

β , γ -Carbon–Carbon Bond Cleavage as a Prelude to Chain Transfer in Ester-Functionalized Norbornene Polymerization

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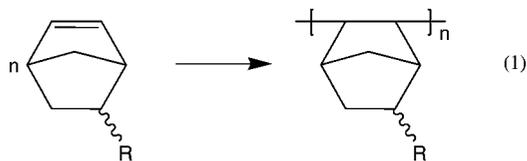
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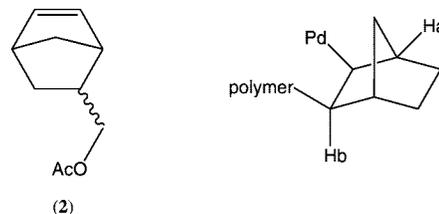
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Vinyl addition poly(norbornene) materials continue to be of interest for electronic and optical applications due to their enticing properties, namely, low dielectric constant, high optical transparency, and high glass transition temperature.¹ Vinyl addition poly(norbornene) properties can be tuned by appropriate and judicious choice of the pendant R group on the norbornene monomer (eq 1). For functionalized group-containing monomers such as esters, polymerization using late transition metals is preferred due to the catalyst's tolerance toward these functionalities. One of the earliest catalysts reported for norbornene vinyl addition polymerization was $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ (**1**).² Further investigations lead ultimately to the conclusion that $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ was responsible for the living polymerization (i.e., absence of chain transfer or termination) of norbornene and its functionalized homologue, 2-acetoxymethyl-5-norbornene (**2**).^{3,4} Most notably and consistent with a living polymerization mechanism was the authors' comment that "the Pd–C bond of the polymer end group remained intact after all of the monomer had been consumed." The living polymerization of norbornene is understandable in view of the lack of suitable β -hydrogens for elimination upon insertion of norbornene monomer into the Pd–C bond. While H_a and H_b are beta to the Pd metal, H_a is in a bridgehead position and would violate Bredt's rule upon elimination. H_b is *anti* to the Pd and as such is improperly oriented for elimination.

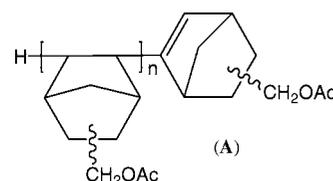


In light of these previous studies we were surprised to find that polymerization⁵ of 2-acetoxymethyl-5-norbornene (**2**) (*endo/exo* ratio = 70/30) with **1** (1000:1 molar ratio) in the presence of 1 equiv of $\text{P}(n\text{-Bu})_3$ afforded a polymer (34% yield of isolated polymer after 17.5 h at 110 °C) with very low number-average molecular weight ($M_n = 1130$). For a living polymerization system, the M_n is related to the ratio of monomer and initiator concentration and can be calculated after taking into account the molecular weight of the monomer and the yield. At a 1000:1 molar ratio and 34% yield, the theoretical M_n is $\sim 56\,000$. Clearly under the conditions employed, some manner of chain transfer was occurring; under these conditions the Pd–C bond

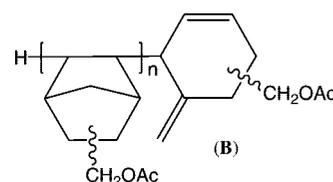
of the growing polymer chain was not remaining intact. Using a wide range of NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) analytical techniques, we were able to discern the nature of the polymer end group and speculate on the chain transfer mechanism.



The MALDI-TOF MS of low molecular weight poly(**2**) is shown in Figure 1.⁶ This remarkably clean spectrum shows only one series of $(M + \text{Na})^+$ molecular ions, e.g., 1849, 2015, 2181, 2347, 2513, etc. After accounting for the sodium ion, the molecular ions observed are consistent with a polymer series with a norbornenyl end group as one possible option (see end-group structure **A**).



