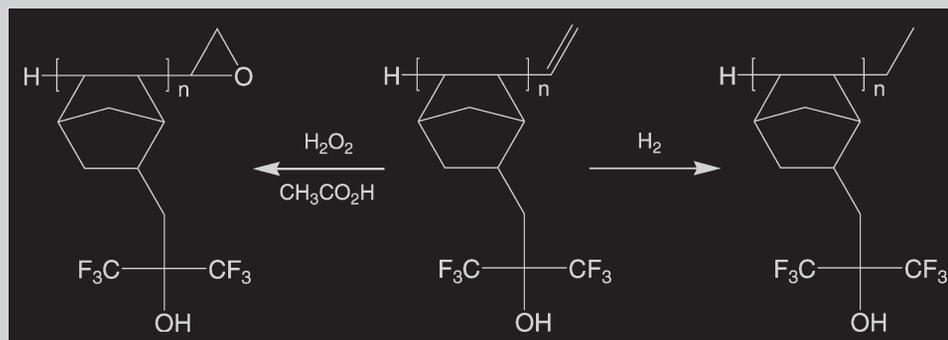


Summary: Homopolymers of a bis-trifluorocarbonyl substituted norbornene (**1**) (α,α -bis(trifluoromethyl)bicyclo[2.2.1]-hept-5-ene-2-ethanol or HFANB) and copolymers of **1** with *t*-butyl ester of 5-carboxylic acid (**2**, *t*-BuEsNB) were produced using palladium catalysts and olefinic chain transfer agents such as 1-hexene and ethylene to control molecular weight. However, these low-molecular-weight polymers exhibited relatively low optical transparencies at 193 nm. In fact, the opacity (measured as optical densities in absorbance units per micron) of thin films of these homo- and copolymers was inversely proportional to their molecular

weight. This relationship is consistent with an end group contribution to the film opacity. Spectroscopic analysis of these polymers by ^1H NMR and MALDI-TOF MS confirmed that 1-hexene and ethylene chain transfer agents generated olefin-terminated vinyl addition polymers. The olefinic end group contribution to optical density can be eliminated by appropriate chemical modification. Both epoxidation and hydrogenation of the polymer olefinic end groups generated very low optical density materials, independent of molecular weight, that are suitable as 193-nm photoresist binder resins.



End group modification of vinyl and hexenyl-terminated homopolymers of **1** by epoxidation or hydrogenation.

The Effect of End Group Modification on the Transparency of Vinyl Addition Norbornene Polymers at 193 nm^a

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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mcp-journal.de>, or from the author.

Introduction

Photolithography is used in the semiconductor industry to transfer circuitry information inscribed on masks onto silicon substrates. To accomplish this task, a liquid photo-sensitive formulation (or photoresist) is spin coated from an organic solvent onto a silicon wafer and dried to form a

photosensitive film. The film is then exposed to light passing through the mask. In areas of the film that are exposed, a photoinduced chemical reaction occurs that changes the solubility of the exposed areas. The film is then developed using a solvent (typically aqueous base developer) to give a three-dimensional relief image of the mask in the photoresist film. Next, the image is transferred to the underlying substrate via plasma etching to which the remaining photoresist film is resistant.^[1]

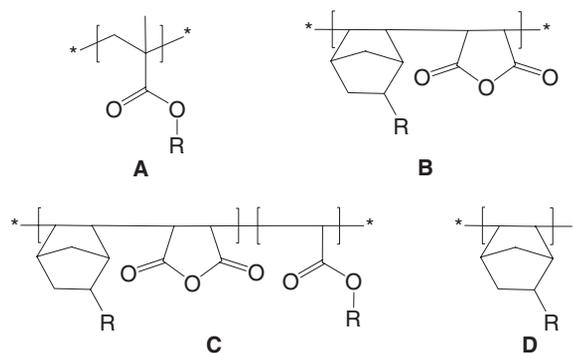
The major component in photoresist formulations (besides organic solvent) is the binder resin. For modern positive tone, chemically amplified photoresists, the binder resin typically contains an acid-labile group that deprotects thermally in the presence of a catalytic amount of acid. The acid is produced as a result of the photolytic decomposition of the photoacid generator (or PAG) which is added to the photoresist formulation. This deprotection provides the “solubility switch” that is necessary for development. The deprotected polymer is soluble in aqueous base whereas the protected polymer is not.^[2]

An important characteristic of photoresist films that impacts lithographic performance is dissolution behavior in developer. This characteristic is profoundly affected by molecular weight and molecular weight distribution of the binder resin.^[3] For example, high-molecular-weight poly(*p*-hydroxystyrene) (PHS) dissolves slower in aqueous base than its low-molecular-weight counterparts. Therefore, control of molecular weight and molecular weight distribution of binder resins is critical.

Another important characteristic of the photoresist film that affects lithographic performance is transparency at the imaging wavelength. Achieving sufficient transparency has required development of new binder resins as imaging radiation has migrated to lower wavelengths in the quest for smaller and smaller features. For example, the shift from i-line and g-line radiation (i.e., ≥ 365 nm) to 248-nm radiation necessitated a change from novolac to derivatives of PHS due to novolac's opacity at 248 nm.

In the recent shift from 248 to 193 nm imaging radiation, the semiconductor industry has auditioned several new polymeric materials as binder resins based on their transparency at 193 nm: methacrylates (A), norbornene/maleic anhydride copolymers (B, COMA-type polymers), norbornene/maleic anhydride/acrylate polymers (C, hybrid polymers), and vinyl addition norbornene polymers (D). Unique among these polymers, vinyl addition norbornene polymers hold the promise of both transparency and excellent etch resistance.^[4] See Scheme 1.

Janiak and Lassahn have reviewed the literature on metal catalysts for the vinyl addition polymerization of norbornene up to 2001.^[5] Vinyl addition norbornene polymers can be synthesized using late transition metal catalysts. Numerous palladium compounds have found utility in catalyzing this reaction. Using these late transition metal catalysts, norbornene monomers possessing pendant functionalities

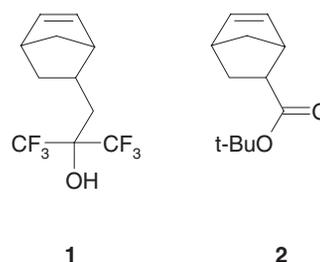


Scheme 1. Some polymeric materials which are transparent at 193 nm: methacrylates (A), norbornene/maleic anhydride copolymers (B, COMA-type polymers), norbornene/maleic anhydride/acrylate polymers (C, hybrid polymers), and vinyl addition norbornene polymers (D).

such as acid-labile groups, hydrophilic groups, base soluble groups, etc. can be polymerized. Many of these functionalities can be used to tailor the properties of photoresist binder resins. Inclusion of these functionalities in vinyl addition norbornene polymers is possible due to the wide functional tolerance of these late transition metal catalysts.^[6]

Recently, several publications have appeared that discuss the incorporation of the bis-trifluorocarbonyl substituted norbornene **1** (α,α -bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-ethanol or HFANB) into photoresist binder resins.^[7,8] This can be achieved by free radical or metal-catalyzed routes. Monomer **1** is of interest since it imparts aqueous base solubility to polymers and the preponderance of carbon-fluorine bonds increases the optical transparency of the polymers especially at short wavelengths. In particular, vinyl addition copolymers of **1** and *t*-butyl ester of 5-norbornene carboxylic acid (**2**, *t*-BuEsNB) were found to have utility as binder resins in 157-nm photoresist formulations.^[8] Terpolymers containing **1** were capable of printing sub 100-nm features at 193 nm.^[9]

In this contribution, we explore the homopolymerization of **1** and the copolymerization of **1** and **2** using palladium catalysts (see Scheme 2). Control of molecular weight of such polymers using olefinic chain transfer agents^[10] and



Scheme 2. Structures of α,α -bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-ethanol (**1**) and *t*-butyl ester of 5-carboxylic acid (**2**).

the impact of end groups on optical density (OD) of such polymers at 193 nm are also presented.^[11]

Experimental Part

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.

