



Palladium Catalyzed Vinyl Addition Poly(norbornenes): Formic Acid as a Chain Transfer Agent. Mechanism and Polymer Optical Properties.

**Pramod Kandanarachchi, Chun Chang, Steven Smith, Patrick Bradley, Larry F. Rhodes^{*},
Robert P. Lattimer[#] and George M. Benedikt[#]**

Promerus LLC, 9921 Brecksville Rd, Brecksville, OH 44141

[#]Lubrizol Advanced Materials, 9911 Brecksville Rd, Brecksville, OH 44141

*Reprinted from
Journal of Photopolymer Science and Technology
Vol. 26, No. 4, 431-439 (2013)*

Palladium Catalyzed Vinyl Addition Poly(norbornenes): Formic Acid as a Chain Transfer Agent. Mechanism and Polymer Optical Properties.

Pramod Kandanarachchi, Chun Chang, Steven Smith, Patrick Bradley, Larry F. Rhodes*, Robert P. Lattimer[#] and George M. Benedikt[#]

Promerus LLC, 9921 Brecksville Rd, Brecksville, OH 44141

[#]Lubrizol Advanced Materials, 9911 Brecksville Rd, Brecksville, OH 44141

Polymers of substituted norbornenes were produced using palladium catalysts in the presence of formic acid (FA) as a chain transfer agent (CTA) which act to control molecular weight as well as to increase conversion. Spectroscopic analysis of these polymers by ¹H NMR and MALDI-TOF MS confirmed that hydrogen-terminated polynorbornenes are generated leading to extremely low optical densities at 193 nm. Deuterium labeling studies were conducted in order to discern possible chain transfer mechanisms.

Keywords: Norbornene, transparency, 193 nm, formic acid, chain transfer

1. Introduction

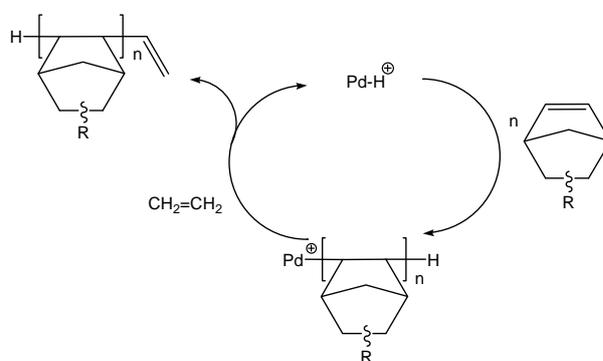
Molecular weight and molecular weight distribution are important properties of binder resins in photopolymer compositions since they affect critical film properties such as dissolution behavior in developer [1]. Techniques to control molecular weight without impacting other properties such as transparency at the imaging wavelength (e.g., 365, 248, or 193 nm) are desirable.

Vinyl addition poly(norbornene) materials have been investigated in photopolymer compositions due to their high optical transparency and etch resistance [2]. However, production of relatively low M_w poly(norbornene) has been challenging since the early methods of molecular weight control agents (or chain transfer agents, CTA), namely α -olefins and ethylene, created materials with olefinic end groups [3] (see Scheme 1) that are opaque to 193 nm light. Chemical transformation of these end groups into more transparent moieties (e.g., epoxides) is possible, however it requires a second process step and as such is not desirable [4].

We developed H₂ as an alternative chain transfer agent which controls molecular weight of poly(norbornene) materials via a σ -bond metathesis reaction.

This CTA produces a low molecular weight polymer with hydrogen end groups that exhibits a

low optical density (OD) at 193 nm [5] (see Scheme 2).

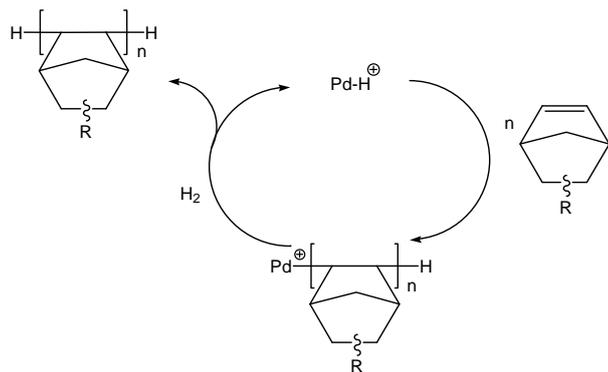


Scheme 1

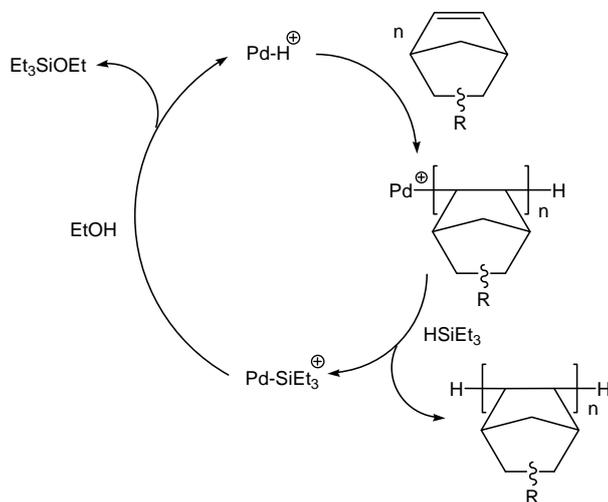
However, H₂ is not attractive due to its high flammability. As a result we investigated other reagents that could possibly undergo a σ -bond metathesis reaction with the nascent Pd-C bond of the growing polymer chain as does H₂, namely silanes (e.g., HSiEt₃) as CTAs in the presence of alcohols, such as EtOH.

