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Palladium Catalyzed Vinyl Addition Poly(norbornenes): Silane Chain Transfer Agents, Hydroxyl Group Activators and Their Impact on Optical Density at 193 nm

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Polymers of substituted norbornenes were produced using palladium catalysts in the presence of silane chain transfer agents (CTA) which act to control molecular weight. Yields were dramatically increased by addition of hydroxylic reagents such as ethanol. 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. Negative tone compositions containing norbornene copolymers with aliphatic and fluorinated alcohol substituents have been demonstrated.

Keywords: Norbornene, transparency, 193 nm, silane, chain transfer

1. Introduction

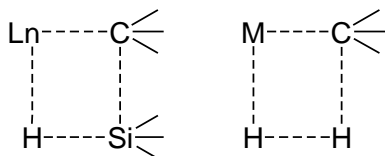
Molecular weight and molecular weight distribution are important properties of binder resins in photopolymer compositions since they affect critical film properties such as dissolution behavior in developer [1]. Ideally, techniques to control molecular weight without impacting other properties such as transparency at the imaging wavelength (e.g., 365, 248, or 193 nm) are desirable [2].

Recently, several publications have appeared that discuss the incorporation of the bis-trifluorocarbonyl substituted norbornene **1** (\pm, \pm -bis(trifluoromethyl)norbornene-2-ethanol) into photoresist binder resins [3, 4, 5]. Previously, we reported that the homopolymerization of **1** and the copolymerization of **1** and **2** (t-butylester of 5-norbornene carboxylic acid) with controlled molecular weight could be achieved using olefinic chain transfer agents and neutral palladium catalysts of the type, Pd(OAc)₂(PR₃)₂. Unfortunately, to obtain low optical densities (ODs) for these polymers at 193 nm a post-polymerization end group modification step such as epoxidation or hydrogenation was required [6].

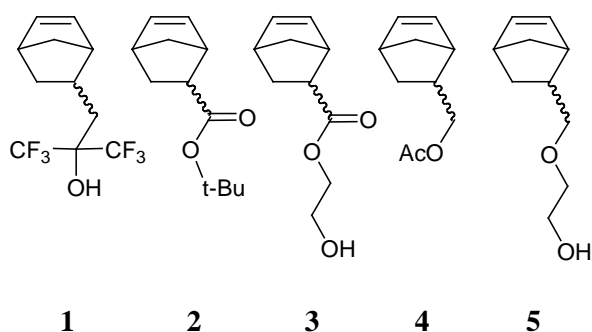
We subsequently found that H₂ is an effective molecular weight control agent for accessing low molecular weight poly(**1**) made using catalysts such as Pd(OAc)₂(PR₃)₂. These homopolymers exhibited very low ODs at 193 nm that were independent of molecular weight [7]. For commercial production however, use of highly flammable hydrogen requires special handling and is not desirable from a safety perspective. Thus, we were tasked with discovering an effective, but commercially viable method for controlling molecular weight without impacting transparency.

Beginning in the mid-90's Marks and co-workers disclosed the use of primary silanes, i.e., RSiH₃, as effective chain transfer agents for olefin polymerization using lanthanide (Ln) metallocene catalysts [8]. This transformation is thought to occur via a four-centered \ddot{A} bond metathesis transition state. It is similar to that conceived for hydrogen CTAs in olefin polymerization catalyzed by transition metals, M (see figure below) and is responsible for appending the silane functionality to the terminus of the polymer.

These reports prompted us to investigate the efficacy of silanes as CTAs in norbornene poly-



merization using palladium catalysts. We found that the poly(norbornene) molecular weight is inversely proportional to the concentration of the tertiary silane and that additives containing hydroxyl functionalities such as ethanol act to improve catalyst activity. Deuterium labeling studies helped elucidate the role of silane and ethanol in the polymerization. We discovered that poly(**1**) made using silane are extremely transparent at 193 nm and that copolymers of monomers **1** and **5** (5-norbornene-2-methanol hydroxyethylether) can be formulated into negative tone photopolymer compositions [9].



2. Experimental

2.1 General.

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

All monomers were obtained from Promerus LLC, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (DANFABA) was purchased from Boulder Scientific, Et₃SiH from Gelest, hexakis(methoxymethyl)melamine (HMMM) from TCI America, Rhodorsil® PI-2074 from Rhodia, and 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) from Sigma-Aldrich. The catalysts used in this study, Pd(OAc)₂(P(*i*-Pr)₂Ph)₂ (**6**), Pd(OAc)₂(PCy₃)₂ (Cy = cyclohexyl) (**7**), and [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**), were prepared according to published procedures [10].

