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Articles

Tandem Homogeneous Metathesis/Heterogeneous Hydrogenation: Preparing Model Ethylene/CO_2 and Ethylene/CO Copolymers

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ABSTRACT: Addition of silica gel to a completed homogeneous metathesis polymerization catalyzed by $Cl_2(Cy_3P)_2RuCHPh$ (**1**) converts the residue of **1** to a highly effective heterogeneous olefin hydrogenation catalyst. Quantitative olefin hydrogenation of the unsaturated polymer under very mild conditions occurs in the presence of a variety of functional groups. This tandem homogeneous metathesis/heterogeneous hydrogenation procedure is used to prepare commercially relevant polyethylene-based materials, such as sequence ordered ethylene/CO_2 and ethylene/CO copolymers as well as telechelic polyethylene.

Introduction

Recent advances in olefin metathesis have established this reaction pathway as a powerful transformation in organic chemistry, where growing confidence of its utility by the synthetic community is demonstrated by the willingness to implicate this reaction in multistep syntheses of natural products.[1] The rapidly expanding scope of this reaction and delineation of structure−reactivity relationships also have allowed its exploitation in metathesis polymerization to prepare polymers with well-defined microstructures.[2] Hydrogenation of these unsaturated backbones provides polymers that may be difficult or impossible to obtain by direct means, where examples include the preparation of perfectly linear polyethylene[3] and telechelic polyethylene,[4] model polyolefins with regularly spaced pendant groups,[5] polyarylene−alkylenes,[6] and ethylene block copolymers with precisely controlled monomer run lengths.[7] Of commercial importance are the hydrogenated polymers of norbornene and polycyclic derivatives of norbornene marketed as Zeonex. Typical routes involve first the synthesis and isolation of unsaturated polymers followed by a second step in which the polymers are hydrogenated with additional reagents and/or catalyst.

A combined metathesis/hydrogenation procedure would be preferred, and recently McLain[8] et al. reported a one-pot procedure for doing so. An ethylene/methyl acrylate copolymer was synthesized first by the ring-opening metathesis polymerization (ROMP) of an ester-functionalized cyclooctene using the ruthenium catalyst $Cl_2(PCy_3)_2Ru{=}CHCH{=}CPh_2$, followed by homogeneous hydrogenation. The hydrogenation step is performed by applying relatively high hydrogen pressures to the completed ROMP reaction at 135 °C, where hydrogen pressures of at least 400 psi were required to maintain catalytic activity of this homogeneous system sufficient to achieve >99% reduction. The hydrogenating species was assumed to be $RuHCl(PCy_3)_2$, and the need for higher pressures most likely stems from decomposition and/or aggregation of this proposed highly unsaturated complex in the absence of excess hydrogen. This type of homogeneous in situ hydrogenation also has been recently reported utilizing a bimetallic ruthenium metathesis catalyst under mild conditions.[9] The dual utility of these ruthenium complexes is not surprising as Ru−phosphine complexes have been known as effective olefin hydrogenation catalysts since Wilkinson's initial observations[10] more than 30 years ago.

We now report a simple two-step metathesis/hydrogenation procedure, which consists of using a ruthenium complex to first drive *homogeneous* metathesis chemistry and then to promote *heterogeneous* hydrogenation in situ. The key step involves the addition of simple chromatographic grade silica gel after the metathesis reaction is completed to serve as a support for the residue of the commercially available ruthenium complex $Cl_2(Cy_3P)_2RuCHPh$ (**1**).[11] The resulting silica supported heterogeneous ruthenium species catalyzes relatively rapid and quantitative olefin hydrogenation under mild conditions (moderate pressures, room temperature) without the need for highly specialized equipment. Further, the conversion of the catalyst to a heterogeneous hydrogenation system facilitates removal of the catalyst and isolation of the hydrogenated products, since the catalyst residue can be mechanically separated by simple filtration. To demonstrate the opportunities that exist, this methodology has been applied in the preparation of saturated aliphatic polymers with high polyethylene character.