Despite the fact these types of mixtures are touted to be a form of “liquid hydrogen” [6], we found that H₂ was not the active chain transfer agent based on the results of a deuterium labeling study. Rather silane controls the polymer molecular weight and alcohol serves to boost the polymerization activity by

regeneration of the catalytically active species, namely a Pd-H cation [7] (see Scheme 3).



Scheme 2

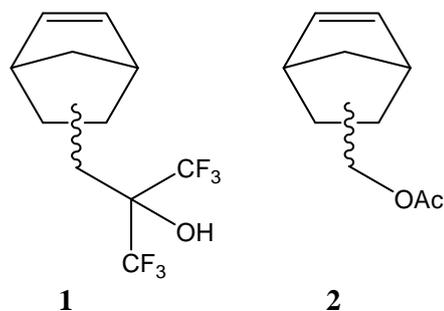


Scheme 3

While poly(norbornene) made with Et_3SiH and EtOH mixtures were also very transparent at 193 nm since the polymer contained hydrogen end groups, the catalyst regeneration step creates an equivalent of Et_3SiOEt . Such by products were of concern since significant quantities present in the polymer might produce non-uniformities during a subsequent etch step due to the etching rate differences between purely organic materials and those comprising silicon moieties [8]. Thus a more process friendly chain transfer agent was sought that provided good molecular weight control, low optical density polymer at 193 nm, no worrisome byproducts that might compromise the final polymer composition, and was safe to handle.

A review of the literature suggested that formic acid (FA) may well provide the sought after solution. Formic acid is known to decompose in the presence of transition metals to form H_2 and CO_2 , and has been used in olefin hydrogenation and in the catalytic asymmetric transfer hydrogenation of ketones and imines [9, 10, 11]. Herein we detail homo and copolymerization experiments of monomers **1** and **2**

which show that formic acid acts as a chain transfer agent and controls molecular weight of the poly(norbornene). However, deuterium labeling studies show that H_2 is not the species that is responsible for the polymer molecular weight control and the mechanism is more complicated than originally anticipated.



2. Experimental

2.1 General.

All manipulations were carried out under an atmosphere of prepurified nitrogen using standard airless or dry box techniques. Anhydrous grade solvents were deoxygenated by sparging with prepurified nitrogen prior to use.

All monomers were obtained from Promerus LLC, $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ (**3**) and $\text{Pd}(\text{acac})_2$ (**4**) were obtained from Aldrich, *N,N*-dimethylanilinium tetrakis(pentafluorophenyl) borate (DANFABA) was purchased from Boulder Scientific Company, formic acid came from Sigma-Aldrich, while the deuterated versions were obtained from Cambridge Isotope Labs. $[\text{Pd}(\text{OAc})(\text{MeCN})(\text{P}(i\text{-Pr})_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**) was prepared according to published procedures [12].

NMR, GPC, and optical density (OD) were determined as previously reported [4]. The MALDI-MS experiments were carried out as reported previously [7].

Polymer conversion was determined gravimetrically using a Mettler Toledo HR73 Halogen Moisture Analyzer. Typically a metal pan containing a glass microfiber mat is weighed and approximately 0.5 mL of polymer solution is added to the pan. The pan is then heated to 200 °C by the analyzer until a constant weight is achieved. The solids content is reported as a percentage of the starting weight, i.e., polymer percent conversion.

2.2 Copolymerization of **1** and **2** (55/45) using catalyst **3** and formic acid as CTA.

In a representative polymerization, monomer **1** (4.49 g, 0.0270 mol), monomer **2** (9.05 g, 0.0330 mol), and toluene (13.6 g) were mixed in a vial equipped with a stirbar. The vial was sealed. Formic acid was added to the vial (18 mole % on monomer, see Table 1 for quantities used for other experiments). The vial was heated to 90 °C and catalyst **3** (0.027 g, 0.060 mmol) in nitromethane (1.31 g) was added.

The reaction mixture was stirred at 90 °C for 17 hours. The reaction mixture was then cooled. Polymer conversion in the reaction mixture was determined by total solids analysis (94%). GPC analysis: $M_w = 4830$; $M_w/M_n = 1.69$. The reaction mixture was purified by removal of catalyst residues. The polymer was precipitated into hexanes and dried overnight in a vacuum oven at 60 °C. GPC: $M_w = 5090$; $M_w/M_n = 1.63$. $^1\text{H NMR}$ (DMSO- d_6): δ 7.3-8.0 (br s, $-\text{C}(\text{CF}_3)_2\text{OH}$), 3.5-4.5 (br s, $-\text{CH}_2-\text{O}(\text{O})\text{CMe}$), 0.8-2.6 (br m, cycloaliphatic protons). Molar ratio of **1** to **2** was determined using the integration of the 7.3-8.0 resonance ($-\text{OH}$ resonance for **1**) and the 3.5-4.5 resonance ($-\text{CH}_2-\text{O}(\text{O})\text{CMe}$ for **2**): 57/43 ratio of 1/2. In the $^1\text{H NMR}$ spectrum, olefinic resonances are observed from 4.7 to 5.0 and 5.3 and 5.9 ppm consistent with a diene end group structure. The polymer was analyzed by MALDI-TOF MS. A major copolymer series of $(\text{M}+\text{Na})^+$ ions was observed that are consistent with a diene end group structure. MS: m/z 903, 961, 1069, 1127, 1177, 1235, 1293, 1343, 1401, 1451, 1509, 1567, 1617, 1675, 1783, 1841, 1891, 1949, etc. The optical density of the dried polymer at 193 nm was determined: $0.55 \mu\text{m}^{-1}$.

