molar mass polymer ($[3AcCHE]_0 \approx 3$ M in chloroform, 48 h, 55% conversion). This reduced reactivity is likely related to the lower ring strain of 3AcCHE compared to 3AcCOE. The polymerization of 3AcCHE also shows preference for the formation of the *E*-HT polymer as shown by the two major olefinic signals in the ^{13}C NMR spectra (Figure 5c). However, several minor olefinic signals are noticeable in comparison to the ^{13}C NMR spectra of poly(3AcCOE) (Figure 5d), indicating that the regularity is lower than that of poly(3AcCOE). Quantitative analysis of the ^{1}H NMR spectrum of poly(3AcCHE) (Figure S35, Supporting Information) revealed a significant decrease of the stereoselectivity (78.4% *E*) but only a slight decrease of the regio-selectivity (95.9% *HT*) relative to poly(3AcCOE).

Hydrogenated polymers. All the acetoxy-substituted polyalkylenamers can be hydrogenated using diimide[25] (Table 2), generating polymers equivalent to VAE samples with 50.5 wt % VA (for 3-, 4-, or 5AcCOE) or 55.1 wt % VA (for 3AcCHE). Since all the starting monomers are racemic compounds, these polymers are expected to be atactic. In all cases, the extent of hydrogenation was >99% and the acetoxy group was not affected as indicated by NMR spectroscopy. We expected that the hydrogenated polymers should retain the regioregularity from their parent polyalkylenamers, and this is supported by ^{13}C NMR analysis of the hydrogenated polymers shown in Figure 6. The polymer obtained from poly(3AcCOE) (a-HP3AcCOE, "a" for atactic) displays a single signal for both the carbonyl carbon and the methine carbon in the ^{13}C NMR spectrum (Figure 6a), supporting a highly regioregular structure. As poly(3AcCOE) has a HT structure, a-HP3AcCOE is the equivalent of a model VAE copolymer with pendent acetoxy group on precisely every eighth backbone carbon.

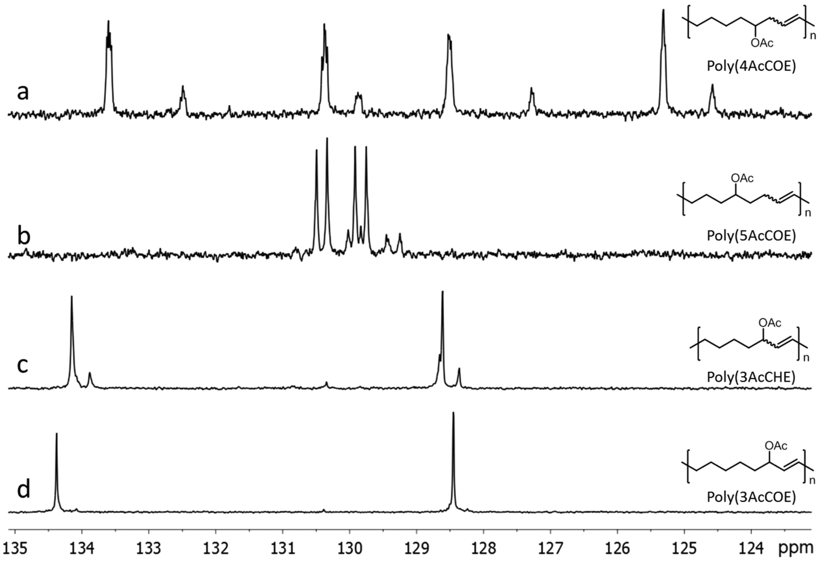


Figure 5. ^{13}C NMR spectra (olefinic region) of poly(4AcCOE) (a), poly(5AcCOE) (b) and poly(3AcCHE) (c). For comparison, ^{13}C NMR spectrum of poly(3AcCOE) in the same region is shown in part d.