Experimental Section

General Considerations. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Gemini series NMR superconducting spectrometer system or a Varian VXR-300. Resonances are referenced to residual protio solvent and reported in δ units downfield from TMS at 0.0 ppm. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. High-temperature gel permeation chromatography was

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performed by Exxon Chemical Company, Baytown Polymers Center, with a Waters GPC system (mixed bed styragel columns) set up specifically for analyzing polyethylene. Molecular weight values were calculated assuming polyethylene Mark−Houwinck coefficients.

Differential scanning calorimetric (DSC) data were obtained with a Perkin-Elmer 7 series thermal analysis system. DSC samples (5−10 mg) were analyzed with ice as coolant and under a helium flow rate of 25 mL/min. All samples were predried at 40−50 °C under reduced pressure ($<$0.1 mmHg) for at least 24 h. The instrument was calibrated for peak onset temperature transitions and peak area using indium as standard. Samples were scanned at a heating/cooling rate of 10 °C/min from room temperature to 150 °C with data collection during the second cycle.

Materials. The ruthenium catalyst (**1**) was prepared according to the literature.[11] Toluene (Fisher, HPLC grade) was distilled from Na/K alloy under argon and degassed. 9-Decenyl acetate (**4**), ethyl 10-undenoate, and 9-decenyl 10-undecenoate (**8**) were obtained by published esterification methods[12] from 10-undecenoic acid and 9-decenol. 1,9-Decadiene, 1-octene, *trans*-7-tetradecene, and 2-chlorobutane were obtained from Aldrich, vacuum distilled from CaH_2, degassed, and stored under argon prior to use. Triene substrate **3** was prepared as reported elsewhere.[13] Diene monomers, **8** and **11,** were degassed and dried by stirring under reduced pressure at 60 °C for 1−5 h before polymerization. Silica gel-60 (Fischer, Selecto Scientific catalog no. 162824, particle size 32−63 μm) was sonicated twice in reagent grade $CHCl_3$, dried under reduced pressure ($<$0.5 mmHg) at 80 °C with magnetic agitation for 48 h, and stored in an argon-purged drybox until use. All manipulations were conducted inside an argon-purged drybox except where noted. Hydrogenations were conducted in glass pressure tubes (Ace Glass) fitted with brass inlet valves via threaded Teflon bushings. Model studies performed at higher pressures were conducted in a glass-lined, stainless steel Parr bomb.

Model Study of Hydrogenation Using *trans*-7-Tetradecene. *trans*-7-Tetradecene (1.0 g, 5.09 mmol) and catalyst **1** (5.2 mg, 0.13 mol %) were combined in a pressure tube containing a magnetic stir bar and stirred 1 h to allow dissolution of catalyst and alkylidine exchange, during which time the purple heterogeneous mixture became a clear maroon solution. A 520 mg sample of silica gel was added, and the tube was immediately sealed, removed to a hydrogen manifold, and exposed to a constant H_2 pressure at room temperature. After 30 min, the reaction was quenched by releasing pressure to the atmosphere and filtered to remove catalyst residue and silica, yielding a clear, colorless liquid. The extent of reduction was estimated by ^{1}H NMR ($CDCl_3$) comparing the resonances at 5.4 ppm (multiplet, internal olefin) to that at 0.88 ppm (triplet, CH_3 group). Experiments at each pressure were conducted in triplicate and the average conversions calculated.

Synthesis of 1,18-Bis(acetoxy)octadecane (7). 9-Decenyl acetate (**4**) (1.0 g, 5.04 mmol) and catalyst **1** (5.2 mg, 52 μmol) were combined in a high-vacuum flask containing a magnetic stir bar. The vessel was sealed, removed to a Schlenk line, and opened to a slight positive pressure of argon. It was heated to 60 °C with vigorous stirring for 4 h, after which reaction was continued for an additional 2 h at ∼0.2 mmHg. The reaction mixture was taken up in 3 mL of toluene and combined with 600 mg of silica gel in a pressure tube, and the whole was exposed to 120 psig of H_2 at 90 °C for 5 h with vigorous stirring. Filtration and evaporation of solvent and traces of hydrogenated **4** yielded the product **7** as a white powder (0.90 g, 96% yield). LRMS: 372 (m + 2). Elemental anal. calcd for $C_{22}H_{42}O_4$: C, 71.31; H, 11.42. Found: C, 71.37; H, 11.50. ^{1}H NMR: δ (ppm, $CDCl_3$) 4.02 (t, 4H); 2.02 (s, 6H); 1.59 (m, 4H); 1.23 (br, 28H). ^{13}C NMR: δ 171.2, 64.65, 29.65, 29.56, 29.52, 29.24, 28.59, 21.02.

