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Acyclic Diene Metathesis Polymerization Using a Modified WCl_6–SnR_4 Olefin Metathesis Catalyst

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In recent years, Wagener et al.[1] and others[2] have successfully employed olefin metathesis to polymerize and copolymerize a variety of acyclic dienes. This reaction, acyclic diene metathesis (ADMET), is a step-growth polymerization in which α,ω-dienes react to produce unsaturated polymers plus ethylene:

$$\underset{\text{acyclic diene}}{(n+1)H_2C{=}CHRCH{=}CH_2} \underset{\text{olefin metathesis catalyst}}{\rightleftharpoons} \underset{\text{polymer}}{H_2C{=}CH(\text{-}RCH{=}CH\text{-})_nRCH{=}CH_2} + nCH_2{=}CH_2 \quad (1)$$

The polymer contains an unsaturated repeat unit, and vinyl end groups are present at both chain termini. Molecular weights increase with diene conversion, which can be driven by removal of evolved ethylene. While there are many olefin metathesis catalysts, Wagener et al. found that conventional catalysts with Lewis acid components (such as $WCl_6/EtAlCl_2$) were not very effective for ADMET due to acid-catalyzed side reactions (vinyl addition and C=C bond migration) which generated impure and intractable products.[3] Pure, characterizable ADMET polymers were produced using Lewis acid-free catalysts: soluble alkylidene complexes of W or Mo, such as $M(=CHCMe_2R)(=N\text{-}2,6\text{-}C_6H_3\text{-i-}Pr_2)[OCMe(CF_3)_2]_2$, where R = Me or Ph, first prepared by Schrock[4] et al. Unfortunately, these alkylidene complexes are not yet commercially available and are difficult to prepare. This prompted us to search for a more readily available but equally selective ADMET catalyst.

In 1976, Ichikawa and Fukuzumi[5] reported highly selective metathesis of simple aliphatic 1-alkenes using a soluble catalyst system consisting of WCl_6, SnR_4, and a weak Lewis base such as an alkyl acetate. The Lewis base component sharply reduced undesired side reactions (double bond migration and addition polymerization), apparently due to neutralization of acidic catalyst species. We now report the successful use of this catalyst system to metathesize 1,5-hexadiene to high-purity 1,4-polybutadiene:

$$\underset{\text{1,5-hexadiene}}{CH_2{=}CHCH_2CH_2CH{=}CH_2} \xrightarrow[\substack{50\text{–}80\ °C \\ WCl_6/SnMe_4/PrOAc \\ \text{benzene}}]{-\text{ethylene}}$$

$$\underset{\text{1,4-polybutadiene}}{CH_2{=}CH(\text{-}CH_2CH_2CH{=}CH\text{-})_xCH_2CH_2CH{=}CH_2} \quad (2)$$

A solution of 1,5-hexadiene (168 mmol), WCl_6 (2 mmol), $SnMe_4$ (4 mmol), and *n*-propyl acetate (8 mmol) in 100 mL of benzene was refluxed for 25 h with a slow flow of nitrogen through the apparatus.[6,7] Significant gas evolution was observed during the first few hours. GC analyses indicated ethylene to be the primary hydrocarbon component of the effluent gas stream; no other hydrocarbon gases were detected except for 1,5-hexadiene and benzene vapors and traces of methane. No vapors of other hexadiene isomers were detected. After 20 h of reflux, evolution of ethylene had virtually ceased and conversion of 1,5-hexadiene was estimated by GC to be greater than 95%. After cooling to room temperature, no insoluble material was detected. Addition of methanol (1 L) to the solution caused formation of a brown, viscous precipitate which was collected by decantation and washed with methanol. After drying at 70 °C under vacuum for 4 h, a brown[8] solid was obtained (5.5 g) with a highly viscous, waxy consistency.