Table 2. Characterization Data of Polymers Derived from Acetoxy-Substituted Cyclic Alkenes

	unsaturated polymer			hydrogenated polymer					
monomer	M_n[a] (kg/mol)	$Đ$[a]	T_g[b] (°C)	VA[c] (wt %)	M_n[a] (kg/mol)	$Đ$[a]	T_g[b] (°C)	T_m[b] (°C)	T_c[b] (°C)
3AcCOE	36.4	1.64	−33	50.6	40.0	1.60	−36	53	9
(R)-3AcCOE	36.4	1.58	−40	50.6	37.4	1.54	−30	91	59
4AcCOE	22.1	1.87	−43	50.6	25.9	1.53	−41		
5AcCOE	41.7	1.74	−40	50.6	51.7	1.57	−42		
3AcCHE	18.4	1.62	−31	55.1	18.9	1.56	−46		

[a] Determined by SEC using polystyrene standards. [b] Determined by DSC on the 2nd heating/cooling cycle at 10 °C/min. [c] Effective vinyl acetate content in the polymer.

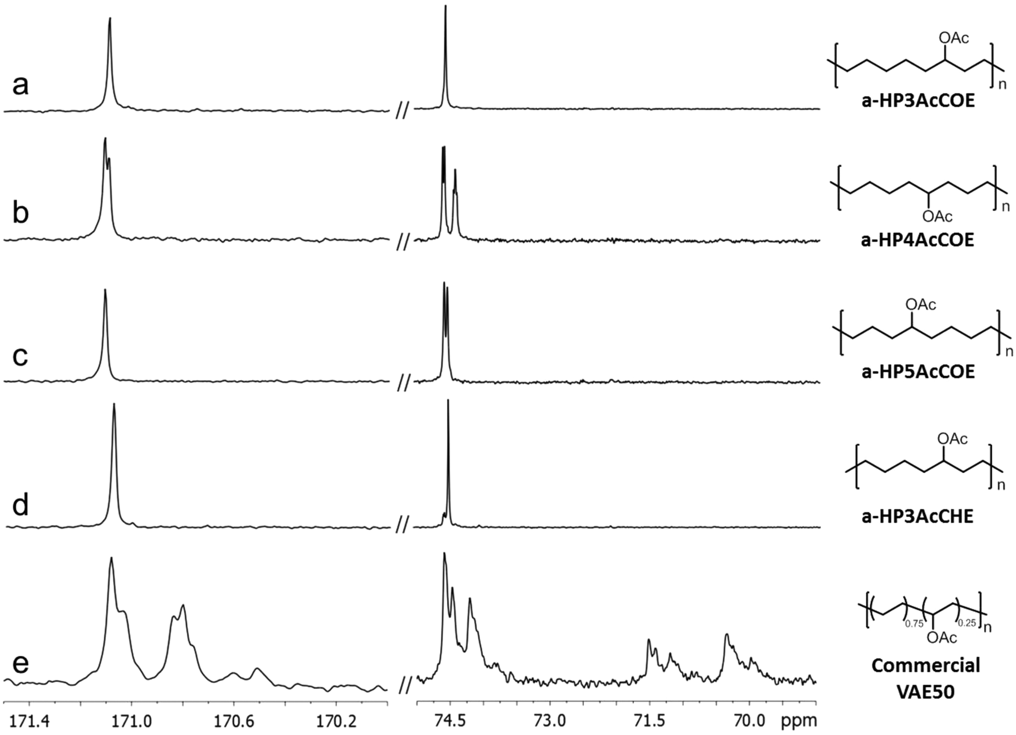
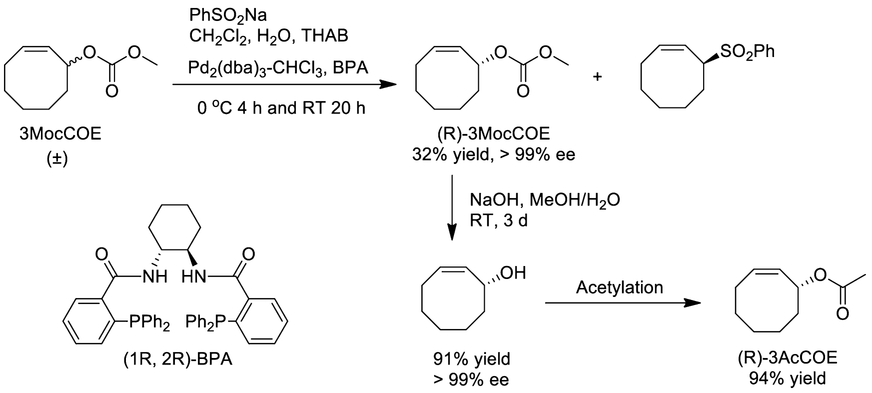