Synthesis of Telechelic Polyethylene (6). 1,9-Decadiene (3.0 g, 21.7 mmol), 9-decenyl acetate (**4**) (0.861 g, 4.34 mmol, 0.2 equiv), and **1** (49 mg, 0.06 mmol) were combined for a total of 800:1 olefin-to-catalyst ratio. Over a period of 6 h, pressure was slowly decreased (intermittent vacuum), eventually reaching a dynamic vacuum of 10^{-2} mmHg, while increasing temperature from 45 to 65 °C. After 24 h, 1.5 g of the crude unsaturated polymer (**5**) was intimately mixed with 2.5 g of silica gel in a pressure tube and exposed to 120 psig of H_2 at 90 °C for 30 min. A 15 mL aliquot of toluene was then added via syringe under H_2 purge, and the vessel was then exposed to 120 psig of H_2 at 90 °C with vigorous stirring for 5 h. Reaction was quenched by release of pressure and filtered while still hot through a heated coarse glass frit to remove catalyst residue and silica. Toluene was removed under reduced pressure to yield 1.45 g of white solid. Elemental anal. calcd for [$C_{102}H_{202}O_4$]: C, 82.07; H, 13.64. Found: C, 82.03; H, 13.70. ^{1}H NMR: δ (ppm) (90 °C, toluene-d_8) 3.98 (t, 4H); 1.73 (s, 6H); 1.50 (m, 4H); 1.30 (br, 220H). $M_n = 1.5 \times 10^3$ (PDI = 1.9, GPC), 1.7×10^3 (^{1}H NMR end group analysis).

Synthesis of an Aliphatic Polyester (10). Diene **8** (3.00 g, 9.31 mmol) and catalyst **1** (12.7 mg, 15.5 μmol) were combined, and ADMET polymerization was conducted as above. The pressure was slowly decreased by applying intermittent vacuum, eventually reaching a dynamic vacuum of 10^{-2}−10^{-3} mmHg while the temperature was slowly increased from 45 to 70 °C, and then reaction was continued for 24 h. Crude yield of unsaturated polyester (**9**): 2.70 g, 97.8%. A 1.00 g chunk of the crude polymer/catalyst residue mixture was combined with 500 mg of silica gel and 10 mL of toluene in a glass pressure tube, and hydrogenation was conducted as above. Note: hydrogen pressure is applied prior to dissolution of the polymer chunk. After 24 h, pressure was released to the atmosphere, and the heterogeneous mixture was filtered while still hot through a coarse glass frit. The polymer precipitated on cooling to below 60 °C. The toluene was evaporated under reduced pressure to yield polyester **10** as a white solid. Yield: 0.96 g, 95% based on 1 g of **9**. Elemental anal. calcd for [$C_{19}H_{36}O_2$]: C, 76.97; H, 12.24. Found: C, 77.06; H, 12.22. ^{1}H NMR: δ (ppm) (90 °C toluene-d_8) 4.02 (t, 2H); 2.17 (t, 2H); 1.56 (m, 4H); 1.28 (br, 28H). ^{13}C NMR: δ 177.0, 139.1, 114.1, 51.21, 45.67, 33.76, 32.47, 29.49, 29.35, 29.05, 28.86, 27.42. $M_n = 1.02 \times 10^4$ (PDI = 2.3, GPC).