NMR, GPC, and optical density (OD) were determined as previously reported [6b]. The MALDI-MS experiments were carried out using a Bruker Reflex III system. Solutions of polymer, 1,8,9-anthracenetriol (dithranol matrix), and sodium trifluoroacetate (NaTFA) were prepared in

tetrahydrofuran solvent (20 mg/mL). Ten μL of the NaTFA solution was added to 1 mL of polymer solution. Equal volumes of polymer and matrix solutions were mixed and spotted on a stainless steel MALDI plate. MALDI experiments were conducted in reflectron mode with delayed extraction at laser powers slightly above the threshold power for detection of sample ions.

2.2 Copolymerization of **1** and **3** using H₂ as CTA

Monomers **1** (74.9 g, 0.273 mol) and **3** (4.92 g, 0.027 mol), along with DANFABA (0.24 g, 0.30 mmol) were weighed into a glass pressure vessel equipped with a stir bar and combined with toluene (200 mL) in the dry box. The vessel was sealed. In the hood, the solution was sparged with hydrogen gas for 15-20 min charged with H₂ (90 psig) and heated to 80 °C. Once the reactor reached 80 °C, Pd(OAc)₂(P(*i*-Pr)₂Ph)₂ (**6**) (0.074 g, 0.12 mmol) was added in a minimum amount of toluene. The mixture was stirred for 18 h. After cooling, the pressure was released and the mixture was poured into heptane to precipitate the polymer. The polymer was filtered and dried at 90 °C in a vacuum oven. Yield 33.4 g (42%). ¹³C NMR (DMSO-d₆, 70 °C): δ 174.24 (m, -C(O)O-), 123.79 (q, ¹J_{C-F} = 287 Hz, -CF₃), 76.27 (br s, -C(CF₃)₂OH), 65.70 (s, -OCH₂CH₂-), 59.77 (s, -OCH₂CH₂-) 30-59 (aliphatic carbons). Molar ratio of **1** to **3** (90/10) was determined using the integration of the 76.27 resonance (for **1**) and the 65.77 resonance (for **3**). GPC: *M*_w = 9250; *M*_n = 4870.

2.3 Copolymerization of **1** and **3** using Et₃SiH as CTA.

In a representative polymerization, monomer **1** (59.2 g, 0.216 mol), monomer **3** (4.37 g, 0.0240 mol) and DANFABA (0.192 g, 0.240 mmol) were weighed into a glass vial equipped with a stir bar and combined with Et₃SiH (3.10 g mL, 0.027 mol) and toluene (160 mL). The vial was capped and the solution was sparged with nitrogen and then heated to 80 °C. To this solution was added Pd(OAc)₂(PCy₃)₂ (**7**) (0.038 g, 0.048 mmol) in a minimum amount of toluene. The mixture was allowed to stir for 18 h. After cooling, the mixture was poured into heptane to precipitate the polymer. The polymer was filtered and dried at 80 °C in a vacuum oven. Yield 48.4 g (76%). GPC: *M*_w = 4500; *M*_n = 3210.

The procedure was repeated using conditions reported in Table 1.

2.4 Polymerization of **1** using Et₃SiH as CTA with and without EtOH.

In a representative polymerization, monomer **1** (10.97 g, 0.040 mol), ethanol (0.20 g, 0.0044 mol), Et₃SiH (0.46 g, 0.0040 mol) and 1.0 mL of a 0.002 M solution of DANFABA in methylene chloride were placed into a vial equipped with a stir bar. The total volume was increased to 27 mL by the addition of toluene and the vial was sealed with a septum cap. The mixture was heated to 80 °C. Once the temperature was reached, 1.0 mL of a 0.00066 M solution of [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**) in methylene chloride was added to the monomer mixture. The mixture was stirred for 17 h. The mixture was then cooled to room temperature and poured into hexane to precipitate the polymer. The polymer was filtered and dried in a vacuum oven at 80 °C. Yield 7.79 g (71%). GPC: $M_w = 4950$; $M_n = 3390$.

The experiment was repeated with decreasing catalyst loading and the results are shown in Table 2. Repeating the experiment without EtOH gave no polymer (see experiment 9 in Table 2).