However, the NMR data collected for poly(**2**) were at odds with the structural assignment of the end group shown in structure **A**. In the ^1H NMR spectrum (see Figure 2), the most notable features are the *two* equal intensity downfield resonances at 4.7–5.0 and 5.6–5.9 ppm. The end group of structure **A** should exhibit only *one* olefinic proton resonance. A combination of ^{13}C NMR and edited ^{13}C NMR using distortionless enhancement by polarization transfer (DEPT-135) techniques revealed that the four olefinic peaks observed at 148.8 and 110.0 ppm and at 131.6 and 127.8 ppm are due to *exo*-cyclic olefin and *endo* cyclic olefin carbons (see Supporting Information). Therefore, end-group structure **B** containing two double bonds is proposed as more consistent with the NMR spectra – this is also in agreement with MALDI-TOF MS analysis (Figure 1). Two-dimensional ^1H – ^{13}C NMR heteronuclear correlation spectra (see Supporting Information) confirmed the assignments in Figure 2. Confidence in our assignments was bolstered by the good agreement between the gel permeation chromatography (GPC) determined number-average molecular weight (M_n) of the purified polymer used for analytical studies (1130) and the calculated M_n by end-group analysis (1328).



A proposed mechanism for the formation of the unusual end-group structure **B** is presented in Scheme 1. The mechanism requires rearrangement of the bicyclic system into a monocyclic system by β , γ -carbon–carbon bond cleavage of the methylene

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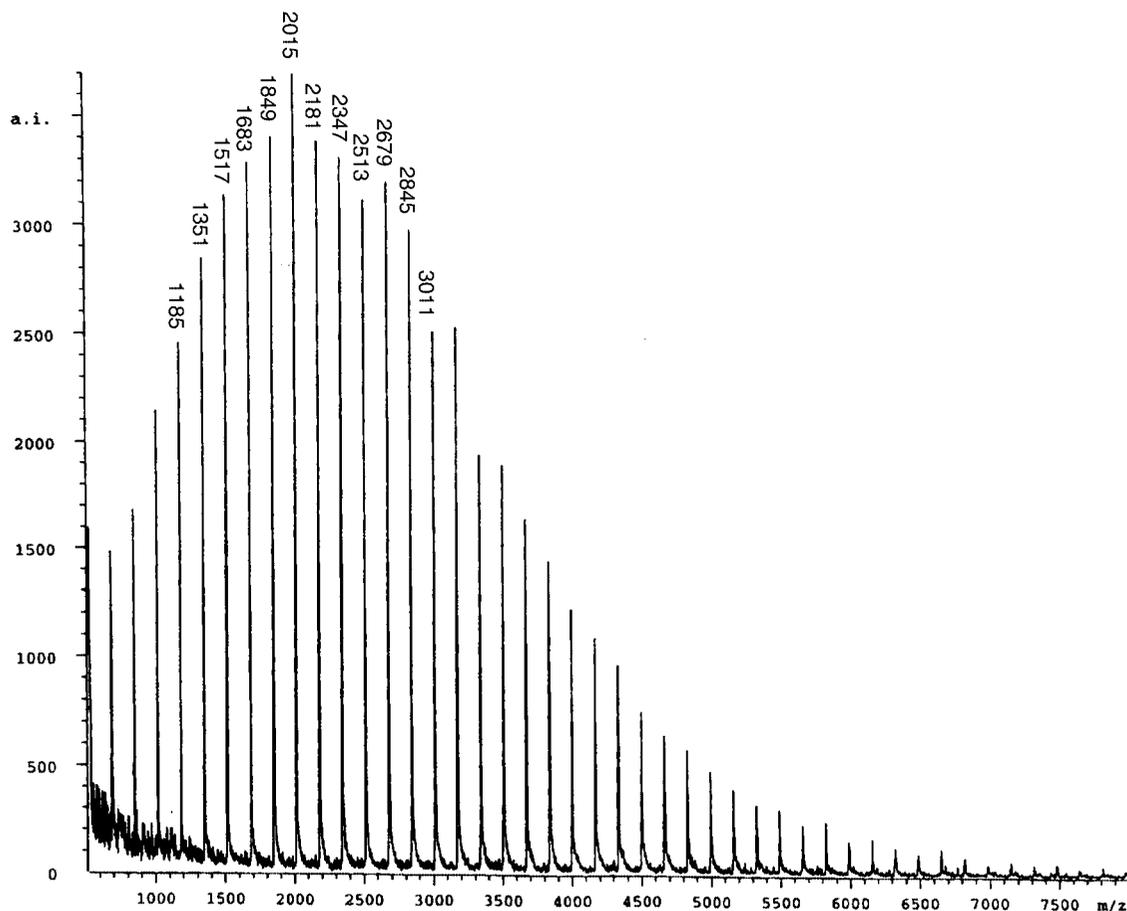


Figure 1. MALDI-TOF MS (in dithanol matrix with added sodium trifluoroacetate, linear mode) of poly(2-acetoxymethyl-5-norbornene) (GPC: $M_n = 1130$, polystyrene standards) made using $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ with some m/z values shown.