Synthesis of 11-Oxo-1,20-heneicosadiene (11). The ketone diene **11** was prepared in two steps via Claisen condensation of ethyl 10-undecenoate to form the β-keto ester diene, followed by dealkoxycarbonylation without isolation of the first step. Claisen condensation: ethyl 10-undecenoate (60 mL, 52.44 g, 247 mmol, 1 equiv) was added dropwise to a stirring suspension of KH [34.97 g (35% w/w in mineral oil), 296.4 mmol, 1.2 equiv] in 300 mL of dry THF at room temperature. After 12 h, the reaction was cooled to 0 °C and quenched by addition of 30 mL of acetic acid, and the solution was poured into cold deionized water. The layers were separated, and the aqueous phase was extracted with ether. The combined organic solutions were washed with deionized water, dried over $MgSO_4$, and concentrated under reduced pressure to a yellow oil. Dealkoxycarbonylation: the crude oil was combined with 93.4 g of LiCl, 450 mL of DMSO, and 20 mL of deionized water, and the mixture was sparged with argon for 30 min. The mixture was then vigorously stirred at 155 °C under argon for 12 h. Upon cooling to room temperature, the mixture separated and the upper phase solidified. The solid was taken up in ether, washed with deionized water, concentrated, and purified by flash chromatography (3% EtOAc/hexanes). Yield 70% for two steps. Elemental anal. calcd for $C_{21}H_{38}O$: C, 82.29; H, 12.50. Found: C, 82.08; H, 12.40. ^{1}H NMR: δ (ppm, $CDCl_3$) 5.78 (m, 2H); 4.92 (m, 4H); 2.35 (tr, 4H); 2.01 (q, 4H); 1.53 (m, 4H); 1.32 (br, 24). ^{13}C NMR: δ 211.6, 139.1, 114.1, 42.78, 33.75, 29.33, 29.27, 29.05, 28.88, 23.87.

Synthesis of a Sequence-Ordered Ethylene/CO Polymer (13). Ketone diene **11** (500 mg, 1.63 mmol) and catalyst **1** (3.3 mg, 4.1 μmol) were combined, and ADMET polymerization was conducted as above. After 30 min, 1 mL of toluene was added under argon to aid stirring, and the reaction was continued in an 80 °C bath with intermittent vacuum for 24 h followed by 8 h at 10^{-2} mmHg. Hydrogenation and isolation as above yielded 445 mg (97%) of polymer **13** as a white solid. ^{1}H NMR: δ (ppm) (108 °C toluene-d_8) 2.15 (t, 2H); 1.57 (m, 4H); 1.35 (br, 28H); 0.91 (t, 0.07H, CH_3 end groups). ^{13}C NMR:

δ 208.1, 42.91, 30.28, 30.25, 30.22, 30.09, 30.02, 29.94, 24.46. $M_n = 9.9 \times 10^3$ (PDI = 3.7, GPC).

Results and Discussion

Model Studies of Silica Mediated Hydrogenation. To study the hydrogenation phase of this new procedure, the conversion of *trans*-7-tetradecene to tetradecane was examined to model the saturation of olefins in polymer structures. In a typical experiment, *trans*-7-tetradecene and catalyst **1** (400:1 molar ratio) were combined and stirred 1 h to allow dissolution of catalyst and alkylidene exchange as would be the case at the end of a metathesis reaction. Silica was added, and the system was exposed to a constant H_2 pressure *at room temperature* with vigorous stirring for only 30 min. Adsorption of the catalyst onto silica was indicated by rapid decolorization of the solution and conversion of the silica to a reddish-brown color. Once the reaction was complete, the extent of hydrogenation of the substrate was estimated from ^{1}H NMR by comparing the resonances due to the olefinic protons to those of the methyl groups. Under these conditions, room-temperature hydrogen pressures of 100, 150, and 200 psig resulted in 41, 90, and >99% reduction of 7-tetradecene to tetradecane, respectively; a pressure of 250 psig at room temperature resulted in quantitative hydrogenation within spectroscopic detection limits. For the sake of comparison, the room-temperature exposure of a homogeneous solution of catalyst **1** and *trans*-7-tetradecene to 120 psig of H_2 for 15 h resulted in less than 30% hydrogenation of the olefin; a duplicate reaction with silica present resulted in quantitative reduction in the same reaction time.