2.5 Polymerization of **1** using decreasing concentration of Et₃SiH as CTA.

In a representative polymerization, toluene (171 mL), monomer **1** (100 g, 365 mmol), ethanol (2.30 mL, 40.5 mmol), and triethylsilane (5.80 mL, 36.5 mmol) were placed into a vial equipped with a stir bar and sealed with a septum cap. The mixture was sparged with nitrogen for 15 min then heated to 80 °C. Once temperature was reached, [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**) (44.0 mg, 0.0365 mmol) dissolved in 1.5 mL of dichloroethane and DANFABA (88.0 mg, 0.110 mmol) dissolved in 1.5 mL of dichloroethane were both injected into the monomer reaction mixture. The mixture was stirred for 18 h. The mixture was then cooled to room temperature and poured into hexane to precipitate the polymer. The polymer was filtered and dried in a vacuum oven for 24 h at 100 °C. Yield 76.5 g (77%). GPC: $M_w = 5350$; $M_n = 3270$.

The procedure was repeated using conditions reported in Table 3.

2.6 Polymerization of **4** using Et₃SiH(D) and EtOH(D).

In a representative polymerization, monomer **4** (6.65 g, 0.040 mol), ethanol (0.20 g, 0.0044 mol), Et₃SiH (0.51 g, 0.0040 mol), 1.0 mL of a 0.006 M solution of DANFABA in methylene chloride and were placed into a vial equipped with a stir bar. The total volume was increased to 27 mL by the

addition of toluene and the vial was sealed with a septum cap. The mixture was heated to 80 °C. Once temperature was reached, 1.0 mL of a 0.002 M solution of [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**) in methylene chloride was added to the monomer reaction mixture. The mixture was stirred for 20 h. The mixture was then cooled to room temperature and poured into hexane to precipitate the polymer. The polymer was filtered and dried in a vacuum oven at 85 °C. Yield 5.33 g (85%). GPC: $M_w = 3390$; $M_n = 1580$.

The procedure was repeated using conditions reported in Table 4.

2.7 Copolymerization of **1** and **5**.

In the drybox, monomers **1** (7.07 g, 0.026 mol) and **5** (0.71 g, 0.0042 mol), DANFABA (0.060 mmol) and Et₃SiH (0.35 g, 0.0034 mol) were added to a vial equipped with a stir bar. Sufficient toluene and 1-methoxy-2-propanol (90:10 volume ratio) to bring the total volume to 20 mL was added. The vial was sealed with a septum cap. The mixture was heated to 80 °C, then 1.0 mL of a 0.012 M solution of Pd(OAc)₂(PCy₃)₂ (**7**) in toluene was added. The mixture was stirred for 18 h. The reaction mixture was then cooled to room temperature and poured into heptane to precipitate the polymer. The polymer was filtered and dried in a vacuum oven at 80 °C. Yield 6.15 g (79%). ¹³C NMR (DMSO-d₆, 70 °C): δ 123.79 (q, ¹J_{C-F} = 287 Hz, -CF₃), 76.25 (br s, -C(CF₃)₂OH), 72.49 (s, -CH₂OCH₂-), 60.75 (s, -CH₂OH), 30-59 (aliphatic carbons). Molar ratio of **1** to **5** (83/17) was determined using the integration of the 123.79 resonance (for **1**) and the 60.75 resonance (for **5**). GPC: $M_w = 4450$; $M_n = 2850$. Optical density (193 nm): 0.13 μm⁻¹.

2.8 Formulation and Imaging of poly(**1/5**).

A solution of 0.25 g of poly(**1/5**) prepared in section 2.7, 0.025 g of HMMM, 0.0075 g of Rhodorsil® PI-2074, 0.005 g of CPTX in 0.75 g of PGMEA was prepared. Approximately 0.50 g of the above formulation was filtered through a 0.2 μm PTFE filter and applied to an hexamethyldisilazane treated wafer. The wafer was spun at 500 rpm for 15 s followed by 2000 rpm for 60 s then soft baked at 75 °C for 90 s. The wafer was image-wise exposed using an ABM mask aligner equipped with a 365 nm band pass filter at a dose of 500 mJ/cm² at 365 nm. The wafer was post-exposure baked at 75 °C for 120 s. Latent images were observed. The wafer was immersed into 0.26 N aqueous TMAH for 4 min. The wafer was removed from developer and rinsed

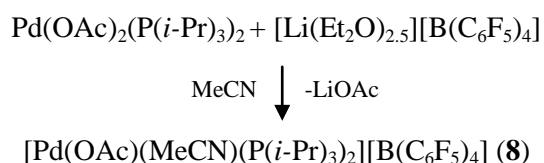
with deionized water and dried with nitrogen. Microscope evaluation of the wafer showed that negative tone images with features of 15 μm x 85 μm were clearly resolved.