2.3 Copolymerization of **1** and **2** (55/45) using catalyst **4** and formic acid as CTA.

In a representative polymerization, a solution of monomer **1** (7.54 g, 27.5 mmol), monomer **2** (3.74 g, 22.5 mmol), catalyst **4** (0.008 g, 0.025 mmol), DANFABA (0.060 g, 0.075 mmol), 12.5 g toluene, and 4.2 g ethyl acetate was made. Formic acid was added to these reaction vessel (6 mole % on monomer, see Table 3 for quantities used for other experiments) and the mixture was heated to 90 °C for 16 hours. The mixture was then allowed to cool to room temperature. Polymer conversion in the reaction mixture was determined by total solids analysis (100%). GPC analysis: $M_w = 3300$; $M_w/M_n = 1.45$. The polymer was then purified to remove residual catalyst, precipitated into heptane and dried in a vacuum oven. GPC: $M_w = 4170$; $M_w/M_n = 1.37$. $^1\text{H NMR}$ (DMSO- d_6): δ 7.3-8.0 (br s, $-\text{C}(\text{CF}_3)_2\text{OH}$), 3.5-4.5 (br s, $-\text{CH}_2-\text{O}(\text{O})\text{CMe}$), 0.8-2.6 (br m, cycloaliphatic protons). Molar ratio of **1** to **2** was determined using the integration of the 7.3-8.0 resonance ($-\text{OH}$ resonance for **1**) and the 3.5-4.5 resonance ($-\text{CH}_2-\text{O}(\text{O})\text{CMe}$ for **2**): 54/46 ratio of 1/2. In the $^1\text{H NMR}$ spectrum, olefinic resonances are observed with relatively little intensity from 4.7 to 5.0 and 5.3 and 5.9 ppm compared to the spectrum obtained for polymer samples made with catalyst **3** (*i.e.*, the ratio of $-\text{OH}$ (from $-\text{C}(\text{CF}_3)_2\text{OH}$) to olefinic resonances calculated from the $^1\text{H NMR}$ integrals of isolated polymers from experiment 6 (16:1) is substantially higher than that of experiment 4 (6:1)). The polymer was analyzed by MALDI-TOF MS. A

major copolymer series of $(\text{M}+\text{Na})^+$ ions was observed that are consistent with hydrogen end groups. MS: m/z 963, 1071, 1129, 1179, 1237, 1295, 1345, 1403, 1461, 1511, 1569, 1619, 1677, 1785, 1893, 1951, etc. The optical density of the dried polymer at 193 nm was determined: $0.22 \mu\text{m}^{-1}$.

2.4 Copolymerization of **1** and **2** (60/40) using catalyst **4** and formic acid as CTA.

A solution of monomer **1** (115 g, 420 mmol), monomer **2** (46.5 g, 280 mmol), catalyst **4** (0.11 g, 0.35 mmol), DANFABA (0.84 g, 1.1 mmol), 180 g toluene, and 60 g ethyl acetate was made. This solution was divided into seven portions. To each portion was added a desired amount of formic acid (see Table 5). The mixtures were heated to the desired temperature (60 °C, 80 °C or 90 °C) for 19 hours. The mixtures were then allowed to cool to room temperature, and total solids analysis (for conversion) and GPC analysis (for molecular weight) were carried out on the resulting mixture. The polymer was then purified to remove residual catalyst and then precipitated into heptane and dried in a vacuum oven. The optical density of the dried polymer at 193 nm was determined and the final molecular weight was determined by GPC analysis. See Table 5 for conversion, molecular weights and optical density results.

2.5 Polymerization of **2** using catalyst **5** using formic acid and deuterated formic acid as CTA.

In a representative polymerization, monomer **2** (23.3 g, 0.140 mmol), DANFABA (0.034 g, 0.042 μmol) were mixed with toluene (31 mL) and added to a reaction vessel. The desired amount of HCOOH (see Table 6) was added. The reactor was sealed and then heated to 100 °C. Catalyst **5** (0.017 g, 0.014 μmol), in ethyl acetate (6.2 ml) was added to the vessel. The mixture was stirred for 18 hours, cooled, and subjected to total solids analysis (for conversion), GPC analysis (for molecular weight) and MALDI-TOF MS analysis (for end-group identification), see Table 6 for results. The procedure was repeated as reported in Table 6 using DCOOH, HCOOD and DCOOD. For HCOOH, only one homopolymer series of $(\text{M}+\text{Na})^+$ ions was observed consistent with hydrogen end groups. MS: m/z 855, 1021, 1187, 1353, 1519, 1685, 1851, 2017, 2183, 2349, 2515, 2681, 2847, etc.

3. Results

3.1 Polymerization studies.

The copolymerization of monomers **1** and **2** (55/45 molar ratio) was carried out using $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ (**3**). In the absence of formic acid a copolymer with a M_w of 5140 was obtained. The optical density of this polymer at 193 nm was relatively high: $0.55 \mu\text{m}^{-1}$. Several copolymerization

experiments were carried out with increasing formic acid concentration. See Table 1 for details. The M_w of the resulting polymer is plotted versus formic acid concentration in Figure 1 along with the accompanying OD which shows essentially no change in M_w or OD as a function of formic acid concentration.

Table 1. Copolymerization of **1** and **2** (55/45) using catalyst **3** with and without formic acid (FA) at 90 °C.

Exp	FA (%)	Conv (%)	Reaction	Precip.	OD (193)	
			Mixture	Polymer		
			M_w	M_w		
1	0	92	5140	5470	0.55	
2	6	100	5140	5640	0.49	
3	12	100	4970	5440	0.50	
4	18	94	4830	5090	0.55	

The isolated copolymer solid from experiment 4 was further characterized by NMR and MALDI-TOF MS techniques. The molar ratio of **1** to **2** was determined to be 57/43 based on the ^1H NMR spectrum which is very close to the starting monomer ratios.