As mentioned previously, McClain[8] suggested the formation of a Ru−H species upon hydrogenolysis of a similar ruthenium carbene, and recent work by Caulton[14] supports this assumption. However, the former indicated that hydrogenation activity is not maintained at lower hydrogen pressures. The greater efficiency in hydrogenation upon addition of silica is most likely due to two contributing factors. One obvious assumption is that immobilization on a heterogeneous support precludes aggregation and any bimolecular modes of decomposition of the hydrogenating species. Second, our work also indicates that the addition of silica to a reacting solution of **1** and olefin leads to the formation of (a) new species, possibly a Ru−hydride, capable of catalyzing olefin migration. Evidence for this assumption comes from experiments in the absence of hydrogen. For example, the homogeneous conversion of 1-octene with catalyst **1** results in only the expected products of clean metathesis, *cis*- and *trans*-7-tetradecene, while stirring 1-octene with silica alone yields only starting material. However, the combination of 1-octene, catalyst **1**, and silica results in a heterogeneous reaction system that produces a homologous mixture of linear internal alkenes from C_6−C_{16}, including odd and even carbon species (GC/MS, DEPT ^{13}C NMR, ^{1}H NMR).

We propose that both olefin metathesis and olefin migration operate simultaneously in the heterogeneous silica system in the absence of hydrogen gas (Figure 1). In this proposed scheme, 1-octene isomerizes to a mixture of four octenes (1-, 2-, 3-, and 4-octene), and each of these octenes then is subject to metathesis chemistry driven by the heterogeneous catalyst residue. The consequence is to broaden the product distribution to internal olefins from C_4−C_{14}, including species with odd numbers of carbons. Continuing the tandem process with the newly available olefins could produce species larger than C_{14}.

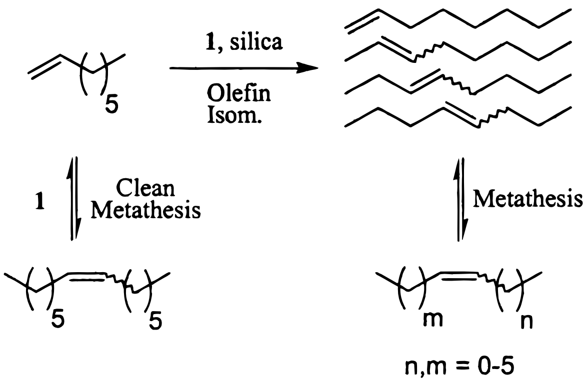

Figure 1. Reactivity of **1** toward 1-octene with and without silica.

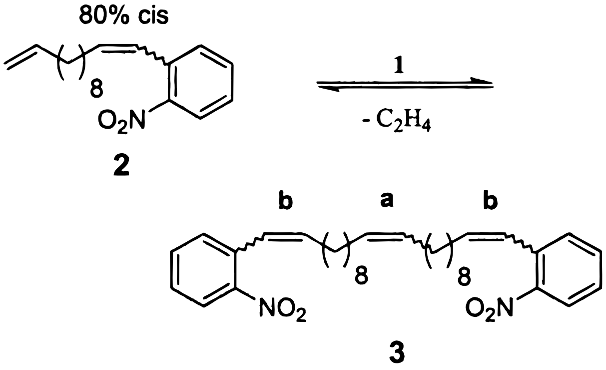

Figure 2. Model compound used for evaluating selectivity of catalyst **1** on silica.

The metathesis observed in these reactions is likely catalyzed by intact ruthenium carbene **1**, which has been simply physisorbed to silica. Olefin migration then may be catalyzed by a new ruthenium species, possibly a metal hydride, which could originate from reaction of **1** with the silanol groups of silica. Further, the presence of olefins with odd numbers of carbons and the absence of detectable branching makes processes such as olefin dimerization via Ziegler−Natta type insertion and elimination unlikely. Incidentally, replacement of **1** in this experiment with the catalyst $Cl_2(Ph_3P)_2RuCHPh$, which has been shown to be *inactive* for acyclic olefin metathesis, only results in production of octenes with olefins in internal positions, without the formation of higher or lower homologues. Therefore, adsorption of the catalyst residue from a homogeneous solution onto silica to produce a heterogeneous catalyst not only provides for high surface area (more available reactive sites) but also likely forms an Ru−H species. This Ru−H species can lead to olefin migration in the absence of hydrogen gas. While systems for tandem olefin metathesis and isomerization are desirable for some applications (e.g., the SHOP method), isomerization is an unwanted side reaction in this case and can be suppressed using moderate hydrogen pressure.