HFANB (**1**) and *t*-BuEsNB (**2**) were obtained from Promerus LLC, *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate (DANFABA) and lithium tetrakis(pentafluorophenyl)borate diethyletherate (LiFABA) from Boulder Scientific, and ethylene and 1-hexene (97%) from Aldrich. Palladium(II) acetate, [(tricyclohexylphosphine)(1,5-cyclooctadiene)(pyridine)iridium]PF₆ and all phosphines were purchased from Strem and used as received.

Instrumental Analysis

The ¹H and ³¹P NMR spectra were recorded on a Bruker AV-500 NMR spectrometer operating at 500.13 and 202.47 MHz, respectively. The ¹³C NMR spectra were obtained on a Bruker AV-200 NMR spectrometer operating at 50.13 MHz at 70 °C using inverse gated proton decoupling, with a 4-s delay between the pulses. These ¹³C samples were prepared in 10 mm NMR tubes in DMSO-*d*₆ (~4 mL) with ~50 mg Cr(acetylacetonate)₃ as a relaxation agent. Chemical shifts for ¹H and ¹³C NMR spectra were referenced using either internal solvent resonances or hexamethyldisiloxane and are reported relative to tetramethylsilane or were referenced to internal tetramethylsilane. The ³¹P NMR spectra were referenced to external 85% H₃PO₄.

Thermogravimetric analysis (TGA) was carried out on copolymer samples of **1** and **2** to determine copolymer composition using a TA instruments model 2950HR (high resolution) thermogravimetric analyzer. The instrument was operated using TA Thermal Advantage Software. Data were analyzed using TA Universal Analysis 2000 software. Samples were heated from room temperature to 550 °C under N₂ at a ramp rate of 10 °C · min⁻¹.

Polymer molecular weights were determined by GPC according to the following procedure. Approximately 50–60 mg of polymer was dissolved in 20 mL of tetrahydrofuran containing 250 mg BHT. The samples were gently shaken to dissolve. The solution was filtered through a 0.2-micron Teflon[®] disposable syringe filter and then injected into the chromatograph. The chromatographic conditions were mobile phase, THF stabilized with 250-ppm BHT; pump, Waters 515 pump at 1.0 mL · min⁻¹; autosampler, Micromeritics Model 708; sample, ~0.25% concentration, 100-μL injection volume; column, 2 Phenomenex Linear (2) columns, plus 1 Phenomenex 50A column, 5 micron, in series; column oven, Waters, 40 °C; Detector, Waters 2410 Refractive Index at 40 °C. The data for analysis were acquired using Waters' Millennium LC/GPC network software, version 3.2. Calibration was obtained using EasiCal polystyrene standards from Polymer Laboratories. The calibration range was 7.5 × 10⁶–162 Da.

Negative ion MALDI-TOF mass spectra were recorded using a Bruker Reflex III instrument in both linear and reflection modes. (The reflection mode gives better mass resolution, which results in better mass measurement accuracy. The linear mode shows less ion fragmentation.) Sinapic acid matrix was prepared as a saturated solution in 1:1 acetonitrile/water. The polymer samples were dissolved in THF (0.1 g · mL⁻¹). Equal volumes of the matrix and sample solutions were mixed prior to syringe deposition on a stainless steel MALDI plate.

Infrared analysis was conducted on a Nicolet Magna 560 FT-IR. Samples were prepared by dissolving the isolated polymer in THF (10 wt.-%). The polymer solution was cast on a zinc selenide crystal forming a polymer film after drying. The sample chamber is purged for 5 min with dry N₂, and 25 scans are collected and averaged at a resolution of 4 cm⁻¹.

Elemental analyses were performed by Robertson MicroLIT Laboratories, Inc., Madison, NJ.

Optical Density Determination

The optical density (OD) of the polymers was determined by the following method. A 15 wt.-% solution of the desired polymer was prepared using propylene glycol methyl-ether acetate (PGMEA). The solution was dispensed onto a 1-inch quartz wafer and spun at 500 rpm for 10 s and 2 000 rpm for 60 s. The wafers were then baked for 60 s at 130 °C on a hotplate.

The optical absorbance was measured at 193 nm using a Cary 400 Scan UV-Vis spectrophotometer using a blank quartz wafer in the reference beam. The thickness of the films was then measured using a TENCOR profilometer after the films were scored. OD of the film was calculated by dividing the absorbance by the thickness (in microns).

Synthesis of *Trans*-Pd(OAc)₂(P(*i*-Pr)₃)₂ (**3**)

Palladium(II) acetate (0.20 g, 0.89 mmol) was dissolved in methylene chloride (3 mL) and cooled to -35 °C. A solution of tri-*i*-propylphosphine (0.29 g, 1.8 mmol) in cyclohexane (7 mL) was cooled to -35 °C and slowly added to the palladium solution. The palladium solution changed from red to yellow-orange. The resulting mixture was concentrated and placed in a freezer at -35 °C. Yellow crystals formed which were isolated and dried in vacuo. Yield 0.35 g (72%).

Elemental analysis for C₂₂H₄₈O₄P₂Pd (545.0): Calcd C 48.49, H 8.88; Found C 48.07, H 8.63.

¹H NMR (C₆D₆): δ = 2.08 (br septet, 6H), 2.00 (s, 6H), 1.32 (m, 36H).

³¹P NMR (C₆D₆): δ = 32.8 (s).

Synthesis of Pd(OAc)₂(PCy₃)₂ (**4**)

Palladium(II) acetate (0.20 g, 0.89 mmol) and tricyclohexylphosphine (0.50 g, 1.8 mmol) were added together as solids and then dissolved in methylene chloride (3 mL). A yellow solution resulted from which a yellow solid precipitated. The solution was stored in a freezer at -35 °C overnight. The yellow solid was collected by filtration and washed with cyclohexane (3 × 10 mL) and dried in vacuo. Yield 0.5 g (72%).

Elemental analysis for $C_{40}H_{72}O_4P_2Pd$ (785.4): Calcd C 61.17, H 9.24; Found C 61.14, H 8.66.

1H NMR (C_6D_6): $\delta = 2.20$ (br d, 14H), 2.13 (s, 6H), 2.00 (br s, 8H), 1.81 (br s, 26H), 1.62 (s, 8H), 1.23 (s, 10H).

^{31}P NMR (C_6D_6): $\delta = 22.9$ (s).

Synthesis of $Pd(OAc)_2(PPh(i-Pr))_2$ (**5**)

Palladium(II) acetate (1.00 g, 4.46 mmol) was dissolved in methylene chloride (35 mL) and di-*i*-propylphenylphosphine (1.73 g, 8.90 mmol) was dissolved in methylene chloride: pentane 50:50 (10 mL). The two solutions were chilled to $-35^\circ C$ and combined with mixing. The resulting red solution was filtered and layered with pentane. After 18 h, yellow crystals formed which are isolated, washed with pentane, and dried under vacuum. Yield 1.20 g (44%).

Elemental analysis for $C_{28}H_{44}O_4P_2Pd$ (613.0): Calcd C 54.86, H 7.23; Found C 54.96, H 7.66.

1H NMR (CD_2Cl_2): $\delta = 7.73$ (m, 4H), 7.40 (m, 6H), 2.38 (m, 4H), 1.38 (d of d, 12H), 1.33 (s, 6H), 1.18 (d of d, 12H).

^{31}P NMR (CD_2Cl_2): $\delta = 29.5$ (s).

Synthesis of $Pd(OAc)_2(PPh_2(i-Pr))_2$ (**6**)

Palladium(II) acetate (1.00 g, 4.46 mmol) was dissolved in methylene chloride (35 mL) and *i*-propyldiphenylphosphine (2.03 g, 8.92 mmol) was dissolved in a 50:50 mixture of methylene chloride and pentane (20 mL). Both solutions were cooled to $-35^\circ C$. The phosphine solution was added to the palladium solution. The mixture was stirred for 3 h at $-35^\circ C$. An orange solution developed with a yellow precipitate. The solvents were decanted and the remaining solid was washed with pentane and dried under vacuum to afford an amorphous yellow solid. Yield 3.04 g (100%).