3. Results and Discussion

3.1 Polymerization studies.

Polymerization of monomers **1** and **3** (90/10 molar ratio, see entry 1 in Table 1) using Pd(OAc)₂(P(*i*-Pr)₂Ph)₂ (**6**) (2500:1 monomer to Pd molar ratio) and DANFABA under 90 psig hydrogen gave the copolymer in 42% yield with a *M_w* of 9250 (*M_n* = 4870). A polymerization at higher (5000:1) monomer to Pd ratio, albeit with a different catalyst, Pd(OAc)₂(PCy₃)₂ (**7**) (see entry 2 in Table 1) in the presence of Et₃SiH (10 mole percent) instead of H₂ gave a copolymer with a *M_w* of 4500 (*M_n* = 3210) in higher yield (76%). At approximately one-tenth the catalysts loading, the Et₃SiH polymerization conditions (see entry 4) gave essentially the same yield of the copolymer as that found for experiment 1 (with H₂).

In addition to neutral palladium phosphine acetate compounds such as **6** and **7**, the cationic palladium reaction products formed from combining, for example Pd(OAc)₂(P(*i*-Pr)₃)₂ with [Li(Et₂O)_{2.5}][B(C₆F₅)₄], can also be used as polymerization catalysts [10a, 11]. Thus several comparative polymerizations were carried out using the cationic complex, [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**).



A higher yield was found for cationic compound **8** compared to neutral compound **7** all else being equal. Compare entries 4 and 6 which were carried out at a 20000:1:3 monomer: Pd:DANFABA molar ratio. Experiment 6 gave 73% yield while experiment 4 gave 44%. At a 50000:1:3 ratio monomer: Pd:DANFABA molar ratio, experiment 8 gave 38% yield. Thus while complex **7** yielded essentially the same amount of polymer as catalyst precursor **8** (compare entries 4 and 8), it required 2.5 times more catalyst. Note that the molecular weights of the copolymers for the Et₃SiH experiments in Table 1 stay essentially the same despite the change in identity and loading of the palladium complexes used.

Table 1. Copolymerization of **1** and **3** (90/10 molar ratio, experiment 4 was 94/6 molar ratio) using Pd(OAc)₂(P(*i*-Pr)₂Ph)₂ (**6**), Pd(OAc)₂(PCy)₂ (**7**), or [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**), and DANFABA in the presence of hydrogen (90 psig) or Et₃SiH (10 mole percent) as CTA.

Expt.	Pd	CTA	Yield (%)	<i>M_w</i>	<i>M_n</i>
1*	6	H ₂	42	9250	4870
2~	7	Et ₃ SiH	76	4500	3210
3@	7	Et ₃ SiH	65	4130	2870
4^	7	Et ₃ SiH	44	4870	3190
5#	8	Et ₃ SiH	73	4550	3050
6^	8	Et ₃ SiH	73	4450	2980
7%	8	Et ₃ SiH	58	4550	3050
8+	8	Et ₃ SiH	38	--	--

Monomer: Pd: DANFABA molar ratio: *2.5K:1:5, ~5K:1:3, #10K:1:3, @12K:1:3, ^20K:1:3, %30K:1:3, +50K:1:3.

Our initial attempts to obtain comparable yields for the homopolymerization of **1** at the lower loadings of complex **8** were frustrated by poor results. As can be seen in Table 2, experiment 9 gave no polymer when **1** was polymerized at a 60000:1 monomer to Pd ratio.

Investigation of the structure of the copolymer of **1** and **3** by ¹³C NMR methods showed some interesting features which led to experiments that dramatically increased the yields for the homopolymerization of **1** (see Figure 1).

Besides the expected carbonyl carbon (a) and the trifluoromethyl carbon (b) and the aliphatic carbon resonances (between 30-50 ppm), four peaks between 4 and 8 ppm (consistent with an alkylsilane) and a peak at 61.08 ppm (f) appeared. Two of the high field peaks (6.78 and 6.15 ppm) were assigned to Et₃SiOSiEt₃ based on literature values. The other two high field peaks (6.58 and 4.42 ppm, g and h) are of equal intensity and are slightly broader than those resonances assigned to Et₃SiOSiEt₃ suggesting that this moiety is associated with the polymer. The chemical shift of the resonance at 61.08 ppm (peak f) and its integration compared to the peak at 4.42 ppm is consistent with formation of a triethylsilyl derivative of monomer **3**. See structure in Figure 1. Based on the integration of peak f relative to e, approximately 30% of the alcohol pendant group was transformed to the triethylsilyl derivative. Treatment of this polymer with acetic acid in the presence of H₂O₂ removed the silyl group regenerating the alcohol functionality.