The hydrogenations described herein deal with isolated olefin moieties within a hydrocarbon chain. To examine the selectivity of this heterogeneous reaction, we attempted the hydrogenation of a model compound **3** (Figure 2) containing multiple reducible sites. As predicted based on recent reports[15] of selectivity in the metathesis of substrates with varied electronic and steric modifications, bond **b** is unreactive under the conditions employed for metathesis catalyzed by **1**. As a result, triene **3** can be obtained from **2** in 95% isolated yield.[13] In situ heterogeneous hydrogenation of **3** revealed certain aspects of relative selectivity of the system reported here. Hydrogenations were conducted at room temperature (24 h) in toluene, and conversions were estimated from ^1H NMR. At 120 psig of H_2, bond **a** is quantitatively hydrogenated. However, bond **b** (cis) is only converted by approximately 90% while **b** (trans) is virtually unreacted. At 800 psig, conversions are near quantitative and approximately 80% for **b**(cis) and **b**(trans), respectively. These observations are in keeping with the selectivity typically observed for sterically hindered cis/trans isomers. In both cases, a diminutive peak was detected (^1H NMR, $\delta \sim 3.6$ ppm) which might be assigned to the NH_2 protons of the aniline moiety resulting from possible reduction of a small percentage of the nitro groups. Reports of hydrogenation with various homogeneous catalysts of general formula $Cl_n(R_3P)_mRuL_n$ indicate pressures in excess of 80 atm are required to obtain good to excellent reduction of aromatic nitro compounds to aniline derivatives in practical reaction times.[16] Optimization of reaction conditions might allow hydrogenation of nitro-functionalized substrates, providing an indirect route to primary amines without the need for the protection/deprotection schemes necessary with currently available metathesis catalysts. Regardless, these results show that under these conditions olefins may be reduced selectively in the presence of aromatic nitro groups.

Under the conditions reported here, the olefin hydrogenation reaction is effective in the presence of a variety of other functionality including esters, ketones, tetraalkyl silanes, and aromatics.[17] However, preliminary studies show that at elevated temperatures and pressures monoalkyl-substituted benzene rings can be reduced while chlorinated alkanes show an inhibitory effect. Repeating the model experiments with *trans*-7-tetradecene, including 5 equiv of 2-chlorobutane, resulted in less than 20% reduction of the olefin after 4 h at 120 psig of H_2 and room temperature. Removal of volatiles and addition of fresh *trans*-7-tetradecene resulted in ~90% reduction after 4 h at 120 psig, revealing that catalytic activity is hindered but not destroyed by the presence of the chlorinated alkane.

The Preparation of Telechelic Polyethylene. One useful application for this new metathesis/hydrogenation procedure is the production of telechelic polyethylene, materials sought after by Hillmyer and Grubbs[4] using ROMP chemistry followed by diimide reduction. To demonstrate utility of our new tandem homogeneous metathesis/heterogeneous hydrogenation approach, we have prepared telechelic polyethylene (**6**) (Figure 3) via acyclic diene metathesis (ADMET) chemistry.

1,9-Decadiene first was condensed under typical bulk homogeneous ADMET conditions in the presence of 9-decenyl acetate (**4**) as a chain limiter. Upon completion of the metathesis reaction, the initial olefin to Ru ratio (800:1) is reduced by one-half to 400:1, and this is therefore the catalyst loading at the beginning of the hydrogenation stage. Subsequent heterogeneous hydrogenation requires the addition of solvent to aid dispersion, but dilution in the presence of active metathesis catalyst would favor formation of lower molecular weight cyclics at the expense of linear species. To avoid this problem, the unsaturated polymer (**5**) first was intimately mixed with silica, and the system was exposed to 120 psig of H_2 for 30 min prior to addition of toluene. Extensive hydrogenation had already occurred at this point, even in the bulk state, to yield a product with sufficient polyethylene character to render it poorly soluble in toluene at room temperature. Hydrogen pressure (120 psig) was reapplied for 5 h while heating in a 90 °C oil bath to prevent precipitation of the product. Simple hot filtration and removal of the solvent under reduced pressure yielded the telechelic polyethylene as a white solid in near quantitative yield.