The molecular ions observed in the MALDI-TOF mass spectrum for the copolymer obtained in experiment 4 are listed in Table 2 below. One major copolymer series was observed which was in excellent agreement with one hydrogen end group and one diene end group (as a Na ion adduct).

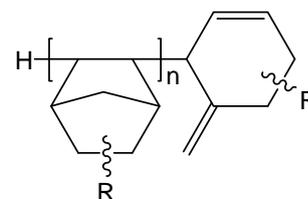


Table 2. List of m/z molecular ions observed in the MALDI-TOF mass spectrum of the copolymer of **1** and **2** from experiment 4 (see Table 1) along with the calculated m/z values in accordance with the number of repeat units of monomers **1** and **2**.

Repeat units		Observed	Calculated
1	2	m/z	m/z^*
2	2	903	903
3	2	1177	1177
4	2	1451	1451
2	3	1069	1069
3	3	1343	1343
4	3	1617	1617
5	3	1891	1891
1	4	961	961
2	4	1235	1235
3	4	1509	1509
4	4	1783	1783
1	5	1127	1127
2	5	1401	1401
3	5	1675	1675
4	5	1949	1949
1	6	1293	1293
2	6	1567	1567
3	6	1841	1841

*assumes hydrogen and diene end group and Na ion adduct.

The copolymerization of **1** and **2** was carried out using catalyst **4** in the presence of 6 and 12% formic acid. The results of these experiments are shown in Table 3. Experiments 5 and 6, in contrast to experiments 2 and 3 (using catalyst **3**), yield lower M_w and substantially lower optical density copolymer.

Table 3. Copolymerization of **1** and **2** (55/45) using catalyst **4** in the presence of formic acid (FA) at 90 °C.

Exp	FA (%)	Conv (%)	Reaction	Precip.	OD (193)	
			Mixture	Polymer		
			M_w	M_w		
5	6	100	3300	4170	0.22	
6	12	100	3050	3590	0.21	

Further analysis of the isolated copolymer solid from experiment 5 using MALDI-TOF MS showed that in contrast to catalyst **3**, catalyst **4** yields a molecular ion series (see Table 4) that is consistent with polymer containing two hydrogen end groups (as the Na adduct) as shown below.

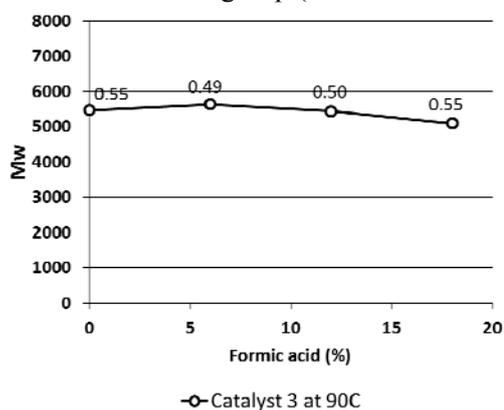
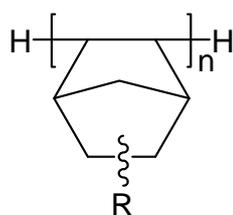


Figure 1. Plot of M_w of copolymer **1/2** (55/45) formed in the reaction mixture formed using catalyst **3** versus formic acid concentration. Optical density (μm^{-1} at 193 nm) of the isolated copolymer is shown beside each data point.

The ^1H NMR spectrum of the copolymer from experiment 4 contains resonances at 4.7 to 5.0 and 5.3 and 5.9 ppm. These resonances are consistent with an *exo*-methylene cyclohexenyl-terminated poly(norbornene) that have been described previously [13]. See the structure in the figure below where R is the functional groups on monomers **1** and **2**.



A more extensive study was carried out for catalyst **4** at a slightly different comonomer ratio: 60/40. In this study the impact of reaction temperature was investigated for different formic acid concentrations. See Table 5 and Figure 2 where the effect of formic acid concentration on copolymer M_w and optical density at 193 nm is plotted. The data shows that both reaction temperature and formic acid play a role in determining the molecular weight of the copolymer. Higher temperature yields lower M_w and higher formic acid concentration lowers M_w . Compared to catalyst **3**, where there is little if any impact of formic acid concentration on OD (see Figure 1), catalyst **4** generally yields a lower OD (see Figure 2).

Table 4. List of m/z molecular ions observed in the MALDI-TOF mass spectrum of the copolymer of **1** and **2** from experiment 5 (see Table 3) along with the calculated m/z values in accordance with the number of repeat units of monomers **1** and **2**.

Repeat units		Observed	Calculated
1	2	m/z	m/z^*
3	2	1179	1179
2	3	1071	1071
3	3	1345	1345
4	3	1619	1619
5	3	1893	1893
1	4	963	963
2	4	1237	1237
3	4	1511	1511
4	4	1785	1785
1	5	1129	1129
2	5	1403	1403
3	5	1677	1677
4	5	1951	1951
1	6	1295	1295
2	6	1569	1569
1	7	1461	1461

*assumes two hydrogen end groups and Na ion adduct.

Finally experiments were carried out to help ascertain the role of formic acid in the formation of homopolymers of **2** using catalyst **5**, $[\text{Pd}(\text{OAc})(\text{MeCN})(\text{P}(i\text{-Pr})_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$. As shown in Table 6, four experiments were carried out using normal formic acid, monodeutero- (both formyl and acid labeled versions) and dideutero-formic acid. The formic acid concentration was kept constant at 30 mole % for these experiments. The conversions of the monomer to polymer were 100% for all of the

experiments. The homopolymer was analyzed by GPC and MALDI-TOF MS techniques.