Elemental analysis for $C_{34}H_{40}O_4P_2Pd$ (681.1): Calcd C 59.96, H 5.92; Found C 58.84, H 5.89.

1H NMR (CD_2Cl_2): $\delta = 7.71$ (m, 8H), 7.45 (m, 12H), 2.75 (m, 2H), 1.36 (s, 6H), 1.13 (d of t, 12H).

^{31}P NMR (CD_2Cl_2): $\delta = 26.9$ (s).

Polymerization of **1** in the Presence of 1-Hexene

Method A

In a typical polymerization, nitrogen sparged **1** (12.0 g, 43.8 mmol) and 1-hexene (0.92 g, 10.9 mmol, 20 mol-% based on the moles of monomer) were combined in a glass vial. A stock solution of $Pd(OAc)_2(PCy_3)_2$ (**4**) (0.0069 g, 0.0088 mmol) and DANFABA (0.035 g, 0.044 mmol) in 10 mL of anisole was made. A 1 mL portion of this solution was added to the monomer/1-hexene solution. Anisole was added to this solution to bring the total volume up to 18 mL. The mixture was heated at $120^\circ C$ for 91 h. After cooling the polymer was precipitated by dropwise addition of the reaction mixture into hexane. The precipitated polymer was isolated by filtration and dried at $90^\circ C$ in a vacuum oven. Yield 10.1 g (84%).

1H NMR ($CDCl_3/DMSO-d_6$): $\delta = 0.5-2.6$ (br m, aliphatic hydrogens, 11H), 6.2-7.1 (br s, OH, 1H), 4.9 (br s, terminal

hexenyl end group hydrogens), 5.4 (br s, internal hexenyl end group hydrogens), 5.6 (br s, terminal hexenyl end group hydrogens).

GPC: $\bar{M}_w = 39\,600$; $\bar{M}_n = 8\,590$.

Method B

In a typical polymerization, nitrogen sparged **1** (26.2 g, 95.6 mmol), 1-hexene (12.1 g, 0.143 mol, 60 mol-% based on the moles of monomer), DANFABA (0.015 g, 0.019 mg), and toluene (26.8 mL) were combined in a glass vial. The mixture was heated to $80^\circ C$. Complex $Pd(OAc)_2(PCy_3)_2$ (**4**) (0.0050 g, 0.0038 mmol) was added as a solution (0.3 mL) in 1,2-dichloroethane. The mixture was stirred for 3 h. After cooling the polymer was precipitated by dropwise addition of the reaction mixture into hexane. The precipitated polymer was isolated by filtration and dried at $90^\circ C$ in a vacuum oven. Yield 17.4 g (66%).

GPC: $\bar{M}_w = 18\,300$; $\bar{M}_n = 9\,140$.

Polymerization of **1** in the Presence of Ethylene

In a typical polymerization, nitrogen sparged **1** (80.0 g, 0.292 mol) and toluene (117 mL) were added to a glass, pressure reactor equipped with a stir bar. The mixture was sparged with ethylene for about 15 min. Then an overpressure of ethylene (14 psig) was applied to the reactor while heating the mixture to $80^\circ C$. After the reactor reached the desired temperature, the ethylene pressure was released and a methylene chloride solution (3 mL) of DANFABA (0.047 g, 0.059 mmol) was added followed by a methylene chloride solution (3 mL) of $Pd(OAc)_2(PPh(i-Pr))_2$ (**5**) (0.0072 g, 0.012 mmol). Ethylene pressure was reapplied and the mixture held at $80^\circ C$ for 18 h. After cooling to room temperature, the ethylene was vented and the mixture was added dropwise to 1 L of rapidly stirring heptane. The solvent was decanted from the precipitated polymer. The polymer was washed with additional heptane. The polymer was then filtered and dried at $70^\circ C$ under vacuum. Yield 42.2 g (53%).

1H NMR ($CDCl_3$): $\delta = 0.5-2.6$ (br m, aliphatic hydrogens, 11H), 2.6-3.3 (br s, OH, 1H), 5.00 (br s, vinyl end group hydrogens), 5.86 (br s, vinyl end group hydrogen).

GPC: $\bar{M}_w = 5\,100$; $\bar{M}_n = 3\,020$.

MALDI-TOF MS Analysis of Vinyl-Terminated Homopolymer of **1**

A homopolymer of **1** synthesized using ethylene as a chain transfer agent ($\bar{M}_w = 4\,710$ and $\bar{M}_n = 3\,260$) was analyzed by MALDI-TOF MS. A series of (M-H)⁻ ions was observed that are consistent with the presence of vinyl-terminated polymer.

MS: $m/z = 1\,671, 1\,945, 2\,219, 2\,493, 2\,767, 3\,021, 3\,315, 3\,589, 3\,863, 4\,137$, etc.

MALDI-TOF MS Analysis of Hexenyl-Terminated Homopolymer of **1**

A homopolymer of **1** synthesized using 1-hexene as a chain transfer agent ($\bar{M}_w = 18\,200$ and $\bar{M}_n = 9\,140$) was analyzed by

MALDI-TOF MS. A series of $(M-H)^-$ ions was observed that are consistent with the presence of vinyl-terminated polymer.

MS: $m/z = 1\,727, 2\,001, 2\,275, 2\,549, 2\,823, 3\,097, 3\,371, 3\,645, 3\,919, 4\,193$, etc.

Copolymerization of **1** and **2** in the Presence of 1-Hexene

Nitrogen sparged **1** (7.68 g, 28.0 mmol), **2** (2.33 g, 12.0 mmol), and 1-hexene (0.84 g, 10 mmol, 20 mol-% based on the moles of monomer) were combined in a glass vial. To this solution was added 8 mL of anisole. Stock solutions of $Pd(OAc)_2 \cdot (PCy_3)_2$ (**4**) (0.031 g, 0.040 mmol) and LiFABA (0.17 g, 0.20 mmol) each in 5.0 mL of anisole were prepared. A 1 mL aliquot of each solution was added to the monomer/1-hexene solution. This mixture was heated to 95 °C for 23 h. The polymer was precipitated by dropwise addition of the reaction mixture to hexane. The precipitated polymer was isolated by filtration and dried at 70 °C in a vacuum oven. Yield 6.1 g (61%).

1H NMR ($CDCl_3$): $\delta = 0.7-3.3$ (br m, aliphatic and hydroxyl hydrogens), 1.4 (br s, *t*-Bu hydrogens), 4.9 (br s, terminal hexenyl end group hydrogens), 5.4 (br s, internal hexenyl end group hydrogens), 5.6 (br s, terminal hexenyl end group hydrogens).

^{13}C (DMSO- d_6 , 70 °C): $\delta = 25-60$ (br m, aliphatic carbons), 76.2 (br s, $-CH_2C(CF_3)_2OH$), 79.3 (br s, $-CO_2C(CH_3)_3$), 123.9 (br q, $J_{CF} = 1\,150$ Hz, $-CH_2C(CF_3)_2OH$), 173.2 and 174.4 (br s, *endo/exo* $-CO_2C(CH_3)_3$).

GPC: $\bar{M}_w = 37\,200$; $\bar{M}_n = 13\,200$.

IR (ZnSe): 3 405 (br, m, OH), 3 228 (br, m, OH), 1 722 (s, CO) cm^{-1} .

TGA showed 10.9% weight loss at about 280 °C due to loss of *i*-butylene from the deprotection of the *t*-butyl carboxylate pendant group on comonomer **2**. This is in agreement with a copolymer containing a molar ratio of 54/46 for monomers **1** and **2**.

