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Carboxy-Telechelic Polyolefins by ROMP Using Maleic Acid as a Chain Transfer Agent

Louis M. Pitet and Marc A. Hillmyer*

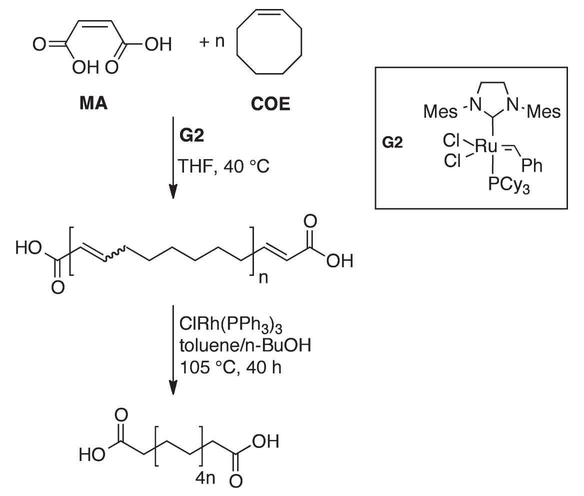
Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, United States

Supporting Information

Functionalized polyolefins are valuable and desirable synthetic targets.[1] More often than not, functional groups are incorporated by postpolymerization reactions.[2] Metathesis polymerizations can enable a straightforward route to functional polyolefins through a polymerization−hydrogenation strategy.[3,4] For example, α,ω-functional (i.e., telechelic) polyolefins are readily prepared by including a symmetric acyclic alkene during ring-opening metathesis polymerization (ROMP) of a cyclic olefin.[5] The simultaneous ring-opening and cross-metathesis (chain transfer, CT) between the propagating center and the chain transfer agent (CTA) results in the chain-end functionality. The efficacy of preparing chains with high functionality (i.e., average number of functional groups per chain, $F_n \rightarrow 2$) rests on the transition metal−alkylidene catalyst being reactive toward the CTA, being able to reinitiate a new chain, and remaining active at low levels relative to the CTA (i.e., $[M]_0 > [CTA]_0 \gg [catalyst]_0$). The latter criterion can be fulfilled by using the highly reactive ruthenium alkylidene having N-heterocyclic carbene ligand (G2) developed by Grubbs.[6] This note describes the use of unprotected maleic acid (MA) as a CTA during ROMP of *cis*-cyclooctene (COE) to provide carboxy-telechelic PCOE with an average degree of polymerization (N) dictated by the ratio of $[COE]_0$:$[MA]_0$ (Scheme 1). The resulting ester-substituted metallo-carbene readily reacts with the cycloalkene/linear poly(alkene), in accordance with the observations by Grubbs and co-workers regarding the reactivity/stability of ester-substituted carbenes.[7] Subsequent hydrogenation provides linear polyethylene (LPE) with retention of the carboxy end-functionality.

Cross-metathesis with vinylic compounds having electron withdrawing groups in the α-position (α-EWGs) such as acrylic amides,[8] acrylic acid,[9] and acrylonitrile[10] emerged in tandem with development of Ru-alkylidene precatalyst derivatives. Success of the CT−ROMP strategy relies on extensive cross-metathesis between a CTA and polymer chains. However, there are only a few examples including acyclic alkenes with α-EWGs during ROMP,[11] despite the ROMP of 1-amide-cyclobutene derivatives being reported.[12] Conventional structures of symmetric CTAs for ROMP contain at least one methylene unit separating the alkene from the functional groups. For example, nitrile-telechelic poly(cyclooctadiene) (PCOD) was prepared with 1,4-dicyano-2-butene and 1,8-dicyano-4-octene as CTAs, the latter of which was reduced with $LiAlH_4$ to provide amino-telechelic polymers.[13] Carboxy-terminal PCOD has been prepared using the CT−ROMP strategy with *cis*-1,4-bis(tert-butoxycarbonyl)-2-butene as a protected CTA and the first generation Grubbs catalyst.[14] Direct preparation of hydroxy-telechelic PCOD was also managed with *cis*-2-butene-1,4-diol as CTA; however, the yields were consistently low and difficulty was encountered controlling molar mass with $[COD]_0$:$[CTA]_0$.[6] Additional methods have been reported for preparing carboxy terminal polynorbornenes by ROMP through termination of a living chain with a vinyl lactone[15] or cleavage of multiblocks.[16] Although α-substituted vinyl compounds are routinely used in cross-metathesis, we could find no examples of CTAs for ROMP with the generic FG−CH═CH−FG structure [FG, functional group].[11]

Scheme 1. Synthesis of Carboxy-Telechelic Poly(cyclooctene) and Polyethylene by a CT-ROMP/Hydrogenation Approach



Four samples were initially prepared by polymerizing COE in tetrahydrofuran at 40 °C with varying concentrations of MA (samples 1−4 in Table 1). The concentration of G2 was kept approximately constant at $[COE]_0$:$[G2]_0 \approx 20{,}000$. Number average degrees of polymerization (N_n) were determined by end-group analysis using ^1H nuclear magnetic resonance (NMR) spectroscopy assuming exactly two end groups per polymer chain and compared to values obtained using size-exclusion chromatograpy (SEC) with multiangle light scattering (MALS) detection.