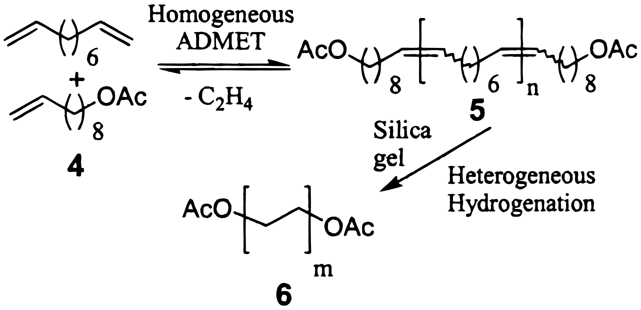

Figure 3. Synthesis of telechelic ester-functionalized polyethylene.

As is the case for all polymers reported here, ^1H and ^{13}C NMR show the complete disappearance of peaks corresponding to 1,2-alkyl-substituted olefinic groups. The monomer/chain limiter ratio in the ADMET polymerization was chosen to give polyoctenamer with DP = 10 ($n = 10$, Figure 3), which upon hydrogenation gives telechelic polyethylene with DP = 48 (Figure 3, $m = 48$), or $M_n = 1.5 \times 10^3$ g/mol. End group analysis (^1H NMR) and high-temperature gel permeation chromatography gave number-average molecular weights of 1.5×10^3 and 1.7×10^3 g/mol, respectively, measurements which are in excellent agreement with the value predicted by the monomer/chain limiter ratio. In addition, the polydispersity ratio of 1.9 agrees well with that expected for an equilibrium polycondensation product.

Further, the acetate content of the telechelic polymer as calculated from ^1H NMR did not decrease from that expected from initial stoichiometry, indicating that these groups remain intact throughout olefin hydrogenation. High-yielding metathesis dimerization/hydrogenation of the chain limiter (**4**) to 1,18-bis(acetoxy)octadecane (**7**) under the same conditions as for preparation of the telechelic polyethylene adds support to the stability of the end groups during hydrogenation.

The Preparation of Ester Functionalized Polyethylene. A second demonstration of the utility of this tandem procedure consists of the formation of polyethylene functionalized with ester groups internal in the chain. Recently, Penelle[18] et al. reported the synthesis of polyesters with regular long alkyl segments within the polymer backbone by classical condensation of long chain aliphatic diols with diacids. Their interest lies in the modification of lamellar crystal structure by introducing regular defects in a polymer with high polyethylene character. Similar polymers may be prepared by the tandem methodology we report herein. This chemistry is shown in Figure 4, and it is identical in scope to the generation of telechelic polyethylene in that ADMET step polymerization is conducted to yield moderate to high molecular weight step polymers, followed by quantitative, silica-mediated hydrogenation.

The polyester **10** (Figure 4) was obtained in near quantitative yield via ADMET condensation of ester

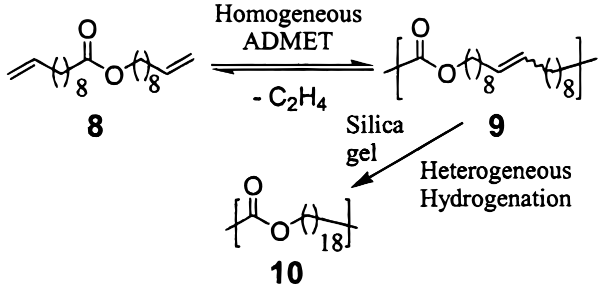

Figure 4. Synthesis of long chain, aliphatic polyester with internal ester groups.