Hydrogenation of Vinyl-Terminated Homopolymer **1**

A vinyl-terminated homopolymer of HFANB (**1**) (1.50 g, $\bar{M}_w = 4\,930$, $\bar{M}_n = 2\,490$), [(tricyclohexylphosphine)(1,5-cyclooctadiene)(pyridine)iridium]PF₆ (21 mg, 0.026 mmol), and toluene (35 mL) were combined in a pressure reactor and stirred until dissolved. The reactor was sealed, charged with H₂ gas (85 psig), and heated to 65 °C for 15 h. The reactor contents were cooled and then filtered, and the solvent was evaporated under reduced pressure. The resulting yellow material was dissolved in acetone (25 mL) along with H₂O₂ (ca. 0.25 mL, 30% w/w). The solution was heated to 56 °C for 30 min and filtered to remove solids. Smopex[®] 110 (Johnson Matthey) (10 mg) was added and the solution was stirred for 30 min. After filtering through a 0.20 μm PTFE filter disk, the acetone was evaporated under reduced pressure to afford a colorless white solid. The material was dissolved in toluene (30 mL), washed with H₂O (3 \times 20 mL), and precipitated by dropwise addition to heptane (150 mL). The product was isolated by filtration and dried in vacuo (70 °C, 12 h) to afford a white amorphous solid. Yield 1.1 g (73%).

1H NMR ($CDCl_3$): $\delta = 0.5-2.6$ (br m, aliphatic hydrogens, 11H), 2.6-3.3 (br s, OH, 1H).

No peaks are observed between 4.9 and 6.1 ppm consistent with hydrogenation of the vinyl end group.

GPC: $\bar{M}_w = 6\,390$; $\bar{M}_n = 4\,110$.

The homopolymer was analyzed by MALDI-TOF MS. A series of $(M-H)^-$ ions was observed that are consistent with the presence of ethyl-terminated polymer.

MS: $m/z = 1\,125, 1\,399, 1\,673, 1\,947, 2\,221, 2\,495, 2\,769, 3\,043, 3\,317, 3\,591$, etc.

Peroxyacetic Acid Treatment of Vinyl-Terminated Homopolymer **1**

Approximately 180 g of vinyl-terminated homopolymer of HFANB ($\bar{M}_w = 4\,710$, $\bar{M}_n = 3\,260$) was dissolved in 937 mL of toluene at 80 °C. To this solution was added 343 mL of glacial acetic acid, 340 mL of 30% hydrogen peroxide, and 180 mL of deionized water. This mixture was heated at 80 °C for 3.5 h. The aqueous and organic layers were permitted to separate and then the aqueous layer was removed. The organic layer was washed three times with a mixture of 500 mL of water and 175 mL of acetone. The organic phase was concentrated to about 900 mL and then poured into heptane (9 L). The resulting polymer was filtered and dried in a vacuum oven at 70 °C overnight. Yield 166.2 g (92%).

1H NMR analysis of the polymer shows that the intensity of the vinyl resonances is substantially reduced. Addition of D₂O to the NMR sample resulted in a shift of the hydroxyl peak of the polymer ($\delta = 2.6-3.3$) downfield to 4.7 ppm, revealing a small resonance at 2.95 ppm assigned to one of the epoxy end group hydrogens. The MALDI-TOF MS of the polymer, $(M-H)^-$, is consistent with formation of epoxy-terminated homopolymer **1**.

MS: $m/z = 1\,687, 1\,961, 2\,235, 2\,509, 2\,783, 3\,057, 3\,331, 3\,605$, etc.

Peroxyacetic Acid Treatment of Hexenyl-Terminated Homopolymer **1**

Approximately 94 g of a hexenyl-terminated HFANB homopolymer ($\bar{M}_w = 28\,300$; $\bar{M}_n = 11\,300$) was dissolved in 310 g of toluene. To this solution about 250 mL of glacial acetic acid and 125 mL of 15% hydrogen peroxide were added. This mixture was heated to 90 °C for 1.5 h and then cooled to room temperature. The top organic phase was separated from the aqueous phase and washed with deionized water to remove any residual acid. The polymer was precipitated from the organic layer by dropwise addition to heptane. The precipitated polymer was isolated by filtration and dried at 65 °C under vacuum. Yield 75.7 g (81%). The 1H NMR ($CDCl_3/DMSO-d_6$) spectrum of the polymer exhibited no resonances between 6.1 and 4.9 ppm consistent with the absence of olefinic groups. The MALDI-TOF MS of the polymer, $(M-H)^-$, is consistent with formation of the epoxy-terminated homopolymer **1**.

MS: $m/z = 2\,017, 2\,291, 2\,565, 2\,839, 3\,113, 3\,387, 3\,661, 3\,935$, etc.

Peroxyacetic Acid Treatment of a Hexenyl-Terminated Copolymer of **1** and **2**

Approximately 20 g of a hexenyl-terminated copolymer of **1** and **2** ($\bar{M}_w = 29\,400$; $\bar{M}_n = 14\,270$) was dissolved in toluene

(140 g). To this solution was added glacial acetic acid (50 g) and hydrogen peroxide (25 g, 30%) diluted in water (25 g). The two-phase mixture was stirred and heated to 85 °C for one hour. The mixture was cooled, the organic layer was separated, and washed three times with water. The organic layer was poured dropwise into heptane to precipitate the polymer. The polymer was isolated by filtration and dried under vacuum. Yield 15 g (75%). GPC: $\bar{M}_w = 30\,200$; $\bar{M}_n = 15\,100$. ^{13}C NMR analysis in DMSO- d_6 showed that the copolymer consisted of 62 mol-% **1** and 38 mol-% **2**. There was no evidence of deprotection of the acid-labile monomer.

Prior to peroxyacetic acid treatment, the OD of the polymer at 193 nm was 0.27 absorption units per micron. After peroxyacetic acid treatment, the OD at 193 nm was 0.12 absorption units per micron.

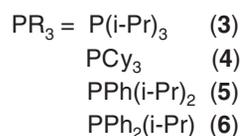
Results

Synthesis and Characterization of $\text{Pd}(\text{OAc})_2(\text{PR}_3)_2$ Complexes

The catalyst precursors used in this study were all based on $\text{Pd}(\text{OAc})_2$ complexed with sterically demanding phosphine ligands. We chose to concentrate on bulky phosphines since these types of ligands, at least with (allyl)palladium derivatives, have been shown to yield the most active complexes for norbornene polymerization.^[12a]

The synthesis of bis(phosphine) complexes of palladium diacetate is rather straightforward. Addition of 2 equiv. of phosphine to palladium diacetate results in formation of the yellow $\text{Pd}(\text{OAc})_2(\text{PR}_3)_2$ product, Equation (1) (Scheme 3). The complexes were isolated in moderate to good yield. They gave satisfactory elemental analyses and were fully characterized by ^1H and ^{31}P NMR spectroscopic methods. See the Experimental Part for details.

Crystals of complex **3** were grown for single crystal X-ray diffraction analysis. Details of this analysis including an ORTEP view of **3** can be found in the *Supporting Information*. Complex **3** exhibits a *trans* coordination of phosphines ligated to a square planar palladium. The solid-state structure of complexes **4**, **5**, and **6** have not been investigated; however, they are almost certainly square planar species with a *trans* disposition of the relatively bulky phosphine ligands.



Scheme 3. Synthesis of bis(phosphine) complexes of palladium diacetate.

Polymerization of **1** and Copolymerization of **1** and **2** using $\text{Pd}(\text{OAc})_2(\text{PR}_3)_2$ Complexes

A series of homopolymerizations of **1** was carried out using several different phosphine adducts of $\text{Pd}(\text{OAc})_2$. DANFABA was employed as a catalyst activator and 1-hexene or ethylene as chain transfer agents.

Two methods were used for homopolymerization of **1** in the presence of 1-hexene. Method A employed a high concentration of monomer (2.5 M) in anisole at 120 °C for 91 h. Method B employed a lower concentration of monomer (1.5 M) in toluene at lower temperature (80 °C) and shorter polymerization times (3 h). Both methods used $\text{Pd}(\text{OAc})_2(\text{PCy}_3)_2$ (**4**) as the catalyst precursor, DANFABA as the cocatalyst, and 1-hexene as the chain transfer agent. Polymerization results are presented in Table 1.