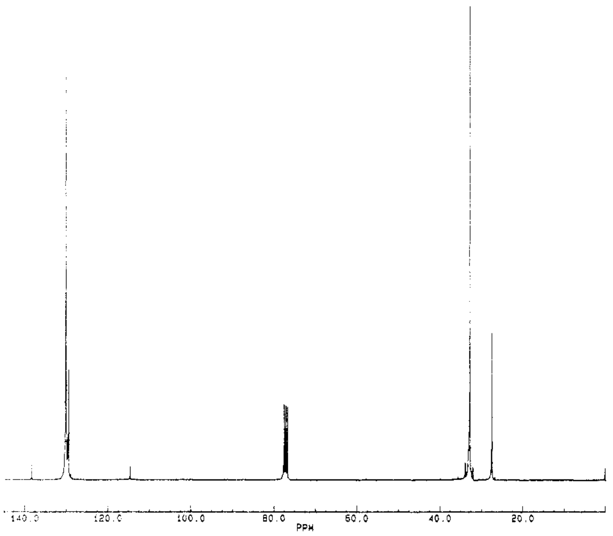

Figure 1. ^{13}C NMR spectrum of the 1,4-polybutadiene product of 1,5-hexadiene metathesis (triplet resonance at 77 ppm from $CDCl_3$ solvent).

The ^{13}C NMR spectrum[9] of this product (Figure 1) was consistent with a very pure 1,4-polybutadiene structure, $(\text{-}CH_2CH{=}CHCH_2\text{-})_n$, with a 4:1 ratio of trans/cis internal C=C bonds and vinyl termination. There was no detectable evidence for saturated (methyl or ethyl) end groups, as judged by a lack of resonances in the 10–25 ppm region. This predominantly *trans*-1,4-polybutadiene structure is virtually identical to that obtained by Wagener et al.[1c] using Schrock metal alkylidene catalysts for 1,5-hexadiene metathesis. From the NMR integration data, the number-average molecular weight of our product was computed to be 2900, assuming a purely vinyl-terminated linear structure with no cyclic or branched species. This value agreed well with GPC molecular weight determination: $M_n = 2970$, $M_w = 7220$, $M_w/M_n = 2.43$ (polystyrene calibration).

These results indicate that metathesis of 1,5-hexadiene using the $WCl_6/SnMe_4/PrOAc$ catalyst proceeded with good selectivity to the 1,4-polybutadiene product. This ADMET polymerization had several key features in common with ADMET as catalyzed by Schrock metal alkylidenes:[1c] (1) little or no C=C bond migration occurred, either in the diene or polymer, leading to a vinyl-terminated 1,4-polybutadiene product, (2) predominantly *trans*-1,4-polybutadiene was obtained, (3) little or no insoluble (cross-linked) polymer was generated, and (4) ethylene was essentially the only gaseous product. However, some differences were noted. First, the $WCl_6/SnMe_4/PrOAc$ catalyst yielded a lower molecular weight polybutadiene ($M_n \sim 3000$) than did the W alkylidene catalyst (M_n 8300–14 000[1c]). Higher molecular weights might be achieved by effecting higher diene conversion, such as by performing

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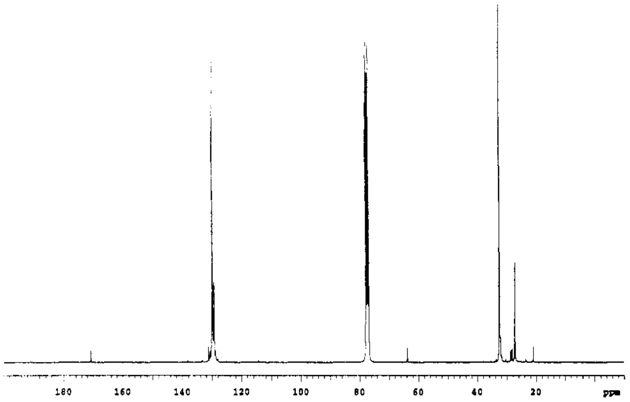

Figure 2. ^{13}C NMR spectrum of the acetoxy-/vinyl-terminated 1,4-polybutadiene product of 1,5-hexadiene/5-acetoxy-1-pentene cometathesis (triplet resonance at 77 ppm from $CDCl_3$ solvent).

the metathesis without solvent diluent (bulk polymerization) as did Wagener et al.[1c] Second, the $WCl_6/SnMe_4/$PrOAc catalyst appears to have lower ADMET activity than the W alkylidene catalyst, judging by the higher temperature (80 °C vs 20–50 °C), longer reaction time (25 h vs several hours), and larger catalyst amount (~1 mol % vs 0.1 mol % relative to hexadiene) we employed.