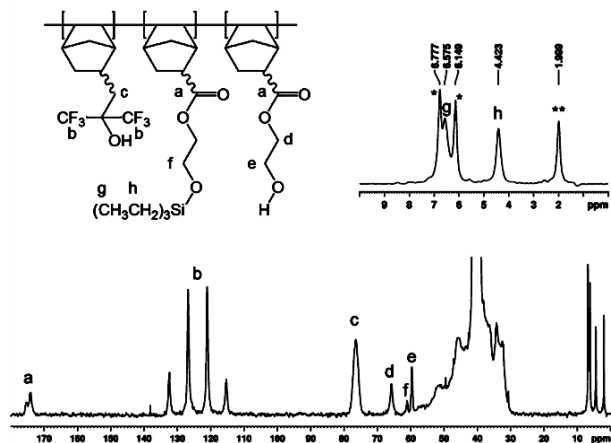


Figure 1. ^{13}C NMR spectrum (DMSO-d_6) of copolymer of **1** and **3** (90/10) made using Et_3SiH as CTA in experiment 3 in Table 1 (*assigned to $\text{Et}_3\text{SiOSiEt}_3$, **HMDS standard).

The reaction of alcohols with silanes (also known as dehydrogenative coupling or silane alcoholysis) finds precedent in the literature. A number of metals are known to catalyze this reaction including both hetero- and homo-geneous varieties of Pd [12].

At this point it occurred to us that the yield of polymerization of **1** might be enhanced by addition of alcohol since the yields of the copolymerization of **1** and **3** (an alcohol norbornene derivative) were higher (38% at 50K:1 monomer to Pd ratio, see entry 8 in Table 1) than the homopolymerization of **1** (0% at 60K:1 monomer to Pd ratio, see entry 9 in Table 2). Thus a repeat of experiment 9 in the presence of EtOH (entry 10 in Table 2) gave a dramatic increase in yield (71%). The limits of this yield enhancement were explored by running further experiments at decreasing catalyst loading. Experiments 11-13 show that reasonable yields of poly(**1**) can be obtained even at a 200000:1 monomer to Pd molar ratio. This translates to a high catalyst activity of 220000 g of poly(**1**)/g of Pd which equals only 4.5 ppm of residual Pd in the polymer. Since low residual metal content is a must for polymers used in the electronics industry, high activity catalysts are always a welcome addition.

Next the impact of Et_3SiH on molecular weight was examined in a series of polymerizations of **1**

listed in Table 3. The polymer molecular weights were found to be inversely proportional to the Et_3SiH concentration. This trend could be consistent with formation of a silane terminated polymer as in the case of olefin polymerization by lanthanide catalysts [8], however further further

Table 2. Polymerization of **1** using $[\text{Pd}(\text{OAc})(\text{MeCN})(\text{P}(i\text{-Pr})_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**) and DANFABA in the presence of Et_3SiH (9 mole %) with and without EtOH (10 mole %) with decreasing catalyst loading.

Expt.	Monomer:Pd: DANFABA	Yield (%)	M_w	M_n
9*	60K:1:3	0	--	--
10 [^]	60K:1:3	71	4950	3390
11 [^]	80K:1:3	64	4800	3250
12 [^]	100K:1:3	52	--	--
13 [^]	200K:1:3	43	--	--

*Without EtOH. [^]With EtOH.

Table 3. Polymerization of **1** using $[\text{Pd}(\text{OAc})(\text{MeCN})(\text{P}(i\text{-Pr})_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**) and DANFABA in the presence of EtOH (10 mole %) with decreasing Et_3SiH concentration.

Expt.*	Et_3SiH mole%	Yield (%)	M_w	M_n
14	9	77	5350	3270
15	5	87	9000	5100
16	3	89	15700	7490
17	2	91	22700	10600
18	1.5	93	31900	13700

*10K:1:3 Monomer:Pd:DANFABA

investigation showed this not to be the case.