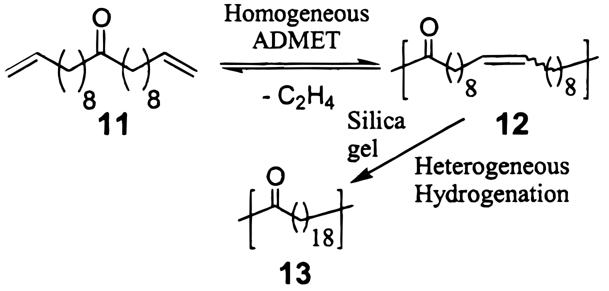

Figure 5. Synthesis of sequence-ordered ethylene/CO copolymer.

diene **8** followed by hydrogenation. Because of its highly crystalline nature ($\Delta H_f = 122$ J/g, $T_m = 97$ °C, DSC) and long ethylene run lengths, polymer **10** displays very limited solubility in typical organic solvents at room temperature but is freely soluble above 60 °C. The structure shown is not entirely correct as the monomer may be statistically incorporated in head−head, head−tail, and tail−tail orientation (1:2:1 ratio) due to the unsymmetrical nature of the ester moiety. WAXS (Cu Kα) analysis of a melt-crystallized sample (annealed 1 h, 80 °C) reveals, in addition to (h,k,0) diffraction peaks characteristic of orthorhombic polyethylene, a peak at $2\theta = 3.92$, with second (7.88) and third (11.85) order reflexes, corresponding to $d = 22.5$ Å, in good agreement with the calculated distance for all trans 18 carbon chains separating collinear ester groups. This method and the polymer characterization are complementary to the reports from Penelle.[18]

Preparation of a Model Sequence-Ordered Ethylene/CO Copolymer. The availability of a series of aliphatic model polymers with relatively distant, precisely spaced functionalities should prove highly useful for studying effects of different groups on polymer crystallinity. The production of such polymers is most easily approached utlilizing step polymerization, chemistry which to some degree limits the scope of functionalities that may be incorporated. This restriction is lifted by incorporating the desired functionality into symmetrical dienes and then condensing to high molecular weight via ADMET, followed by hydrogenation. Recent examples include precisely branched polyethylene[5b] and sequence ordered ethylene/vinyl acetate[5a] model copolymers. We applied the method reported here to provide a further example of such well-defined polymers, in this case, the preparation of the sequence-ordered ethylene/CO copolymer **13** shown in Figure 5.

While strictly alternating ethylene/CO polymers and random versions with very low CO contents exist, there is no published method for the preparation of high molecular weight sequence ordered copolymers with controlled ethylene run lengths. Thus, the model polymer **13** was prepared in fashion similar to polyester **10** by ADMET condensation of the symmetrical ketone-functionalized diene **11** followed by heterogeneous hydrogenation. Crystallization of the unsaturated precursor polymer **12** during the first few minutes of the ADMET reaction prevented stirring, even at 70 °C. A small amount of toluene was added as diluent to facilitate the ADMET reaction, and these reaction conditions employed resulted in lower molecular weight and broader PDI than typically realized utilizing ADMET polymerization.

Not surprisingly, the melting point of the polyketone **13** ($T_m = 134$ °C, $\Delta H_f = 127$ J/g) is approximately the same as ADMET polyethylene[3a,b] produced via condensation of 1,9-decadiene to polyoctenylene followed by diimide reduction. It may be expected that the carbonyl moieties of **13** provide very little perturbation to the lamellar crystal lattice of polyethylene due to similar space filling by carbonyl and methylene groups. In addition, the regular disparity in electron density of the sequence ordered chains permits their observation by X-ray similar to the ester groups of polyester **10**. This should provide an additional measurable dimension greater than the boundaries of the polyethylene unit cell yet order(s) of magnitude less than the crystal thickness of large lamella. This represents an exciting opportunity to probe the crystal modifications of polyethylene on a sublamellar scale using the carbonyls as regularly spaced “labels”, perhaps allowing facile measurement of attributes such as inclination angles.

Conclusions

The method reported herein is an effective one-pot route for forming carbon−carbon bonds in the synthesis of polymers and small molecules. Addition of silica as a support for the ruthenium complex not only facilitates hydrogenation at low to moderate pressures but also simplifies purification of products. In addition to demonstrating opportunities in commercially relevant polymers, this process proves highly suited to the preparation of sequence-ordered model polymers. We are currently extending this chemistry to the synthesis of other polyolefin-like polymers with varied main chain and pendant functionalities, including models for common commercial ethylene/polar monomer copolymers and ethylene block copolymers to produce elastomers. We are also investigating utility for the hydrogenation of unsaturated functional groups other than isolated olefins.

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