Table 5. Copolymerization of **1** and **2** (60/40) using catalyst **4** in the presence of formic acid (FA) at different temperatures.

Exp	FA (%)	Conv (%)	Reaction Mixture M_w	Precip. Polymer M_w	OD (193)
7*	6	76	6360	6670	0.17
8*	12	97	4660	4910	0.17
9*	18	86	4530	4960	0.17
10^	6	100	4500	4710	0.21
11^	12	100	3710	4140	0.17
12#	6	97	3860	4120	0.27
13#	12	97	3380	3700	0.21

*60 °C. ^80 °C. #90 °C

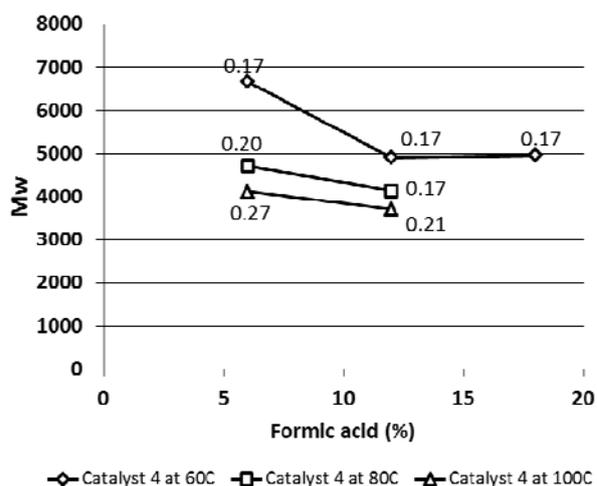


Figure 2. Plot of M_w of copolymer **1/2** (60/40) formed in the reaction mixture formed using catalyst **4** versus formic acid concentration and reaction temperature. Optical density (μm^{-1} at 193 nm) of the isolated copolymer is shown beside each data point.

As in the case of catalyst **4**, catalyst **5** also creates a polymer with hydrogen end groups based on the molecular ion polymer series observed in the mass spectrum. When HCOOD or DCOOH (experiments 15 and 16) was employed, a molecular ion series was observed consistent with both hydrogen and deuterium end groups on the same polymer, but no significant quantity of dihydrogen terminated polymer ($\leq 5\%$) was observed and no evidence was found for the dideuterium terminated polymer series. For experiment 17 where DCOOD was used, 94% of the polymer series observed was due to the dideuterium terminated polymer and the remaining 6% was due to the monodeuterium terminated polymer.

Note that the molecular weight for the homopolymer formed using HCOOH and HCOOD is significantly lower than that found using DCOOH and DCOOD. For example, the M_w (4090) of

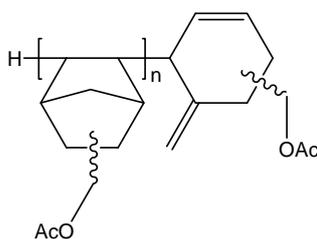
experiment 14 (HCOOH) doubled in experiment 16 (DCOOH).

Table 6. Homopolymerization of **2** using catalyst **5** in the presence of 30% formic acid (FA), both deuterated and non-deuterated.

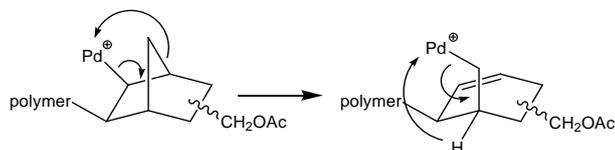
Exp	FA (30%)	Conv (%)	M_w	M_n	MALDI-TOF MS result
14	HCOOH	100	4090	1630	H-(2) _n -H
15	HCOOD	100	3460	1500	H-(2) _n -D
16	DCOOH	100	8220	2380	D-(2) _n -H
17	DCOOD	100	8410	2970	D-(2) _n -D

4. Discussion

It has been reported previously, that in the polymerization of monomer **2** using a phosphine derivative of catalyst **3**, the last inserted monomer undergoes an unusual β , γ -carbon-carbon bond cleavage prior to the molecular weight limiting β -hydrogen elimination chain transfer step [13]. The final polymer product was shown by a combination of MALDI-TOF MS and NMR analytical techniques to comprise an *exo*-methylene cyclohexenyl end group (see figure below).



The proposed mechanism of β , γ -carbon-carbon bond cleavage and the β -hydrogen elimination chain transfer step is shown below.

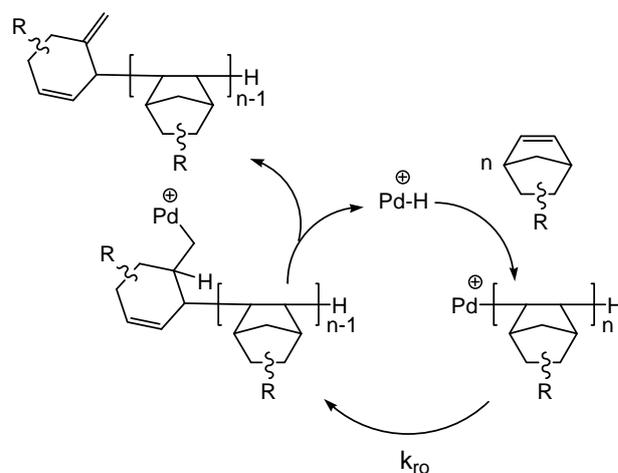


A similar *exo*-methylene cyclohexenyl end group was observed for the copolymer of **1** and **2** prepared with catalyst **3** based on NMR and MALDI-TOF MS data. Catalyst **3** was immune to polymer molecular weight regulation by formic acid. As a result, the optical density did not change as a function of formic acid concentration and the OD was relatively high due to the presence of olefin containing diene end groups. A mechanism incorporating the molecular weight limiting β , γ -carbon-carbon bond cleavage governed by the rate of the ring-opening step k_{ro} can be envisioned (see Scheme 4).