3.2 Elucidation of polymerization mechanism.

In order to confirm the formation of silane terminated polymer, a sample of poly(**4**) from experiment 19 (see Table 4 for details) was submitted for MALDI-TOF mass spectral analysis. The resulting spectrum is given in Figure 2. Only one significant polymer series is observed in the MALDI-TOF mass spectrum and it is consistent with hydrogen end groups at both ends of poly(**4**). Since sodium was added to the polymer to aid ionization, poly(**4**) with 15 repeat units, one sodium ion, and two hydrogen end groups would exhibit a molecular ion of 2515 as is observed in the mass spectrum. Unexpectedly, there is no evidence of a silane terminated polymer.

The presence of hydrogen-terminated polymer suggested that H_2 might be involved in the chain transfer step since the dehydrogenative coupling reaction of alcohols with silanes evolves H_2 . A mechanism that is consistent with this purported chain transfer step and the MALDI-TOF mass spectral data is represented in Scheme 1. A palladium hydride, generated from the reaction of complex **8** and Et_3SiH (discussed below), initiates the polymerization. Hydrogen (from the dehydrogenative coupling of Et_3SiH and EtOH)

terminates the polymer chain, regenerating the cationic Pd-H catalyst. Evidence for palladium hydride comes from a separate NMR experiment in CD₂Cl₂. Reaction of 1 equiv. of complex **8** with 1 equiv. of Et₃SiH shows a mixture of unreacted complex **8** and what is likely to be [Pd(H)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**9**). A hydride triplet is observed at δ -15.21 ppm ($J_{\text{PH}} = 7\text{Hz}$) in the ¹H NMR spectrum and a singlet at δ 55.67 ppm in the ³¹P{¹H} NMR spectrum. These resonances are consistent with **9** [13].

Table 4. Polymerization of **4** using [Pd(OAc)(MeCN)(P(*i*-Pr)₃)₂][B(C₆F₅)₄] (**8**) and DANFABA in the presence of EtOH or EtOD (10 mole %) and Et₃SiH or Et₃SiD (9 mole %).

Expt.*	Silane	Ethanol	M_w	M_n	End groups
19	Et ₃ SiH	EtOH	3390	1580	H/H
20	Et ₃ SiH	EtOD	3640	1840	H/D
21	Et ₃ SiD	EtOH	4360	1700	D/H
22	Et ₃ SiD	EtOD	4440	1820	D/D

*10K:1:3 Monomer: Pd: DANFABA.

If the mechanism in Scheme 1 were operative, deuterium labeling of the silane (Et₃SiD) or of ethanol (EtOD) would result in a 1:2:1 statistical mixture of three polymeric isotopomers (assuming no significant kinetic isotope effects): poly(**4**) i.e., hydrogen at each terminus, poly(**4**-d₁) i.e., hydrogen at one terminus and deuterium at the other terminus, and poly(**4**-d₂) i.e., deuterium at each terminus, respectively

Surprisingly, when a mixture of EtOD and Et₃SiH or a mixture of EtOH and Et₃SiD were employed, only one polymer series was observed in the MALDI-TOF mass spectrum in each case: poly(**4**-d₁), a deuterium and hydrogen terminated polymer (see entries 20 and 21 in Table 3). Clearly, the mechanism in Scheme 1 is not operative.

A mechanism that is more consistent with the experimental observations is presented in Scheme 2. A palladium hydride cation (generated by the reaction of the complex **8** with Et₃SiH) initiates the polymerization. The growing polymer chain is terminated by Et₃SiH to form the hydrogen-terminated polymer and generate a cationic Pd-SiEt₃ intermediate. This intermediate reacts with EtOH to regenerate the Pd-H cation and forms the coupled product, Et₃SiOEt (observed by mass spectrometry) [14].

A report by Widenhoefer is particularly germane to the proposed mechanism in Scheme 2 in which