Figure 6. Partial ^{13}C NMR spectra of a-HP3AcCOE (a), a-HP4AcCOE (b), a-HP5AcCOE (c), a-HP3AcCHE (d), and commercial VAE50 (see text for details) (e). Left: carbonyl carbon. Right: methine carbon.

Scheme 3. Preparation of Enantiomerically Pure 3AcCOE



For comparative purposes the ^{13}C NMR spectra of hydrogenated poly(4AcCOE) (a-HP4AcCOE) (Figure 6b) and poly(5AcCOE) (a-HP5AcCOE) (Figure 6c) show multiple signals for the carbonyl and methine carbons, indicating their regioirregularity. Polymer a-HP4AcCOE has a more complex spectrum than a-HP5AcCOE. This is caused by the fact that the spacing between the pendent acetoxy groups is either 4, 7, or 10 carbons for a-HP4AcCOE, and 6, 7, or 8 carbons for a-HP5AcCOE, so the difference of chemical environment of the carbonyl and methine carbons is more exaggerated for a-HP4AcCOE than for a-HP5AcCOE. On the other hand, a commercial sample of a VAE copolymer with 50 wt % VA

(VAE50, M_n = 83.7 kg/mol, M_w/M_n = 4.01, purchased from Scientific Polymer Products, Inc.) exhibits a complex set of ^{13}C signals (Figure 6e), confirming its irregular and inhomogeneous structure.

Isotactic Precision VAE. The regio-selective ROMP of enantiomerically pure 3AcCOE should give precision polymers that are regio-selective, *E*−*Z* stereoselective and isotactic. To synthesize a pure enantiomer of 3AcCOE we initially utilized the enzyme-catalyzed kinetic resolution of secondary alcohols (or acetates) as this has been shown to give product with good to excellent enantioselectivity.[26] We performed transesterifcation of 3-hydroxy cyclooctene and vinyl acetate catalyzed by a lipase (Amano PS, from *Burkholderia cepacia*) in *n*-hexane (Scheme S1, Supporting Information). The 3AcCOE obtained from this reaction was enriched with the (R)-enantiomer, but the enantiomeric excess (ee) never exceeded 55%, as determined by comparison of its optical rotation with that of the pure enantiomer obtained by the method described below.

Gais and co-workers developed a highly efficient method to prepare various enantiomerically pure allylic compounds using a chiral palladium complex.[27] We utilized a modified version of this method to prepare enantiomerically pure 3AcCOE. As shown in Scheme 3, 3-(methoxycarbonyl)cyclooctene (3MocCOE) was treated with sodium benzenesulfinate in the presence of catalytic amount of $Pd_2(dba)_3 \cdot CHCl_3$ and the chiral Trost ligand (BPA) in CH_2Cl_2/H_2O. After 24 h reaction at ambient temperature, unreacted 3MocCOE was isolated in 32% yield and >99% ee ((*R*)-enantiomer) as determined by comparison of its optical rotation with that of the pure enantiomer reported in literature.[27] Hydrolysis of the methoxycarbonyl group gave the corresponding 3-hydroxycyclooctene, and the optical rotation of which ($[\alpha]^{20}_D = -52.4°$, c = 1.0, CH_2Cl_2) was identical to the reported value of an enantiomerically pure sample ($[\alpha]^{20}_D = -52.4°$, c = 1.46, CH_2Cl_2).[27a] This compound was further converted into the corresponding (*R*)-3AcCOE by acetylation ($[\alpha]^{20}_D = -89.2°$, c = 1.0, *n*-hexane; lit.[28] for the *R* enantiomer of unknown ee, $[\alpha]^{25}_D = -50.5°$, c = 5.08, *n*-hexane; lit.[29] for the S enantiomer of 50% ee, $[\alpha]^{29}_D = +47.0°$, c = 5.01, *n*-hexane). Since the stereochemistry of the chiral center should not be affected during the acetylation, we presume that this product is also enantiomerically pure (i.e., > 99% ee).[30]