On the other end of the spectrum, in the presence of formic acid, catalyst **5** generates only dihydrogen terminated poly(**2**) with no indication that β , γ -

carbon-carbon bond cleavage (i.e., ring opening) occurred.

Literature references suggest that in the presence of palladium catalysts formic acid could decompose to form H_2 and CO_2 . Hydrogen, once formed, can act as a chain transfer agent to control polymer molecular weight as has been published previously [5]. If H_2 were acting as a chain transfer agent, the deuterium labeling study for the homopolymerization of monomer **2** with either the formyl or acid labeled formic acid, i.e., DCOOH or HCOOD, would produce a 1:2:1 statistical mixture of three polymeric isotopomers: poly(**2**), i.e., hydrogen at each terminus; poly(**2**- d_1), i.e., hydrogen at one terminus and deuterium at the other; and poly(**2**- d_2), i.e., deuterium at each terminus, respectively. The results in Table 6 show that the poly(**2**) is essentially isotopically pure. When HCOOD or DCOOH was employed essentially 95% or greater of the observed polymeric molecular ions were monodeuterated; one deuterium is present at the polymer terminus. This clearly shows that H_2 from decomposition of formic acid is not involved in the mechanism by which the polymer molecular weight is controlled.

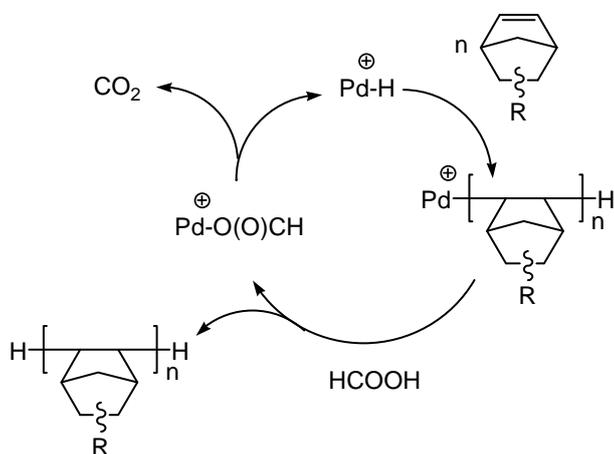


Scheme 4

Another mechanism was sought that explained the facts accumulated in this study (see Scheme 5). In the polymerization reaction mixture a palladium hydride cation is generated by the reaction of formic acid. This active center inserts several norbornene monomers. The growing polymer chain ultimately reacts with the acidic hydrogen of formic acid to form a dihydrogen terminated poly(norbornene) and a palladium formate cation. The formate complex loses carbon dioxide reforming the cationic palladium hydride catalyst.

There are several precedents in the literature for the transformations depicted in Scheme 5. For example, palladium acetate complexes are known to react with formic acid to make palladium hydrides [14]. Indeed,

the ^1H NMR spectrum of a THF- d_8 /toluene- d_8 reaction mixture of catalyst **5** and 100 equiv of formic acid after 4 h at 55 °C shows a hydride signal at δ -15.5 ppm and a singlet at δ 55.6 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. These signals are consistent with formation of what is likely to be $[\text{Pd}(\text{H})(\text{MeCN})(\text{P}(i\text{-Pr})_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ [15].



Scheme 5

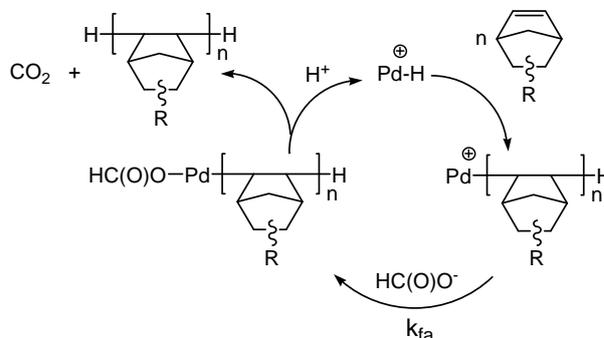
The molecular weight limiting step, reaction of the acid proton of formic acid with the Pd-C bond of the growing polymer chain, has been proposed in the terpolymerization of CO, ethylene and propylene [16].

Loss of CO_2 from a Group 10 formate complex to create a Group 10 hydride has been described by several authors [9c, 17, 18].

While the mechanism in Scheme 5 does account for a route in which the label from monodeuterio-formic acid is regioselectively applied to the polymer (i.e., at the end or the beginning of the polymer chain) as well as accounting for a step that controls molecular weight, it does not account for the higher molecular weight observed for the deuterio-formyl labeled formic acid experiments 16 and 17 compared to that produced in experiments 14 and 15. The higher molecular weight observed in these two experiments is likely due to a primary kinetic isotope effect during the molecular weight rate determining step involving breaking of the formyl-hydrogen (deuterium) bond of formic acid. Based on the M_n values found for experiments 14 and 16, a k_H/k_D of ~ 1.5 can be calculated. This is similar to the primary kinetic isotope effect reported by Bercaw and coworkers which suggested that β -H elimination was the predominant molecular weight determining step [19].