For polymerization method A, the isolated yields were good (~70–85%) and were in general higher than those obtained using polymerization method B (~50–70%). This is to be expected considering that method A used a higher concentration of monomer, the polymerization was carried out at higher temperatures and for longer times than method B. In both cases, increasing concentrations of 1-hexene (10–60 mol-% of the monomer) reduced the molecular weight of the HFANB homopolymer. The number-average molecular weights ranged from ~8 600 to 3 500 for polymer made using method A. Method B gave on average higher \bar{M}_n s. In general, method A gave broader polydispersity indices. In order to reach low molecular weight, a considerable amount of 1-hexene was required. At these higher concentrations of 1-hexene, the volume of monomer and 1-hexene in the reaction mixture was actually greater than the volume of solvent used. Thus, a potentially more effective chain transfer agent was explored: ethylene.

HFANB homopolymerization results using ethylene as a chain transfer agent and three different complexes,

Table 1. Polymerization of **1** in the presence of 1-hexene.

Experiment	Complex	Hexene ^{a)}	Yield			\bar{M}_w/\bar{M}_n
			Yield	\bar{M}_w	\bar{M}_n	
%						
Method A						
1	4	20	84	39 600	8 590	4.61
2	4	30	85	23 900	5 930	4.03
3	4	40	86	16 300	4 600	3.54
4	4	50	83	11 700	3 840	3.04
5	4	55	80	9 430	3 450	2.73
6	4	60	70	8 550	3 770	2.27
Method B						
7	4	10	53	128 000	53 600	2.39
8	4	30	72	47 900	17 300	2.77
9	4	45	58	20 100	10 400	1.93
10	4	60	66	18 300	9 140	2.00

^{a)} 1-Hexene concentration reported in mol-% based on monomer.

Table 2. Polymerization of **1** in the presence of ethylene.

Experiment	Complex	Ethylene	Yield	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
		psig	%			
11	6	0	42	384 000	155 000	2.48
12	6	2	54	65 900	25 600	2.57
13	6	6	64	22 100	9 120	2.42
14 ^{a)}	6	8	56	15 300	7 020	2.18
15 ^{b)}	6	9	57	14 700	6 040	2.43
16 ^{a)}	6	14	57	10 100	4 480	2.25
17	5	14	53	5 100	3 020	1.69
18	5	17	43	4 050	2 570	1.58
19	4	14	53	8 640	4 540	1.90

^{a)} Average of two runs.

^{b)} Average of three runs.

4, **5**, and **6**, in the presence of DANFABA are presented in Table 2. These experiments were carried out at 80 °C for 18 h in toluene. The isolated yields from each polymerization experiment ranged from about 40 to 65%. For complex **6**, the number-average molecular weight of the polymer made in the absence of ethylene was 155 000 (see experiment 11). As the ethylene pressure was increased, the isolated polymer exhibited lower molecular weight. The minimum number-average molecular weight observed was 4 480 when 14 psig ethylene pressure was employed (see experiment 16).

The nature of the phosphine does seem to have an effect on the molecular weight of the isolated polymer. For example, under identical conditions (14 psig ethylene), homopolymer of **1** made with complex **6** exhibited an \bar{M}_n of 4 480 while that made using complex **5** gave a significantly lower molecular weight ($\bar{M}_n = 3 020$, compare experiments 16 and 17). Complexes **4** and **6** give essentially the same homopolymer molecular weight; $\bar{M}_n = 4 540$ for homopolymer of **1** made with complex **4** (see experiment 19). A plot of the effect of ethylene pressure on \bar{M}_n is shown in Figure 1 for all three catalyst precursors.

The copolymerization of monomers **1** and **2** using Pd(OAc)₂(PCy₃)₂ (**4**) and LiFABA in the presence of

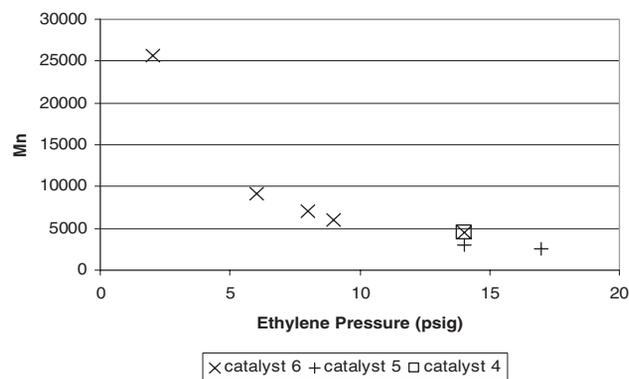


Figure 1. Effect of ethylene pressure on HFANB homopolymer \bar{M}_n as a function of complex used.

1-hexene as a chain transfer agent was investigated. The copolymerizations were carried out at 95 °C for 18 h in anisole at a 70:30 molar feed ratio of monomers **1** and **2**. Results of these copolymerizations are presented in Table 3. Five copolymerizations were carried out with an increasing concentration of 1-hexene. The isolated yields of these copolymers were very similar irrespective of the concentration of 1-hexene used. A significantly higher catalyst loading (5 000:1 monomer to palladium molar ratio) was used for the copolymerizations, as compared to the homopolymerizations of **1**. Analogous to the homopolymerization study, increasing the concentration of 1-hexene resulted in a lowering of the copolymer molecular weight. The composition of the isolated copolymers was determined using TGA (10 °C · min⁻¹). In each case, initial weight loss begins around 200 °C and continues until about 240 °C. No more weight loss occurs until decomposition of the polymer at about 420 °C. The initial weight loss is due to thermal deprotection of the *t*-butyl ester group of monomer **2**, and, therefore, is indicative of the concentration of monomer **2** in the copolymer. Using this technique, the copolymers in Table 3 were found to contain monomer **2** between 40 and 46 mol-%. ¹³C NMR spectrometry is in agreement with the results obtained using TGA. The mole ratio of monomers **1**

Table 3. Copolymerization of **1** and **2** in the presence of 1-hexene using complex **4**.

Experiment	Hexene ^{a)}	Yield	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	TGA composition ^{b)}	¹³ C NMR composition ^{c)}
		%					
20	20	61	37 200	13 200	2.81	10.9%, 54/46	–
21	30	60	28 600	11 700	2.44	10.5%, 55/43	–
22	40	60	18 900	8 500	2.21	10.5%, 55/43	–
23	50	59	14 400	7 000	2.06	10.3%, 56/44	–
24	60	68	11 200	5 000	2.23	9.2%, 60/40	61/39

^{a)} 1-Hexene concentration reported in mol-% based on monomer.

^{b)} wt.-% loss, molar ratio of **1/2**.

^{c)} Molar ratio of **1/2**.

and **2** determined by ^{13}C NMR spectrometry for the copolymer made in experiment 24 was 61:39 while a mole ratio of 60:40 for the same copolymer was determined by TGA.