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Table 1. Degree of Polymerization (N_n) Measured by SEC-MALS and NMR Spectroscopy of Carboxy-Telechelic Poly(cyclooctene)s

sample no.	CTA	$[COE]_0$:$[CTA]_0$	N_n[a] (NMR)	N_n[b] (SEC)	PDI
1	MA	10	15	52	2.49[e]
2	MA	50	53	71	2.30[e]
3	MA	100	94	119	1.83
4	MA	200	210	236	1.77
5	FA	50	*d*	645	2.05
6	2HA	50	*d*	688	1.88

[a] Calculated from the ratio of relative integration from repeat unit and end-group protons in the ^{1}H NMR spectrum. [b] Determined by size-exclusion chromatography (SEC) with multiangle light scattering (MALS) detection in THF, using d*n*/d*c* for PCOE determined previously (d*n*/dc_{PCOE} = 0.110 mL/g) (ref 17). [c] Determined from size-exclusion chromatography in $CHCl_3$ at 30 °C compared with polystyrene standards. [d] End-group signals were not observed in the ^{1}H NMR spectrum of this sample. [e] A small shoulder containing monomeric and/or oligomeric units was included in analysis, and thus PDI values are larger than expected for an equilibrium process with chain transfer.

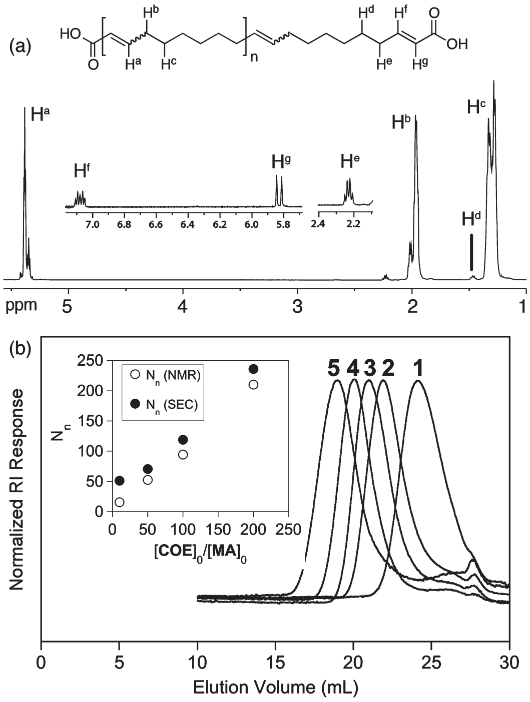


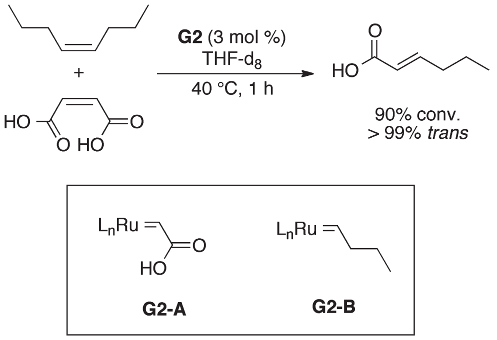
Figure 1. (a) ^{1}H NMR ($CDCl_3$) spectra for the carboxy-telechelic PCOE 2 ($[COE]_0/[MA]_0 = 50$). (b) SEC chromatograms for samples 1−5 and relationship between N_n and $[COE]_0/[MA]_0$ for samples 1−4 (inset).