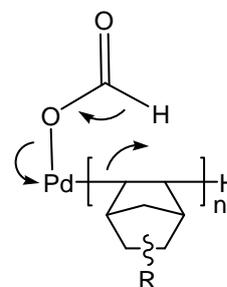
To account for this final observation, another mechanism was considered that invoked the intermediacy of a neutral palladium formate complex governed by rate constant k_{fa} and formic acid concentration. In Scheme 6, the palladium hydride cation inserts norbornene to form a growing polymer chain. The cationic palladium reacts with the formate

ion to yield the neutral formate species. From this intermediate CO_2 and the dihydrogen terminated polymer is generated. The palladium hydride can be regenerated by reaction with a proton from formic acid.



Scheme 6

There are two scenarios that are possible for the last step of the catalytic cycle in Scheme 6. The neutral formate complex could transfer the formyl proton to the Pd-C bond of the norbornyl ligand and extrude CO_2 in a concerted fashion and form a Pd(0) complex that reacts with H^+ to regenerate the palladium hydride catalyst (Scheme 7). Or in a stepwise fashion the formate could lose CO_2 to form an intermediate hydride complex that then reductively eliminates the dihydrogen-terminated polymer forming a Pd(0) species complex that reacts with H^+ to regenerate the palladium hydride catalyst. See Scheme 8.



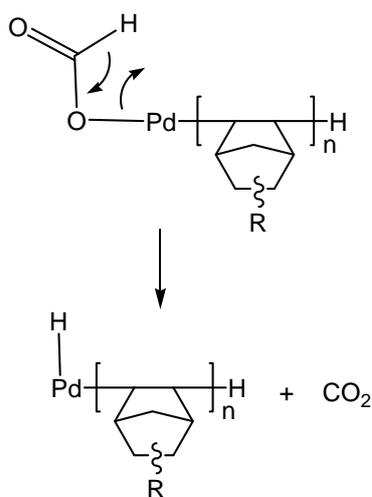
Scheme 7

In either case breaking of the formyl C-H(D) bond in formic acid is required prior to termination of the polymer chain and as such is possibly the cause of the isotope effect that is observed in the M_n of the polymer formed in experiments 14-17.

In the case of catalyst **4** in the presence of formic acid, NMR and MALDI-TOF MS analysis of copolymer **1** and **2** showed that the major molecular ion series was based on hydrogen terminated polymers. Thus, the optical density at 193 nm was substantially lower than copolymers made using catalyst **3** since copolymers with *exo*-methylene cyclohexenyl end groups were less prevalent. In general, as the concentration of formic acid is

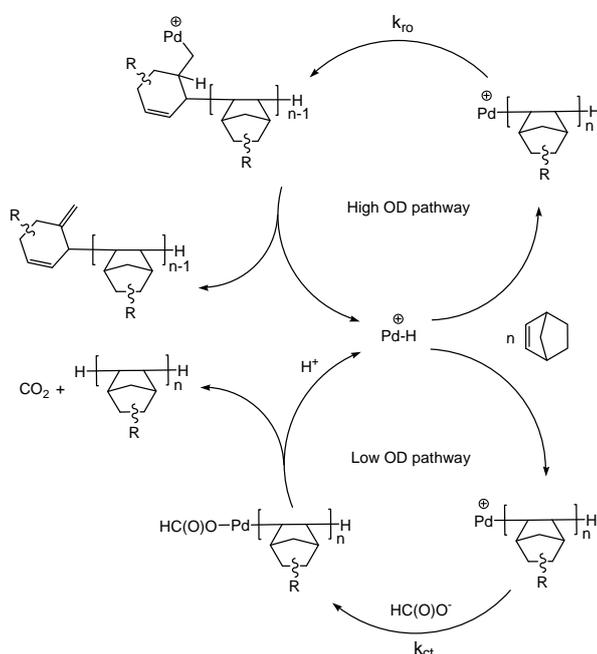
increased with catalyst **4** the OD of the copolymer decreases despite the decrease in molecular weight.

The optical density measurements in Table 5 suggest that the chain transfer mechanism operative for catalyst **4** is a competition between intramolecular ring opening by β,γ -carbon-carbon bond cleavage (governed by k_{ro}) followed by β -hydrogen elimination and chain transfer to formic acid (regulated by k_{fa} and the concentration of formic acid). This competition can be depicted as in Scheme 9 where the ring opening route is considered a high OD pathway and the formic acid route is considered a low OD pathway.



Scheme 8

By determining how temperature and formic acid concentration control the partitioning of the two mechanistic pathways, reaction conditions can be developed that favor low optical density polymers that would be suitable for semiconductor applications.



Scheme 9

5. Conclusions

Formic acid can be an effective CTA for some Pd catalyzed vinyl addition polymerizations of norbornene monomers. Molecular weights, optical densities, deuterium labeling, MALDI-TOF MS, and NMR studies support a chain termination event involving chain transfer to formic acid (low OD pathway) in competition with intramolecular ring opening (high OD pathway). By controlling reaction conditions, the partitioning between these two pathways can be controlled so that low OD polymers are produced.

Acknowledgments

We thank Ms. Jennifer Thorensen for GPC support and Dr. Andrew Bell for comments.