End Group Analysis of Homopolymers of **1** and Copolymers of **1** and **2**

The end groups of both homopolymers of **1** and copolymers of **1** and **2** were investigated by ^1H NMR and by MALDI-TOF MS techniques. A representative ^1H NMR spectrum in CDCl_3 of a relatively low molecular weight homopolymer of **1** ($\bar{M}_n = 3260$) made using ethylene as a chain transfer agent is shown in Figure 2(a). The peaks in the 0.5–2.6 ppm region of the spectrum account for protons on the aliphatic carbons 1–8. The hydroxylic proton 9 is assigned to the broad chemical shift appearing between 2.6 and 3.3 ppm. This assignment is confirmed by addition of D_2O to the NMR tube (see *Supporting Information*) which results in a shift of the hydroxylic hydrogen resonance to ~ 4.8 ppm by H/D exchange. In Figure 2(a), two small, broad resonances are observed in the olefinic region of the spectrum at 5.00

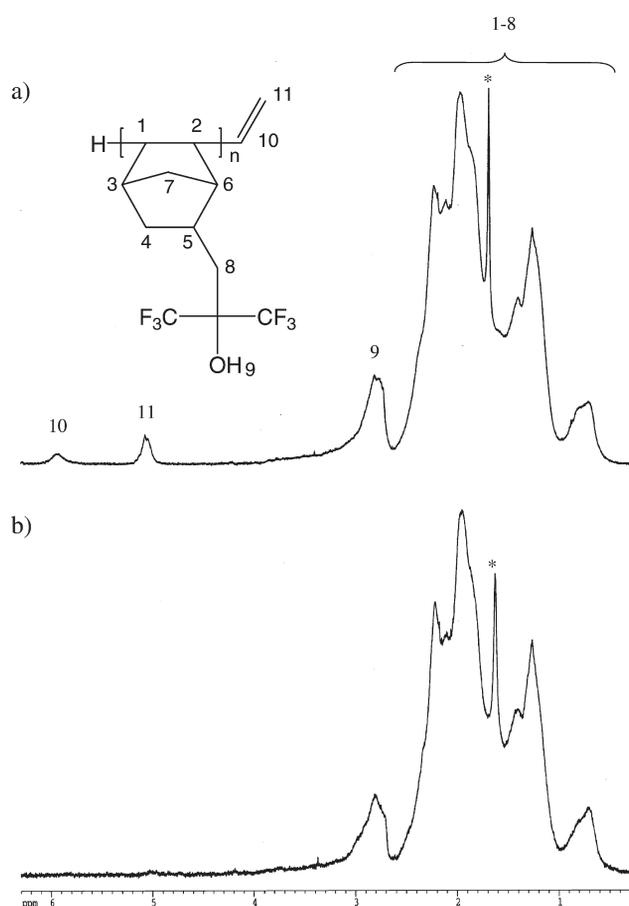


Figure 2. ^1H NMR spectrum of (a) vinyl-terminated homopolymer of **1** and (b) peroxyacetic acid-treated, vinyl-terminated homopolymer of **1**. (* = water).

and 5.86 ppm. These two resonances are assigned to the vinyl terminus (protons on carbons 10 and 11) of the polymer chain derived from chain transfer to ethylene.^[10a]

A MALDI-TOF MS (negative ion mode) trace of the same homopolymer of **1** is presented in Figure 3(a). Only one significant polymer series is observed and it is consistent with a vinyl and hydrogen-terminated poly(HFANB). Since in the negative ion mode loss of H^+ from the hydroxyl group occurs, an HFANB polymer chain with a degree of polymerization of 10 and a vinyl and hydrogen end group would exhibit a molecular ion of 2767 as is observed in the mass spectrum. A much less intense polymer series is observed [marked with * in Figure 3(a)] due to fragmentation loss of CF_3H (70 Da) from a pendant group.

Similar analysis of a homopolymer of **1** synthesized using 1-hexene as a chain transfer agent was consistent with the formation of hydrogen and hexenyl-terminated poly(HFANB). In the ^1H NMR spectrum, taken in $\text{CDCl}_3/\text{DMSO}-d_6$, the aliphatic protons are observed between 0.5 and 2.6 ppm while the hydroxylic proton is shifted down-field and appears as a broad peak between 6.2 and 7.1 ppm. In the olefinic region of the spectrum, a broad singlet is seen at about 5.4 ppm and two much smaller broad singlets are observed at about 5.6 and 4.9 ppm. The larger peak is consistent with a hexenyl end group containing an internal olefin. The two smaller resonances are consistent with a hexenyl end group containing a terminal olefin. The latter presumably arises from a palladium-catalyzed isomerization of the hexenyl end group from an internal to a terminal position.^[12a] The internal olefinic end group could be in the 2, 3, 4, or 5 position (see Scheme 4); ^1H NMR analysis cannot discern between these possibilities. Based on integration of the peaks due to internal versus terminal olefins, the percentage of chains containing a terminal olefinic hexenyl end group is small, only about 15–20%. In the MALDI-TOF MS trace of this homopolymer, the only significant polymer series is due to the hydrogen and hexenyl-terminated poly(HFANB). See *Supporting Information*.

In the ^1H NMR spectrum of copolymers of **1** and **2** in which 1-hexene was used as a chain transfer agent, a broad singlet was also observed at about 5.4 ppm due to a hexenyl end group with an internal olefin. Resonances consistent with small concentrations of copolymers containing hexenyl end groups with a terminal olefin are also observed.

Optical Density of Homopolymers of **1**

The OD of different molecular weight homopolymers of **1** made using both ethylene and 1-hexene (methods A and B) as chain transfer agents was measured at 193 nm. The results of these OD measurements (in absorbance units per micron) are graphed as a function of \bar{M}_n in Figure 4. An inverse relationship exists between OD and molecular weight for the homopolymer of **1**; as the molecular weight decreases, the OD increases. At approximately 8000 \bar{M}_n ,

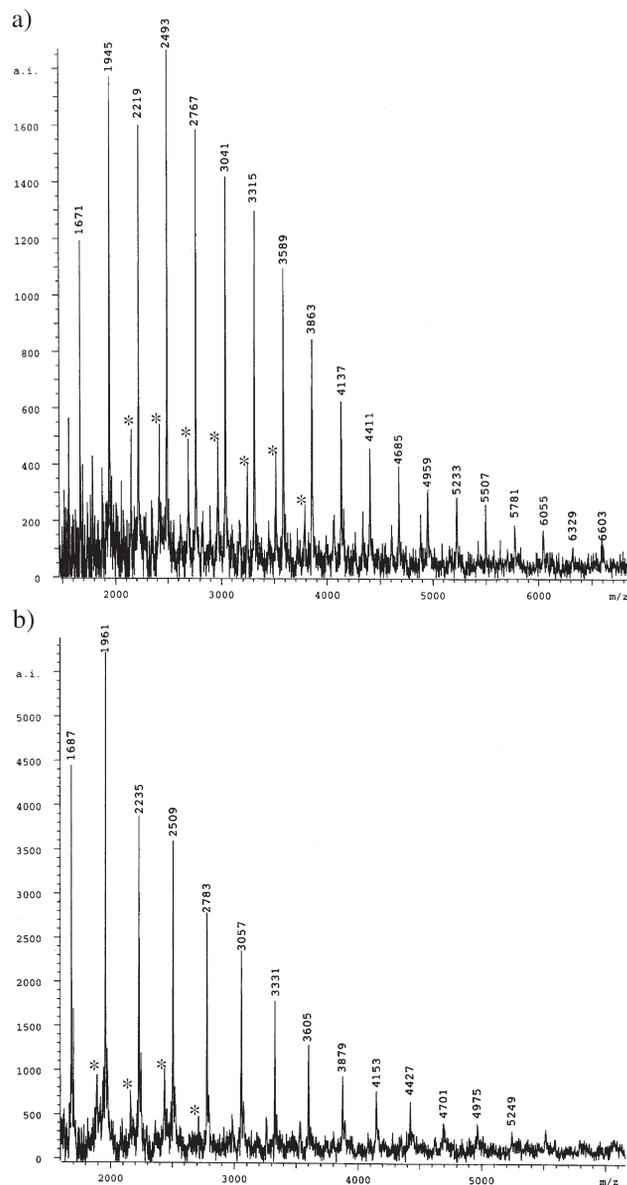


Figure 3. MALDI-TOF MS of vinyl-terminated homopolymer of **1** before (a) and after peroxyacetic acid treatment (b). (* = loss of CF_3H).

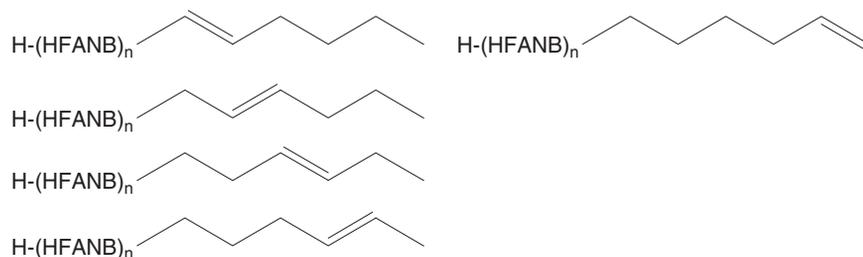
the OD is about 0.20 absorbance units per micron, while at lower molecular weight, about $3\,000 \bar{M}_n$, the OD increases to about 0.35 absorbance units per micron. At very high molecular weight ($\bar{M}_n = 53\,600$), the OD is extremely low, 0.07 absorbance units per micron.