Having identified a readily available ADMET catalyst, we then sought to prepare functionalized polymers through this chemistry. Since ADMET is a step-growth polymerization, it should be possible to synthesize α,ω-difunctional telechelic polymers through cometathesis of the acyclic diene with a functionalized 1-alkene ($H_2C{=}CHR'X$):

$$nH_2C{=}CHRCH{=}CH_2 + 2H_2C{=}CHR'X \underset{\text{ADMET catalyst}}{\rightleftarrows} XR'HC{=}CH(\text{-}RCH{=}CH\text{-})_nR'X + (n+1)C_2H_4 \quad (3)$$

The functional alkene should also serve as a molecular weight control agent. This cometathesis to produce difunctional telechelics is similar in some respects to other olefin metathesis chemistries which have been used to synthesize telechelic polymers, including ring-opening metathesis polymerization (ROMP) of cyclic olefins with functional alkenes[10] and metathesis degradation[11] of polybutadiene with functional alkenes.

To demonstrate the ADMET cometathesis (eq 3), we performed a reaction of 1,5-hexadiene ($R = CH_2CH_2$) with 5-acetoxy-1-pentene ($X = OAc$; $R' = CH_2CH_2CH_2$) using $WCl_6/SnMe_4/$PrOAc catalyst. A solution of 1,5-hexadiene (200 mmol), 5-acetoxy-1-pentene (10 mmol), WCl_6 (2 mmol), PrOAc (8 mmol), and $SnMe_4$ (4 mmol) in 25 mL of chlorobenzene[6] was charged into a glass reflux apparatus[7] under a static nitrogen atmosphere. The solution was heated to 65 °C via an oil bath, at which point reflux began and rapid evolution of ethylene gas was observed (as detected by GC). The temperature was gradually raised to 80 °C over 3 h and then held at 80 °C for 3 h, at which point gas evolution had slowed markedly. A rapid purge flow of nitrogen (500–1000 mL/min) was then begun through the apparatus, and the solution was maintained at 80 °C under this nitrogen purge overnight for 15 h. Afterward, a viscous brown residue remained in the reaction flask; most of the solvent and volatile liquids had evaporated. Workup[12] yielded 7.5 g of a colorless, cloudy, viscous liquid product.

An IR spectrum of this product showed a strong carbonyl absorption at 1750 cm^{-1}. The ^{13}C NMR spectrum (Figure 2) was consistent with a 1,4-polybutadiene structure (80% trans) with both acetoxy (major) and vinyl (minor) end groups.[13] The acetoxy/vinyl end group ratio was about 5/1, and no other end-group types were detected. The acetoxy end-group resonances were not due to the presence of unreacted 5-acetoxy-1-pentene, since a rigorous evaporative removal of volatile liquids had been performed.[12] Molecular weight was determined by GPC: $M_n = 970$, $M_w = 2680$ (polystyrene calibration).

These results indicate that the ADMET coreaction of 1,5-hexadiene with 5-acetoxy-1-pentene did proceed, yielding a low molecular weight 1,4-polybutadiene product with a high proportion of acetoxy end groups. The product was not purely acetoxy-terminated since some vinyl end groups were observed. Also, we cannot rule out the possible presence of cyclic 1,4-polybutadiene species, since these cannot be distinguished from acyclic 1,4-polybutadienes by NMR. However, in principle, it should be possible to obtain diacetoxy acyclic products (acetoxy termination only) through further metathesis, that is, metathesis of the remaining vinyl end groups to produce internal olefin species plus ethylene. If desired, the diacetoxy polymers should be hydrolyzable to diols. Experiments are in progress to determine the generality of this approach and the compatibility of the catalyst system with other functionalized end groups.