The reactivity of (*R*)-3AcCOE in ROMP was no different from the racemic 3AcCOE. Likewise, ROMP of (*R*)-3AcCOE was also regio- and *E*/*Z* stereoselective, as indicated by the identical spectroscopic data for the resulting polymer. Also, poly(*R*-3AcCOE) is optically active, exhibiting significant optical rotation ($[\alpha]^{20}_D = +55°$, c = 1.0, $CHCl_3$) that has the opposite sign to the monomer. The optical rotation of poly(R-3AcCOE) was also dependent linearly on the ee of the monomer (Figure S2, Supporting Information). Chemical hydrogenation of poly(R-3AcCOE) gives corresponding VAE (i-HP3AcCOE, "i" for isotactic) which has a both precision and isotactic structure. However, the optical rotation of i-HP3AcCOE is close to zero ($[\alpha]^{20}_D = +2.4°$, c = 1.0, $CHCl_3$) because effective mirror planes of symmetry are present due to the high levels of regioregularity as in the case of isotactic and syndiotactic polypropylenes which are optically inactive.[31]

Thermal Characterization. DSC was employed to characterize the thermal behavior of the unsaturated and saturated polymers (Table 2). All of the unsaturated polymers are completely amorphous materials with T_g values < −30 °C (Figure S64, Supporting Information). Although poly(3AcCHE) also shows a comparably high T_g, its higher VA content may be a more dominating factor than its structure regularities.

The DSC profile of a-HP3AcCOE displays a broad endotherm (curve 1 in Figure 7a) during the heating cycle and a broad exotherm (curve 7 in Figure 7b) during the cooling cycle. These thermal transitions can be related to the melting (T_m = 53 °C) and crystallization (T_c = 9 °C) of the polymer, respectively. A glass transition (T_g = −36 °C) was also observed. The i-HP3AcCOE shows much higher T_m and T_c (91 and 59 °C, respectively). The greater heat of fusion of i-HP3AcCOE (ΔH_m = 67 J/g) relative to that of a-HP3AcCOE (ΔH_m = 39 J/g) as well as its barely distinguished T_g at −30 °C suggests a considerably higher degree of crystallinity for i-HP3AcCOE. The shoulder/secondary peak appears on the low temperature side of the major melting transition suggests there exist more than one type of crystal structure in i-HP3AcCOE. Interestingly, the heat of fusion of a-HP3AcCOE or i-HP3AcCOE is greater than that of the analogous ROMP-derived precision polymer with methyl substituent (ΔH_m = 30 J/g)[11] despite the smaller size of the methyl group. This is likely due to the dipolar nature of the acetoxy groups.