End Group Modification of Vinyl and Hexenyl-Terminated Homopolymers of **1**

The behavior observed in Figure 4 is at odds with the desire to employ low-molecular-weight and low-OD vinyl addition norbornene polymers as binder resins made using olefin chain transfer agents. Extremely low OD is only attained at high molecular weight. Thus, a method of reducing the optical absorbance of such end groups that was independent of molecular weight was sought. One possible avenue of investigation would be to chemically transform the polymer end groups into less absorbing species.

The first method that we employed was hydrogenation [see Equation (2) in Scheme 5]. It was expected that the resulting saturated end groups would be substantially less absorbing than the starting olefinic end groups. To exemplify this strategy, a relatively low molecular weight homopolymer of **1** ($\bar{M}_n \sim 2\,500$) was treated with hydrogen in the presence of Crabtree's catalyst, [(tricyclohexylphosphine)(1,5-cyclooctadiene)(pyridine)iridium] PF_6 . The metallic residue was scavenged from the reaction mixture by using Smopex[®] 110 (a thionium chloride functional polyethylene resin). The homopolymer of **1** was isolated by precipitation and was found to exhibit a somewhat higher molecular weight ($\bar{M}_n \sim 4\,100$) than the starting polymer due to slight fractionation of the lower molecular weight species. Nevertheless, the complete absence of peaks at 5.00 and 5.86 ppm in the ^1H NMR spectrum of the resulting polymer proved that all of the olefinic end groups were hydrogenated [see Equation (2) in Scheme 5]. The hydrogenated polymer was further characterized by MALDI-TOF MS, negative ion mode (see *Supporting Information*). For a degree of polymerization 10, the ethyl-terminated polymer of **1** should exhibit an $(\text{M}-\text{H})^-$ of 2769 as was observed.

The OD of the hydrogenated polymer (~ 0.07 absorbance units per micron) was found to be much lower than a non-hydrogenated polymer of similar molecular weight



Scheme 4. Possible positions of double bonds in olefinic end groups.

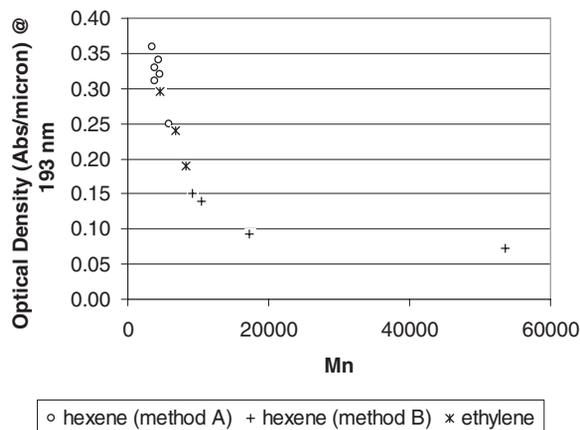
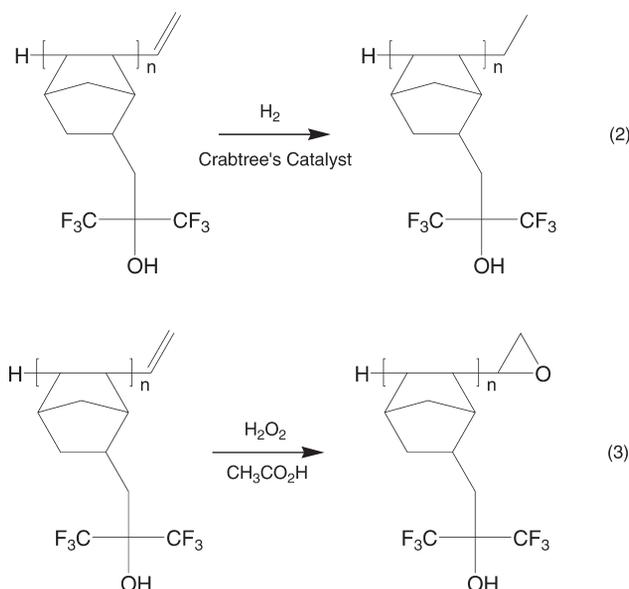


Figure 4. Effect of homopolymer **1** molecular weight, made using both 1-hexene and ethylene as chain transfer agents, on optical density at 193 nm.

(≥ 0.30 absorbance units per micron). The resulting OD is plotted in Figure 5 along with OD versus \bar{M}_n between $\sim 3\,500$ and $17\,000$ for olefin-terminated homopolymers of **1**.

Another method of end group modification that was explored to reduce the OD of olefin-terminated polymers was epoxidation using peroxyacetic acid [see Equation (3) in Scheme 5]. The method was particularly attractive since it did not require further addition of metal catalysts to the binder resin. Both vinyl and hexenyl-terminated homopolymer **1** were treated with mixtures of acetic acid and hydrogen peroxide at elevated temperatures. After workup,



Scheme 5. End group modification of vinyl and hexenyl-terminated homopolymers of **1** by hydrogenation (2) and epoxidation (3).

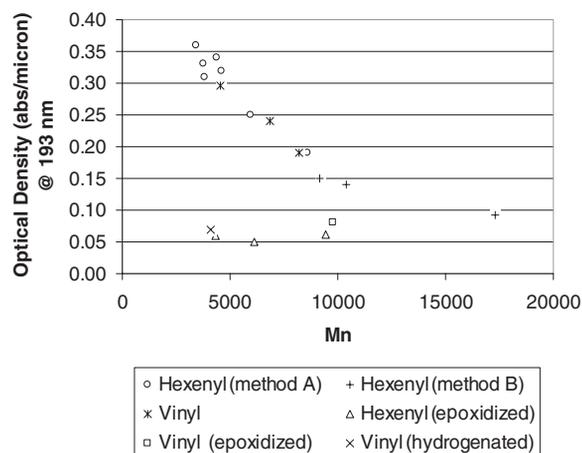


Figure 5. Effect of end group modification (epoxidation or hydrogenation) on optical density at 193 nm for both hexenyl and vinyl-terminated homopolymers of **1**.

the peroxyacetic acid-treated, vinyl-terminated polymer was analyzed by ^1H NMR. Essentially all the vinyl resonances were consumed [see Figure 2(b)]. Addition of D_2O to the NMR tube shifted the polymer hydroxylic protons down-field, revealing a broad resonance at about 2.95 ppm which is assigned to an epoxy end group hydrogen (see *Supporting Information*). In the case of the hexenyl-terminated polymer, no olefinic residues were observed by ^1H NMR spectrometry after peroxyacetic acid treatment (see *Supporting Information*). The mass spectrum (MALDI-TOF) of the peroxyacetic acid-treated, vinyl-terminated homopolymer is presented in Figure 3(b). It is consistent with the formation of an epoxy-terminated homopolymer. For a homopolymer of **1** with a degree of polymerization 10 and hydrogen and an epoxy end group as shown in Equation (3) (Scheme 5), the $(\text{M}-\text{H})^-$ would be 2783 as was observed in Figure 3(b). Similar results are obtained for the hexenyl-terminated homopolymer (see *Supporting Information*).

The optical densities at 193 nm of four such peroxyacetic acid-treated homopolymers of **1** (three hexenyl-terminated and one vinyl-terminated) with different molecular weights were determined. These results are plotted as function of \bar{M}_n in Figure 5. All four polymers, with \bar{M}_n s from about 4 000–10 000, exhibited ODs between 0.06 and 0.08 absorbance units per micron which were substantially lower than that observed for the untreated olefin-terminated homopolymers.