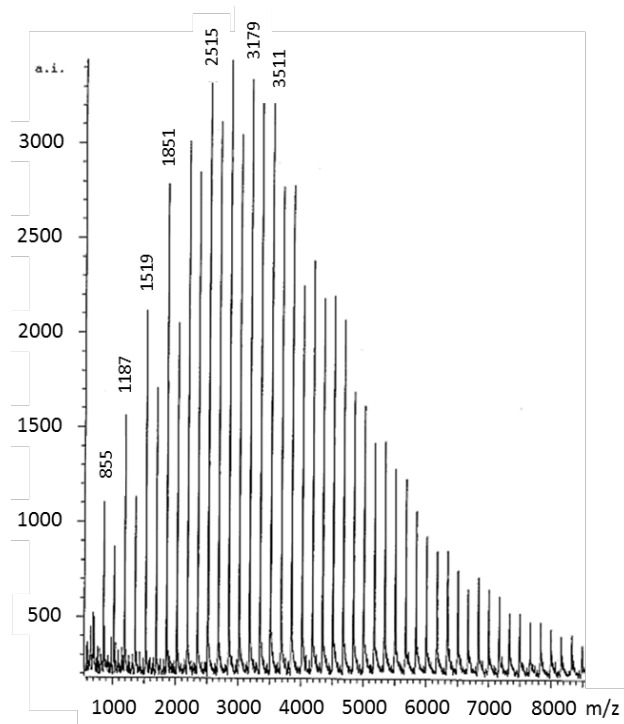
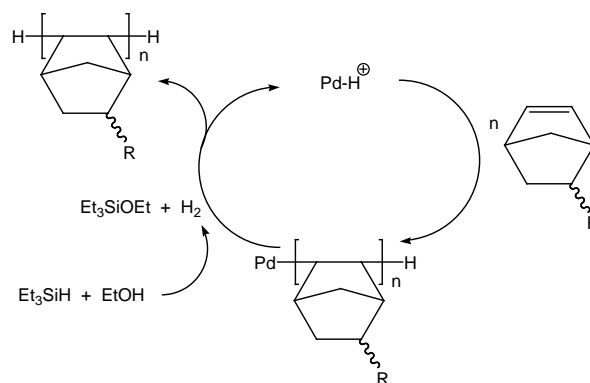
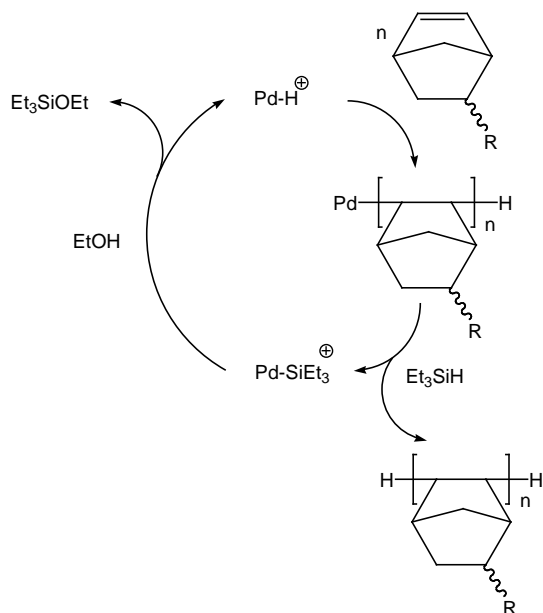


Figure 2. MALDI-TOF MS of homopolymer of **4**.



Scheme 1.

the reductive cyclization of dimethyl diallylmalonate was catalyzed by Pd in the presence of silane and water [15]. The mechanism proposed by Widenhoefer involves insertion of one arm of the diallylmalonate into a Pd-H bond followed by a cyclization reaction with the second arm. The cyclized product is eliminated from the Pd complex coordination sphere by reaction with Et₃SiH to form a Pd-SiEt₃⁺ intermediate, presumably via a \bar{A} bond metathesis transition state. This complex reacts with water to regenerate the Pd-H⁺ species thus closing the catalytic cycle. This mechanism, supported by deuterium labeling studies as well, contains all the essential elements that are presented in Scheme 2.



Scheme 2.

Experiments 9 and 10 in Table 2 clearly show that EtOH promotes the polymer yield for **1**. The yield enhancement is presumably due to the regeneration of the Pd-H⁺ intermediate in Scheme 2 which is more likely to insert the norbornene monomer than a Pd-SiEt₃⁺ species.

Experiments in Table 2 also show that the alcohol functionality present in monomer **1** is insufficiently reactive to promote polymerization at low catalyst loadings. This is presumably due to the high degree of steric hindrance in the –C(CF₃)₂OH pendent group functionality compared to ethanol.

3.3 Optical density of poly(**1**) at 193 nm.

Homopolymers of **1** made using hydrogen as CTAs exhibited very low optical densities at 193nm [7]. The fact that the poly(norbornene) obtained using Et₃SiH in the presence of EtOH contain hydrogen termini, suggested that the optical densities of these polymers at 193nm would also be very low. A comparison of the OD of poly(**1**) made in the presence of H₂ and Et₃SiH (with EtOH) CTAs as a function of *M_n*, given in Figure 3 below, show this to be the case. In addition the OD of poly(**1**) using olefins (hexene and ethylene) as CTAs are shown [6b]. As expected, the OD of these olefin terminated polymers increase dramatically as the *M_n* decreases unlike the hydrogen terminated polymers.