The ^{1}H NMR spectrum of a poly(cyclooctene) (PCOE) sample with $[COE]_0$:$[MA]_0$ = 50 (Figure 1a) shows signals associated with the repeating units of PCOE and the olefinic protons adjacent to the carboxylic acid end groups (also see Figure S1). The "external" olefinic proton (H^g) appears at 5.8 ppm with doublet of triplet multiplicity (doublet, $^3J_{gf}$ = 15.6 Hz; triplet, $^4J_{ge}$ = 1.6 Hz). The "internal" terminal olefinic protons (H^f) appear downfield at 7.1 ppm with doublet of triplet multiplicity and coupling constants (doublet, $^3J_{fg}$ = 15.5 Hz; triplet, $^3J_{fe}$ = 7.0 Hz) consistent with *E* configuration. The strong EW carboxyl groups influence the methylene protons α (H^e) to the "internal" terminal olefinic carbon, causing a slight downfield shift compared to the main repeating unit methylene signals. The value of the triplet coupling constant attributed to the olefinic protons H^f suggests coupling to the methylene protons H^e at 2.23 ppm (triplet, $^3J_{ed}$ = 7.4 Hz; doublet, $^3J_{ef}$ = 7.0 Hz; doublet $^4J_{eg}$ = 1.6 Hz) and is consistent with the assignments depicted in Figure 1a. Further structural corroboration is provided by two-dimensional ^{1}H−^{1}H correlated NMR spectroscopy (COSY) (Figure S2). The integration values of the end-group signals compared with the repeat units are in good agreement with the targeted degree of polymerization assuming quantitative monomer consumption and exactly two functional groups per polymer chain. The high polymer yield for each sample (>90% in all cases) suggests near-quantitative monomer conversion. Molecular weight control by $[COE]_0$:$[MA]_0$ is further evidenced by the relative elution volumes observed in SEC chromatograms (Figure 1b). The values of N_n of the polymer samples 1−4 as determined by NMR spectroscopy and SEC−MALS scale linearly with $[COE]_0$:$[MA]_0$ (inset of Figure 1b). The discrepancy between *N* measured by NMR spectroscopy and SEC for sample 1 possibly arises from aggregation of the carboxylic end groups due to their relatively high concentration at this low molar mass. In that case, the scattering intensity of the aggregates would be artificially high. For sample 1, the NMR results likely give a more accurate degree of polymerization.

The spectra for carboxyl terminal PCOE clearly reveal only one distinct signal for each of the protons H^{d-g} corresponding to an exclusive *trans* configuration about the terminal double bond adjacent to the carboxyl end group. This feature contrasts with the analogous polymerization with 1,4-disubstituted-2-butene CTAs, in which signals associated with both *cis* and *trans* configurations are observed.[6,18] Once incorporated into the chain, the end group is essentially nonreactive. Indeed, when COE was polymerized with G2 in the presence of either fumaric acid (FA, i.e., *trans* isomer of maleic acid) or *trans*-2-hexenoic acid (2HA), carboxyl end groups were not observed by ^{1}H NMR spectroscopy, and high molecular weight polymer was obtained (entries 5 and 6 in Table 1; also see Figure 1b). Cross-metathesis between *cis*-4-octene (4Oct) and MA provides direct evidence for the preferred stereochemical orientation of the Ru−alkylidene species during each metathetical cycle. An equimolar mixture of MA and 4Oct using 3 mol % (per double bond) G2 catalyst in THF-d_8 at 40 °C formed predominantly 2HA (Scheme 2).

The ^{1}H NMR spectrum of the product (Supporting Information) reveals greater than 90% conversion to 2HA product having essentially pure *E* configuration about the double bond.[19] The presence of a sterically unencumbered Ru−alkylidene active species (G2-B in Scheme 2) is crucial to efficient metathesis with MA. The electron-deficient Ru−alkylidene G2-A is nearly prohibited from cross-metathesizing with MA; reaction with 4Oct is far more favorable. Indeed, self-cross-metathesis of maleic acid under identical conditions converted only 2.5 mol % of the double bonds to the *E* configuration.[20] The proposed metathetical cycle (Figure S6) entails the preferred reaction between G2-A with 4Oct. Of course, isomerization of *Z*-4Oct to *E*-4Oct may well proceed throughout the reaction, and thus G2-A could react with either isomer. We suggest that *E*-2-hexenoic acid is the thermodynamically preferred product (Figures S3−S5). The chemical shifts, splitting patterns, and coupling constants for the olefinic protons α (5.75 ppm; doublet, ^3J = 15.6 Hz) and *β* (6.87 ppm; doublet, ^3J = 15.4 Hz; triplet, ^3J = 7.2 Hz) to the

Scheme 2. Cross-Metathesis between MA and 4Oct To Synthesize *trans*-2-Hexenoic Acid[a]



[a] The two possible reactive Ru—alkylidene species are shown resulting from MA metathesis (G2-A) or 4Oct metathesis (G2-B).