Similarly, a copolymer of **1** and **2** (62:38 molar ratio) made using 1-hexene as a chain transfer agent ($\bar{M}_n = 15\,100$) exhibited an OD of 0.12 absorbance units per micron at 193 nm after peroxyacetic acid treatment. Prior to treatment, the polymer was much more absorbing (OD = 0.27 absorbance units per micron, $\bar{M}_n = 14\,270$). There was no indication (^{13}C NMR) of significant deprotection of this copolymer after peroxyacetic acid treatment.

Discussion

Polymerization of ester-functional norbornene monomers using the palladium catalyst, $\text{Pd}(\text{MeCN})_4^{2+}$, was first reported by Risse.^[13] It was later found that solvated (η^3 -allyl)palladium cations [accessed by abstraction of chloride from (η^3 -allyl)palladium chloride dimer with silver hexafluoroantimonate] were substantially more effective catalysts for functional norbornene monomer polymerization.^[14] These catalysts were even capable of polymerizing hydroxyl and carboxylic acid functional norbornenes. Vinyl addition polymerization of **1** and copolymerization of **1** and **2** using solvated (η^3 -allyl)palladium cations has been reported by Willson et al.^[18b] However, molecular weight control using this system was difficult at best. In order to reach molecular weights (M_w) of less than 9 000, ≥ 5 mol-% catalyst needed to be employed; 1-hexene did not effectively reduce the molecular weight of the polymer using this catalyst system. Furthermore, this catalyst deprotected the *t*-butyl ester groups in the polymer apparently caused by in situ creation of strong acid during polymerization.

A comparison of the performance of the catalysts described herein with those published previously is enlightening. For the homopolymerizations of monomer **1** carried out using catalyst **4**, the molar ratio of monomer to palladium was substantially lower than that necessary for the solvent-stabilized cationic (η^3 -allyl)palladium catalysts: 25 000:1 (in the case of ethylene as a chain transfer agent) or 50 000:1 (in the case of 1-hexene as a chain transfer agent). Clearly, catalysts derived from $\text{Pd}(\text{OAc})_2(\text{PCy}_3)_2$ are extremely active for polymerization of **1**. On the other hand, higher catalyst loadings (5 000:1 monomer to Pd molar ratio) are necessary for copolymerization of **1** and **2**. Functional monomers such as, for example, ester norbornenes have been shown to impede the effectiveness of palladium polymerization catalysts.^[15] Presumably, coordination of the metal by the ester functionality is responsible for the need to use higher catalyst loadings in the copolymerization of **1** and **2**.

Unlike that reported for solvent-stabilized (η^3 -allyl)palladium cations,^[16] phosphine-stabilized cationic (η^3 -allyl)palladium norbornene polymerization catalysts respond quite well to 1-hexene as a chain transfer agent in norbornene copolymerization. It is therefore not surprising that molecular weight control for polymers of **1** or copolymers of **1** and **2** using the catalysts derived from $\text{Pd}(\text{OAc})_2(\text{PR}_3)_2$ is attainable by addition of 1-hexene to the reaction mixture. However, in both cases, substantial amounts of 1-hexene were required to access low-molecular-weight polymers. Our previous work suggested that 1-hexene may not perform very effectively as a chain transfer agent due to an isomerization side reaction converting 1-hexene to the less reactive 2-hexene and 3-hexene isomers.^[12a] Ethylene was investigated as a chain transfer agent since it cannot undergo deleterious isomerization side reactions

and it is readily separated from the reaction mixture. Ethylene was found to be very effective in reducing the molecular weight of homopolymers of **1**; M_n less than 5 000 were accessible when ethylene pressures of about 15 psig were used.

The nature of the phosphine does seem to have an effect on the molecular weight of the isolated polymer. The reason for the effect of ligand on molecular weight of the HFANB homopolymer, however, is not straightforward. If steric or electronic factors of the phosphine ligands alone were responsible for the observed molecular weight dependence, one would expect the molecular weight trend to follow the order of decreasing steric bulk [$\text{PCy}_3 > \text{PPh}(i\text{-Pr})_2 > \text{PPh}_2(i\text{-Pr})$] or decreasing electron-donating ability [$\text{PCy}_3 > \text{PPh}(i\text{-Pr})_2 > \text{PPh}_2(i\text{-Pr})$] of the phosphines. This is not the case since complex **4**, which contains the most electron donating and sterically demanding PCy_3 phosphine, yields HFANB homopolymer with essentially the same molecular weight as complex **6** which contains the least donating and least sterically demanding phosphine in the series.^[17]

Homopolymers of **1** and copolymers of **1** and **2** synthesized using catalysts derived from $\text{Pd}(\text{OAc})_2(\text{PR}_3)_2$ were found to contain hydrogen and olefinic end groups arising from ethylene (i.e., vinyl end groups) or 1-hexene (i.e., hexenyl end groups) chain transfer agents. Similar end groups were observed in polynorbornene made using phosphine-stabilized cationic (η^3 -allyl)palladium polymerization catalysts and 1-hexene.^[12a]

The ability to readily observe end groups in the polymers isolated in this study allows conclusions to be made about the polymerization initiation and termination (chain transfer) steps and ultimately about the active catalyst species. As reported previously,^[12a] the presence of hydrogen and olefinic end groups in the same polynorbornene chain strongly suggests that the active catalyst is a palladium hydride. As such, initiation would occur by insertion of norbornene into the Pd–H bond followed by propagation of the polymer chain. Only when insertion of the α -olefin takes place can β -hydrogen elimination occur forming the olefinic-terminated polynorbornene and regenerating the Pd–H catalyst species.^[12c] At this juncture, it is unclear how the purported Pd–H species is initially formed. Alternatively, in the presence of α -olefin chain transfer agents, there remains the possibility that phosphine-stabilized allylic palladium species are created which could initiate polymerization.^[18] In any event, once the first polymer chain is initiated, chain transfer to an α -olefin regenerates the Pd–H active species.

Optical density measurements show that as the molecular weight of the homopolymers of **1** decreases, the polymer becomes more opaque. This trend suggests that polymer end groups are influencing OD. As the molecular weight decreases, the relative concentration of polymer end groups grows. If the end groups absorb at 193 nm, then an increase

in OD would be expected. The presence of olefinic end groups in homopolymers and copolymers of monomer **1** has been established using both $^1\text{H NMR}$ and MALDI-TOF MS techniques. Ethylene exhibits a π to π^* transition at 165 nm. Substitution of ethylene results in a bathochromic shift of this absorbance. Tetra alkyl substituted alkenes exhibit a λ_{max} below 200 nm, but the band widths are sufficiently broad such that significant absorption can occur above 200 nm.^[19] Thus, it appears reasonable that an increased concentration of absorbing olefinic end groups is responsible for the increase in OD at lower molecular weights shown in Figure 4. At high molecular weight the end group concentrations are small and their contribution to absorbance should vanish. Indeed at $\bar{M}_n = 53\,600$ an OD of ~ 0.07 absorbance units per micron is observed, suggesting that the inherent absorption of homopolymer **1** is exceedingly small at 193 nm. End groups in other polymer systems have been found to play a role in photoresist sensitivity and transparency.^[20]

Modification of the olefinic end groups of the homopolymer of **1** or the copolymer of **1** and **2** by hydrogenation or epoxidation gave substantially lower OD films. Clearly, the resulting aliphatic and epoxy end groups are less absorbing at 193 nm than the unsaturated end groups. Aliphatics are relatively transparent at 193 nm and epoxides exhibit a λ_{max} at ~ 170 nm.^[18] In addition, the OD response of the peroxy-acetic acid-treated polymers is invariant to changes in molecular weight. Thus, by transformation of the olefin end group chromophores in homopolymers of monomer **1** or copolymers of **1** and **2** to less absorbing species, low-OD polynorbornenes can be accessed irrespective of their molecular weight. Therefore, end group modification has been demonstrated as a valid method for OD reduction for polynorbornene binder resins that could be used in positive tone photoresists.

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