3.4 Negative tone imaging of poly(**1/5**).

Several years ago, Willson and co-workers reported that blends of poly(**1**) and polymers of the

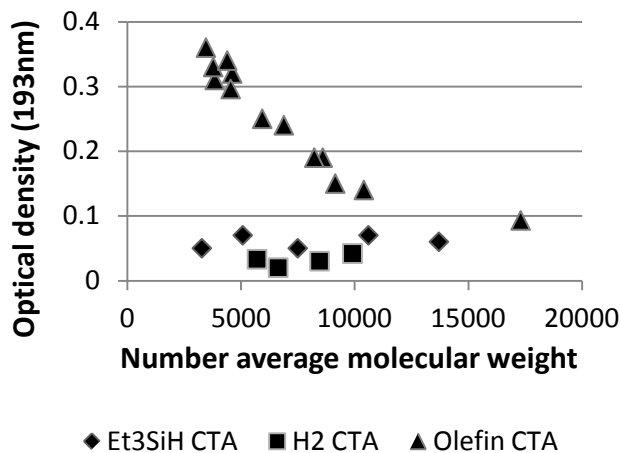
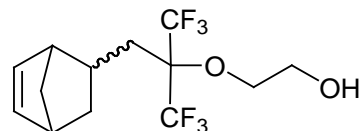


Figure 3. Relationship between *M_n* and OD (μm⁻¹ at 193 nm) for poly(**1**) made using Et₃SiH, H₂ and olefin CTAs.

hydroxyethyl derivative of **1** (see structure below) could be formulated into negative tone acting compositions with tetramethylmethoxy glycoluril (TMMGU, Powderlink 1174) and a suitable photoacid generator (PAG) [16].



Our ability to copolymerize monomer **1** with glycol containing monomers such as **3** and **5** suggested that a negative tone-acting formulation could be developed using similar crosslinkers and PAGs. Copolymerization of **1** and **5** was carried out using Pd(OAc)₂(PCy₃)₂ (**7**) and DANFABA in the presence of Et₃SiH as a chain transfer agent.

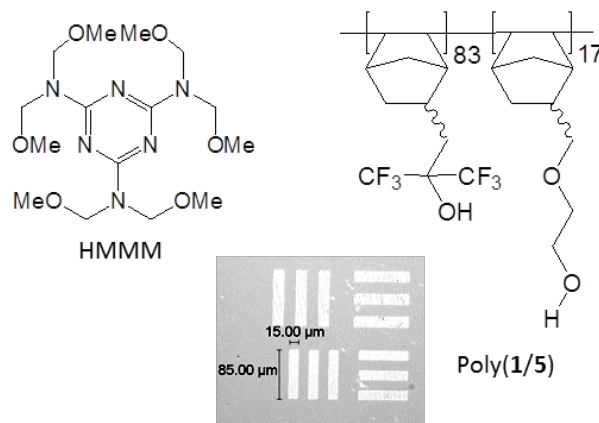


Figure 4. Negative tone imaging results for poly(**1/5**) formulated with HMMM, Rhodorsil® PI-2074, and CPTX at 365nm.

The low molecular weight ($M_w = 4450$) copolymer (83/17 ratio of **1** to **5**), as expected, exhibited a low OD at 193 nm ($0.13 \mu\text{m}^{-1}$).

Poly(**1/5**) was formulated with HMMM, Rhodorsil[®] PI-2074, and CPTX. After image wise exposure (at 365 nm) of films containing these ingredients and development with 0.26 N TMAH, negative tone features were observed with features of $15 \mu\text{m} \times 85 \mu\text{m}$ clearly resolved (see Figure 4). Similar compositions have been disclosed for 193 nm negative tone imaging [17].

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14. Experiment 10 (Table 2) was repeated, but instead of precipitating the polymer, the reaction mixture was analyzed by field ionization mass spectrometry. In addition to solvents, monomer,

and Et₃SiH, a molecular ion peak appeared at 160 *m/z* consistent with the formation of triethylsilane ethoxide (fragment ion observed at 131 *m/z* was assigned to Et₂SiOEt⁺).

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