References

- (a) P. C. Tsiartas, L. L. Simpson, A. Qin, C. G. Willson, R. D. Allen, V. J. Krukonis, P. M. Gallagher-Wetmore, *Proc. SPIE-Int. Soc. Opt. Eng.*, **2438** (1995) 261. (b) L. F. Thompson, C. G. Willson, M. J. Bowden, "Introduction to Microlithography" 2nd Edition; American Chemical Society: Washington, DC, 1994, p 197.
- (a) B. L. Goodall, "Cycloaliphatic Polymers via Late Transition Metal Catalysis", in: Late Transition Metal Polymerization Catalysis, B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler, Eds., Wiley-VCH, Weinheim 2003, p. 141. (b) B. L. Goodall, S. Jayaraman, R. A. Shick, L. F. Rhodes US 6136499 (2000). (c) U. Okoroanyanwu, T. Shimokawa, J. Byers, C. G. Willson, *Chem. Mater.* **10** (1998) 3319. (d) U. Okoroanyanwu, T. Shimokawa, J. Byers, C. G. Willson, *J. Mol. Catal. A: Chem.* **133** (1998), 93. (e) T. Wallow, P. Brock, R. DiPietro, R. Allen, J. Opitz, R. Sooriyakumaran, D. Hofer, J. Meute, J. Byers, G. Rich, M. McCallum, S. Schuetze, S. Jayaraman, K. Hullihen, R. Vicari, L. F. Rhodes, B. Goodall, R. Shick, *Proc. SPIE-Int. Soc. Opt. Eng.* **3333** (1998) 92. (f) P. R. Varanasi, J. Maniscalco, A. M. Mewherter, M. C. Lawson, G. Jordhamo, R. D. Allen, J. Opitz, H. Ito, T. I. Wallow, D. Hofer, L. Langsdorf, S. Jayaraman, R. Vicari, *Proc. SPIE-Int. Soc. Opt. Eng.* **3678** (1999) 51. (g) P. R. Varanasi, A. M. Mewherter, M. C. Lawson, G. Jordhamo, R. Allen, J. Opitz, H. Ito, T. Wallow, D. Hofer, *J. Photopolym. Sci. Technol.* **12** (1999) 493.
- (a) B. L. Goodall, D. A. Barnes, G. M. Benedikt, L. M. McIntosh, L. F. Rhodes, *Proc. Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng.* **76** (1997) 56. (b) B. L. Goodall, D. A. Barnes, G. M. Benedikt, S. Jayaraman, L. M. McIntosh, L. F. Rhodes, R. A. Shick, *Polym. Prepr.* **39(1)** (1998) 216. (c) J. Lipian, R. A. Mimna, J. C. Fondran, D. Yandulov, R. A. Shick, B. L. Goodall, L. F. Rhodes, J. C. Huffman, *Macromolecules* **35** (2002) 8969.

4. C. Chang, J. Lipian, D. A. Barnes, L. Seger, C. Burns, B. Bennett, L. Bonney, L. F. Rhodes, G. M. Benedikt, R. Lattimer, S. Huang, V. W. Day, *J. Macromol. Chem. Phys.*, **206** (2005) 1988.
5. C. Chang; J. Lipian, C. Burns, L. F. Rhodes, R. P. Lattimer, *J. Photopolym. Sci. Technol.* **23** (2010) 715.
6. M. A. Brook, *Silicon in Organic, Organo-metallic, and Polymer Chemistry*; John Wiley and Sons, Inc.: New York, 2000; p 176.
7. C. Chang; D. Barnes, L. D. Seger, L. F. Rhodes, R. P. Lattimer, G. M. Benedikt, *J. Photopolym. Sci. Technol.* **25** (2012) 2161.
8. M. K. Boggiano, Ph. D. Thesis, University of North Carolina at Chapel Hill, 2006, p. 90 and references therein.
9. (a) R. S. Coffey, *Chem. Commun.*, **1967**, 923. (b) T. Yoshida, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.*, **100** (1978) 3941. (c) R. S. Paonessa, W. C. Trogler, *J. Am. Chem. Soc.*, **104** (1982) 3529. (d) Y. Gao, J. K. Kuncheria, H. A. Jenkins, R. J. Puddephatt, G. P. D. Meilleur, D. Rivard, P. D. Harvey, I. Gauthron, D. Lucas, Y. Mugnier, *Inorg. Chem.*, **39** (2000) 2909.
10. J. R. Hyde, M. Poliakoff, *Chem. Commun.*, **2004** 1482.
11. (a) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.*, **118** (1996) 2521. (b) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.*, **118** (1996) 4916. (c) J. Zhang, P. G. Blazeca, M. M. Brunedl, Y. Huang, *J. Org. Chem.*, **74** (2009) 1411. (d) S. A. Yap, *J. Chem. Soc., Dalton Trans.*, **2000**, 3212. (e) Gladiali, E. Alberico, "Transfer Hydrogenations", in: *Transition Metals for Organic Synthesis*, M. Beller, C. Bohm, Eds., Wiley-VCH, Weinheim 2004, p. 145.
12. N. Thirupathi, D. Amoroso, A. Bell, J. D. Protasiewicz, *Organometallics*, **26** (2007) 3157.
13. J. McDermott, C. Chang, L. F. Martin, L. F. Rhodes, G. M. Benedikt, R. P. Lattimer, *Macromolecules* **41** (2008) 2984.
14. N. Y. Kozitsyna, A. M. Ellern, M. Y. Antipin, Y. T. Struchkov, I. I. Moiseev, *Mendeleev Commun.*, **1(3)**, (1991), 92.
15. A. Bell, D. Amoroso, J. D. Protasiewicz, N. Thirupathi, US 20050187398 (2005).
16. A. Vavasori, L. Ronchin, L. Toniolo, *Appl. Cat. A: General*, **389** (2010) 108.
17. D. J. Darensbourg, P. Wiegrefe, C. G. *J. Am. Chem. Soc.* **112** (1990) 5759.
18. V. V. Grushin, C. Bensimon, H. Alper *Organometallics*, **14** (1995) 3259.
19. D. Veghini, L. M. Henling, T. J. Burkhardt, J. E. Bercaw, *J. Am. Chem. Soc.*, **121** (1999) 564.