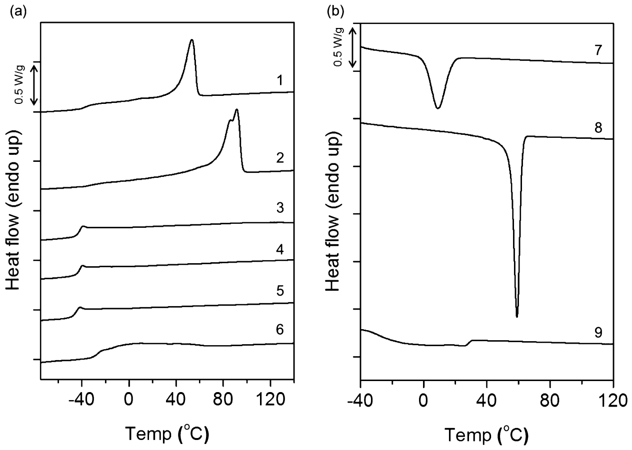


Figure 7. DSC profiles of various VAE copolymers at 10 °C/min. (a) Heating curves of a-HP3AcCOE (1), i-HP3AcCOE (2), a-HP4AcCOE (3), a-HP5AcCOE (4), a-HP3AcCHE (5), and commercial VAE50 (see text for details) (6). (b) Cooling curves of a-HP3AcCOE (7), i-HP3AcCOE (8), and commercial VAE50 (see text for details) (9).

The T_m of a-HP3AcCOE and i-HP3AcCOE are remarkably high compared to analogous ethylene/vinyl acetate copolymers produced by radical copolymerization. The T_m of commercial EVA increases with increasing E content. However, HP3AcCOE (50 wt % VA) melts at the temperature close to the range of T_m of ADMET-derived precision EVA with 20 wt % VA[20] or commercial EVA with 30−40 wt % VA.[32] Such distinct and defined melting and crystallization behaviors have not been observed in the case of other precision polyethylene derivatives with even lower frequency of substitution (on every 9th or 15th carbon).[33]

Using the conditions of run 1 in Table 1 and the typical hydrogenation procedure, we synthesized a series of HP3AcCOE from 3AcCOE samples with different ee's prepared by mixing appropriated amounts of racemic 3AcCOE and enantiomerically pure (R)-3AcCOE. DSC analysis of this series of polymers shows a linear relationship between T_m (and T_c) and the ee of monomer (Figure 8a). The heat of fusion also increases with ee (Figure 8b). This result indicates that the crystallinity and melting point of HP3AcCOE is influenced by tacticity in a predictable way, which allows for precise control of crystallinity and related properties.

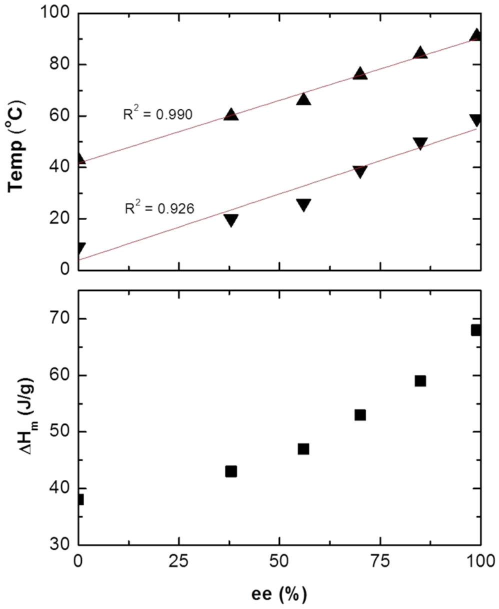


Figure 8. Dependence of thermal properties of HP3AcCOE on the ee of 3AcCOE. (a) Temperatures of melting (T_m, ▲) and crystallization (T_c, ▼). (b) Heat of fusion (ΔH_m).

In contrast, the commercial sample VAE50 shows ambiguous and broad melting and crystallization transitions that spans nearly 100 °C (curves 6 and 9 in Figure 7), accompanied by a much lower heat of fusion (ΔH_m = 17 J/g), suggesting much lower crystallinity than the precision VAE. DSC of the regio-irregular a-HP4AcCOE or a-HP5AcCOE only show glass transitions (curves 3 and 4 in Figure 7a). The more randomly distributed substituents suppress crystallinity in the polymer, resulting in amorphous material as seen in other substituted polyethylene (PE) systems.[34] This phenomenon was also observed with some ethylene–ethylene–acrylic copolymers (e.g., ethylene–ethylene–methyl α-chloroacrylate copolymer), where the periodic copolymer is semicrystalline but the random analogue is amorphous.[35] Interestingly, we found that a-HP3AcCHE is amorphous (curve 5 in Figure 7a) even though it is also highly regioregular (95.8% HT). This result seems to suggest that a minimum run of 7 methylene units between the acetoxy groups is required for crystallinity of VAE/EVA copolymers. This observation also agrees with the result from model studies of methyl-substituted PE,[36] which suggested that crystallinity only exists with less than an average of 15 methyl branches per 100 carbon atoms (there are 14.3 acetoxy branches per 100 carbon atoms for HP3AcHE while 12.5 branches per 100 carbon atoms for HP3AcCOE).