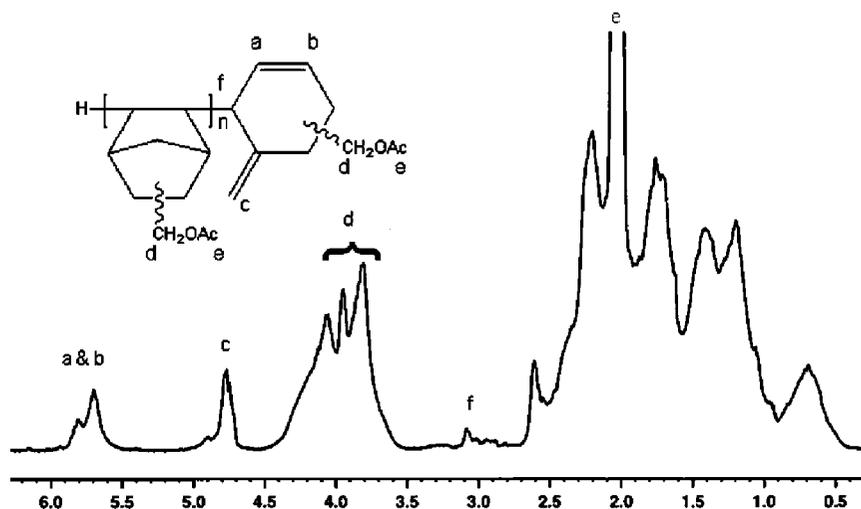


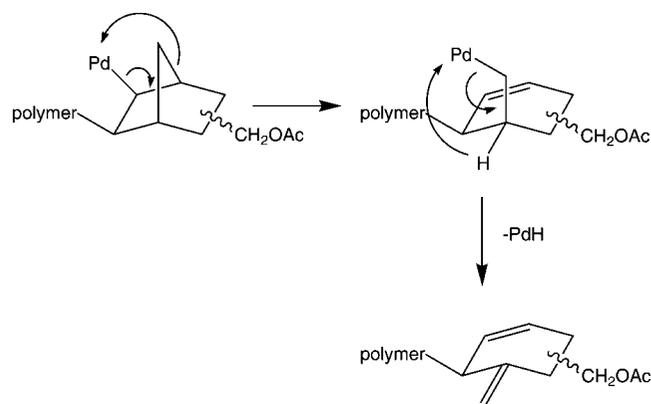
Figure 2. ^1H NMR (CDCl_3) spectrum of poly(2-acetoxymethyl-5-norbornene) (GPC: $M_n = 1130$, polystyrene standards) made using $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$.

bridge. An *endo*-cyclic double bond is formed and the Pd migrates to the former methylene bridge carbon. While previously the Pd was not beta to readily accessible hydrogens, in the resulting intermediate the Pd can freely rotate so as to align itself for H elimination from the β -tertiary carbon. Consequently, an *exo*-cyclic double bond is formed, and the Pd–H species eliminated can undergo subsequent chain initiation. Thus, in this system β , γ -carbon–carbon bond cleavage is a prelude to chain transfer in the polymerization of the ester-functionalized norbornene **2**. Similar end groups have been observed for a Ni

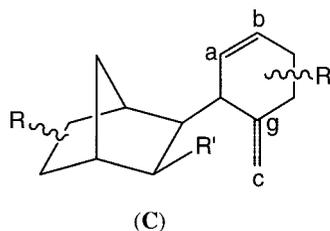
catalyst ($(\eta^3\text{-allyl})\text{Ni}(\eta^2\text{-OCCF}_3)_2$) in the polymerization of *tert*-butyl-5-norbornene-2-carboxylate (*endo/exo* ratio = 80/20) (see Supporting Information).