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(6) All reagents employed were obtained from Aldrich. 1,5-Hexadiene (98%) was purified by distillation, passage through a column of silica/13X sieves, and storage over 4-Å sieves. Benzene and chlorobenzene (HPLC grade) were purified by passage through a column of silica gel and 13X sieves and then stored over 4-Å sieves. *n*-Propyl acetate (99%) and tetramethyltin (99+%) were dried over 4-Å sieves. Tungsten hexachloride (99.9%) was used as obtained and stored under nitrogen. 5-Acetoxy-1-pentene (98%) was stored over 4-Å sieves.

(7) The reaction was performed using a 250-mL three-neck round-bottom glass flask (with magnetic stirbar) fitted with a water-cooled reflux condenser. The apparatus was purged with nitrogen prior to introduction of reagents. A catalyst solution was prepared by dissolving, in order, WCl_6, *n*-propyl acetate,

and tetramethyltin in benzene under nitrogen. The catalyst solution was then syringed into the three-neck flask under nitrogen. GC analyses of gaseous and liquid organics were performed using an HP-5790 FID GC with a 30-m DB-1 capillary column.

(8) The brown color was probably due to the presence of residual tungsten species. X-ray fluorescence analysis: 0.76 wt % W; 0.024 wt % Cl.

(9) Quantitative ^{13}C NMR was performed using chloroform-*d* as the solvent, with chromium acetylacetonate added as a relaxation agent. A Bruker AC300 spectrometer was employed to obtain 75-MHz proton-decoupled spectra, with chemical shifts reported in ppm downfield from TMS. Spectral data: 129–130 (multiplet, relative intensity 100, internal olefinic carbons), 114.5 (s, rel. int. 1.97, $=CH_2$ vinyl carbon), 138.3 (s, rel. int. 1.89, $-CH=$vinyl carbon), 32.7 (s, rel. int. 72, methylene carbon adjacent to internal trans $-C=C-$), 27.4 ppm (s, rel. int. 18, methylene carbon adjacent to internal cis $-C=C-$). Weak resonances were observed at 33.8 and 32.0 ppm, each with a relative integration of about 1–2, probably methylene carbons α or β to vinyl end groups (the triplet resonance at 77 ppm is $CDCl_3$ solvent). Assignments for backbone carbon resonances were made by reference to previously published spectra of polybutadienes. See: Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983; p 202 and references cited therein.

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(12) The viscous brown residue was dissolved in 100 mL of toluene, and the solution was stirred vigorously with 75 mL of aqueous 1 N NaOH under a static nitrogen atmosphere at 80 °C for 3 h and then cooled. The organic layer was separated, washed with water, and dried with $MgSO_4$. Toluene was removed by evaporation under dynamic vacuum ($\sim$5 Torr) at 80–90 °C. This evaporation treatment was sufficient to remove any liquids which might remain from the reaction, including 5-acetoxy-1-pentene, 1,5-hexadiene, chlorobenzene, propyl acetate, and tetramethyltin.

(13) ^{13}C NMR data (acquired using a Varian VXR-300 spectrometer): 129–131 (multiplet, rel. int. 455, internal olefinic carbons), 114.5 (s, rel. int. 1.93, $=CH_2$ vinyl carbon), 138.2 (s, rel. int. 2.35, $-CH=$ vinyl carbon), 32.6 (s, rel. int. 355, methylene carbon adjacent to internal trans $-C=C-$), 27.3 (s, rel. int. 88, methylene carbon adjacent to internal cis $-C=C-$), 170.9 (s, rel. int. 10.2, carbonyl carbon of acetoxy end group), 63.9 (s, rel. int. 11.0, methylene carbon adjacent to acetoxy end group), 20.9 ppm (s, rel. int. 10.5, methyl carbon of acetoxy end group). Six weak resonances were detected between 23.5 and 35.5 ppm, with a cumulative relative integration of about 40, probably a combination of methylene carbons α or β to vinyl end groups and methylene carbons β or γ to acetoxy end groups. Assignments for acetoxy end-group carbon resonances were made by comparison to the spectrum of 5-acetoxy-1-pentene.