X-ray Scattering Measurements. The semicrystalline structure of both a-HP3AcCOE and i-HP3AcCOE was supported by wide-angle X-ray scattering (WAXS) measurements. One-dimensional (1D) WAXS of samples that were stretched to their respective maximum elongations (~500% for a-HP3AcCOE and ~200% for i-HP3AcCOE) at room temperature (above their glass transition temperatures) are shown in Figure 9. As compared to unstretched samples (Figure S3, Supporting Information), the 1D WAXS profiles of these stretch samples exhibited considerably lower intensity amorphous halo signals, indicating a significant increase of crystallinity upon stretching. Small angle X-ray scattering (SAXS) of unaligned samples gave broad primary scattering peaks with d ~ 12–14 nm (Figure S4, Supporting Information), indicating these polymer possesses lamellae structure of alternating crystalline and noncrystalline regions, as observed in typical polyethylene.[37]

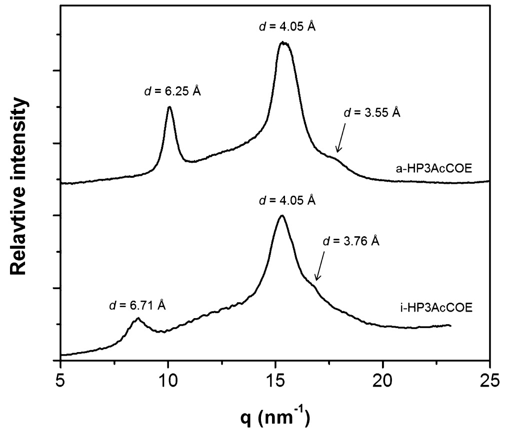


Figure 9. Room temperature 1D WAXS patterns of stretched samples of a-HP3AccOE (top) and i-HP3AcCOE (bottom) with the X-ray incident beam perpendicular to the stretching direction. Patterns derived from azimuthal integration of the indicated area in Figure S5(b) and S6(b), Supporting Information, respectively. Curves are shifted vertically for clarity.

Polyethylene can adopt orthorhombic or triclinic unit cells[36,38] and we posit that the crystal structures adopted by a-HP3AcCOE and i-HP3AcCOE belong to one of these crystal families given their structural similarity to polyethylene. For orthorhombic polyethylene the primary scattering peak is at d = 4.08 Å and for triclinic it is at d = 3.80 Å. Since the acetoxy side group must occupy space in the unit cell, and thus lead to expansion relative to linear polyethylene, a triclinic unit cell is the more likely candidate. In both WAXS patterns the distinct peaks at 6.25 and 6.71 Å likely arise from acetoxy–acetoxy correlations in the unit cell of the crystal structure. Given that these distances are shorter than the distance between adjacent acetoxy groups on the same chain in the fully extended conformation, the chains in the unit cell are likely interdigitated with the polar acetoxy groups on different chains shifted along one axis in the unit cell. While further studies are needed to elucidate the crystal structures of a-HP3AcCOE and i-HP3AcCOE, we can unambiguously conclude that the WAXS patterns of both a-HP3AcCOE and i-HP3AcCOE are unusual for EVA/VAE, as only an amorphous halo has been seen when the VA content >40–45%.[39] Therefore, these observations can be certainly related to the precise microstructure of these polymers.