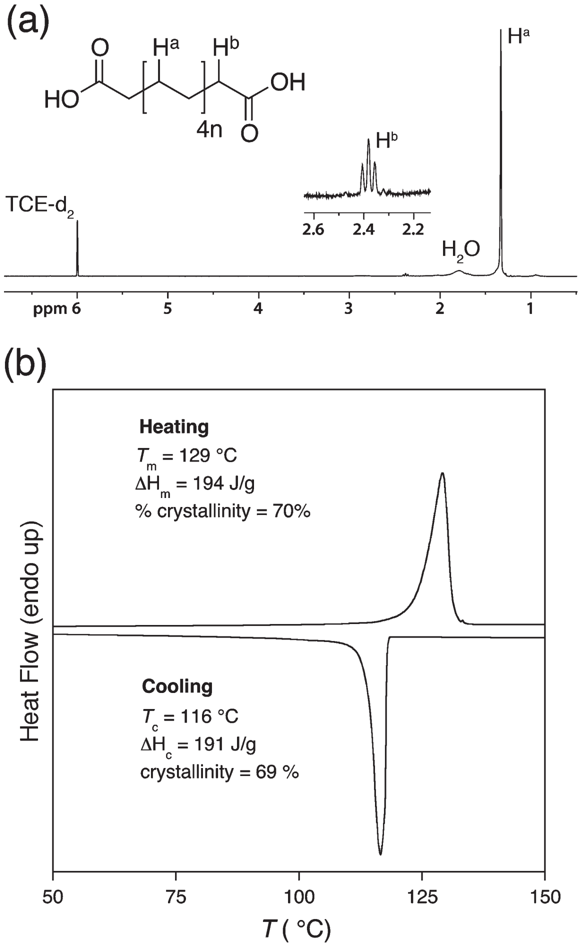


Figure 2. (a) ^{1}H NMR spectrum showing the saturated backbone protons and end-group protons adjacent to the carboxyl end groups magnified. (b) DSC thermogram for the cooling cycle and the second heating cycle and the corresponding phase change temperatures (T), enthalpies (ΔH), and crystallinities.

carboxyl group in the 2HA are identical to the signals seen in the PCOE samples and commercially available *trans*-2HA. The values are consistent with all *trans* configurations about the double bonds adjacent to the end groups in the polymers.

Hydrogenation of the carboxy-telechelic PCOE represents a convenient path toward LPE[21] with reactive end functionality (see Scheme 1). Attempts at heterogeneous hydrogenation with a silica-supported Pt catalyst provided saturated materials, although reduction of the carboxyl groups to hydroxyl functionality was not entirely preventable. This observation is consistent with reports by Wagener and co-workers in hydrogenating unsaturated polyolefins having pendant carboxyl functionality.[22] Alternatively, hydrogenation with Wilkinson's catalyst [tris(triphenylphosphine)rhodium(I) chloride][23] provided essentially quantitative saturation of backbone double bonds without reduction of carboxyl groups. The ^{1}H NMR spectrum obtained in $CDCl_2CDCl_2$ (1,1,2,2-tetrachloroethane-d_2; TCE-d_2) at 100 °C shows the signals for the methylene protons α to the carboxyl groups (Figure 2a). The position of the peak is in agreement with analogous protons in the model compound stearic acid [$CH_3(CH_2)_{16}COOH$]. The relative integration of the signals from the end groups compared with the repeating unit provides a value for the degree of polymerization, N_n, for the linear polyethylene (8-carbon repeating unit; N_n = 17) that agrees reasonably well with the unsaturated PCOE precursor (N_n = 15). IR spectroscopy provides further evidence for the polymer retaining the carboxyl end groups during hydrogenation, especially upon comparison with a model spectrum of stearic acid (Figure S7).

The thermograms (heating rate = 10 °C min^{-1}) from differential scanning calorimetry (DSC) reveal temperatures of melting (T_m = 129 °C) and crystallization (T_c = 116 °C) that are consistent with a completely linear saturated hydrocarbon backbone. The melting and crystallization enthalpies are typical for LPE (ΔH_m^0 = 277 J g^{-1}).[24] This carboxy-telechelic LPE offers the possibility to further functionalize the chain ends and create hybrid soft materials that combine the physical attributes of LPE and with other materials. This straightforward approach to carboxyl functional LPE enhances the convenience with which similarly complex materials can be prepared utilizing metathesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, ^{1}H and ^{13}C NMR spectra, IR spectra for model compounds and polymers, and a mechanistic reaction scheme for cross-metathesis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hillmyer@umn.edu.

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(19) We assume the *cis* isomer of the 2HA would exhibit significant differences in chemical shift in either ^1H or ^{13}C NMR spectra to clearly observe and quantify if it were present. The different isomers can clearly be detected for the reactants (*cis*- vs *trans*-4-octene and maleic vs fumaric acids).

(20) The commercial maleic acid contained 1.2 mol % *trans* double bonds. The cross metathesis reaction led to 3.7 mol % *trans*.

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