While β , γ -carbon–carbon bond cleavage reactions are well-known for strained three- and four-ring systems, they are less common in five- and six-membered or larger rings.⁷ Nevertheless, there are some examples of nickel- and palladium-mediated β , γ -carbon–carbon bond cleavage and β -hydrogen elimination to form norbornene dimers in the literature. The earliest report was from 1979 in which a combination of Ni(II) acetylacetonate,

Scheme 1



triethylaluminum, and triethylphosphite resulted in a dimer of norbornene (where R and R' = H in structure C).⁸ The assignments for the endocyclic and exocyclic double bond carbons a, b, c, and g in C, 129.8, 127.0, 109.1, and 149.3 ppm, respectively (where R and R' = H), are comparable to those assigned in B.



The coupling reaction of norbornene catalyzed by nickel phosphine halide complexes in the presence of sodium borohydride yielded the same dimer structure in C (R = H) as well as other isomers depending on the nickel compound used.⁹ Similar isomeric mixtures were formed in the presence of nickel halides depending on whether mono- or bidentate phosphines were used.¹⁰ Chiusoli and Catellani observed a termination process involving β , γ -carbon-carbon cleavage. They investigated palladium-catalyzed reactions of norbornene in the presence of phenyl bromide and found that the phenyl-substituted dimer C (R = H and R' = Ph) was formed.¹¹

We have carried out a survey of reactivity studies in which an array of phosphorus donor ligands have been employed in norbornene polymerizations catalyzed by **1**. We intend to publish our findings in the near future.

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Supporting Information Available: NMR spectra for poly(**2**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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- (5) Nitrogen-sparged **2** (9.97 g, 60.1 mmol) and toluene (14.96 g) were combined in a glass vial equipped with a stirbar. In a separate vial, catalyst **1** (0.0265 g, 0.0600 mmol) was dissolved in nitromethane (4 mL) and ethyl acetate (4 mL). P(*n*-Bu)₃ (0.0121 g, 0.0600 mmol) was added to the catalyst solution. The monomer solution was heated to 110 °C, and the catalyst solution was injected into the monomer solution. The reaction was allowed to stir at 110 °C for 17.5 h. After cooling to room temperature, the polymer solution was filtered to remove black palladium metal and was evaporated to dryness and then dissolved in a minimum of toluene. The toluene solution was poured into hexanes (4–5 times the polymer solution volume) to form a polymer precipitate. The precipitated polymer was filtered and dried under vacuum at 80 °C overnight. Yield 3.36 g (34%). GPC: $M_w = 1770$, $M_n = 1130$, $M_w/M_n = 1.56$. ¹H NMR (CDCl₃): δ 0.5–2.7 (br m, aliphatic hydrogens, 12H), 2.7–3.1 (br m, -CH, ring H on carbon f), 3.5–4.5 (br m, -CH₂-OC(O)Me, 2H), 4.7–5.0 (br s, >C=CH_2 , *exo*-cyclic olefinic end-group hydrogens), 5.6–5.9 (br m, -CH=CH-*endo*-cyclic olefinic end-group hydrogens). ¹³C NMR (CDCl₃): δ 170.9 (-OC(O)Me), 148.8 (>C=CH_2 *exo*-cyclic, non-protonated, olefinic end-group carbon), 131.6 and 127.8 (-CH=CH-*endo*-cyclic olefinic end-group carbons), 110.0 (>C=CH_2 *exo*-cyclic olefinic end-group carbon), 67.8 (*exo*-CH₂-OC(O)Me), 66.1 (*endo*-CH₂-OC(O)Me), 42.0 (-CH, ring carbon f), 30–60 (aliphatic carbons), 21.0 (CH₂-OC(O)CH₃). MALDI-TOF MS, linear mode (dithranol matrix with added sodium trifluoroacetate to aid cationization): a series of (M + Na)⁺ ions was observed that is consistent with the presence of diene-terminated polymer, e.g., $m/z = 1849, 2015, 2181, 2347, 2513$, etc.
- (6) The GPC molecular weights were referenced to poly(styrene) standards which helps explain the slight discrepancy between the reported GPC M_n value and the maximum intensity molecular weight observed in the MALDI-TOF MS.
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