Mechanical Properties. Figure 10 shows the representative stress–strain curves for a-HP3AcCOE, i-HP3AcCOE and the commercial VAE50 at room temperature. The Young's modulus of i-HP3AcCOE (133 ± 23 MPa) is about 50% higher than that of a-HP3AcCOE (90 ± 15 MPa), and both are more than 30–40 times higher than that of VAE50 (3.1 ± 0.4 MPa). Between the two regioregular polymers, a-HP3AcCOE has

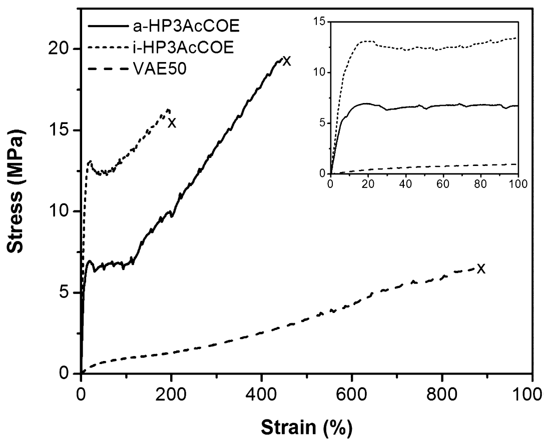


Figure 10. Representative stress−strain curves of a-HP3AcCOE, i-HP3AcCOE and the commercial VAE50. Inset: amplification of the low strain region. The mark “x” denotes failure.

higher tensile strength (24 ± 5 vs 14 ± 5 MPa) but lower yield strength (6.9 ± 0.3 vs 11 ± 2 MPa) than i-HP3AcCOE. These two polymers also exhibit much higher tensile strength than the random VAE50 (8.6 ± 1.5 MPa). i-HP3AcCOE fails at only 180−220% elongation while a-HP3AcCOE can be elongated to 450−500% its original length, but they are both less ductile than VAE50 that exhibits ultimate elongations of 900−1000%. Both a-HP3AcCOE and i-HP3AcCOE behave as typical semicrystalline thermoplastics. The mechanical behavior of each polymer is consistent with the degree of crystallinity of the respective polymer.[40] The result of tensile tests highlights the effect of microstructural regularity (i.e., sequence and tacticity) on the mechanical properties such as stiffness, toughness and ductility of compositionally similar polymers.

■ CONCLUSIONS

We have described the synthesis of several model linear VAE (>50 wt % VA) copolymers by ROMP of acetoxy-substituted cyclic alkenes and subsequent hydrogenation. All monomers can be prepared through simple reactions and in high yields. The polymer obtained from 3AcCOE was found to be highly regio-and stereoregular, and thus eventually led to a precision VAE analogue (a-HP3AcCOE). By employing enantiomerically pure 3AcCOE, the same ROMP procedure afforded an optically active polymer with both regularly and isotactically placed side chains, from which an isotactic precision VAE (i-HP3AcCOE) was obtained. This result showcases a functionalized example of the precision polymers that we reported previously by the regio- and stereoselective ROMP of 3-substitued COE.[11] Both a-HP3AcCOE and i-HP3AcCOE exhibit unusual thermal and mechanical properties due to their semicrystalline structures, which is the consequence of their high structure regularity. The presence of substantial crystallinity is unprecedented in any VAE copolymer with such high substituent frequency. Regio-irregular counterparts were synthesized from 4AcCOE and 5AcCOE; and both polymers have essentially no crystallinity. Furthermore, increase of the substitution frequency by polymerizing 3AcCHE resulted in a precision yet amorphous VAE analogue. These ROMP-derived VAE represent two distinct types of model polymers of the microstructurally inhomogeneous commercial VAE, one of which possesses a substantial degree of crystallinity and the other of which is completely amorphous. The works presented here not only create an efficient pathway to approach functionalized precision polymers but also demonstrate the achievement of different levels of control over polymer structure, which provides useful information for understanding the structure−property relationship of a wider range of polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data for all monomers and polymers. 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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