Optical Density at 193 nm of Vinyl Addition Poly(norbornene) Made Using Hydrogen as a Chain Transfer Agent

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Technical Paper

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Homopolymers of a bis-trifluorocarbinol substituted norbornene (1) (α,α-bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-ethanol or HFANB) were produced using a palladium catalyst and hydrogen as a chain transfer agent to control molecular weight. As the hydrogen pressure increased, the molecular weight of poly(1) decreased. Spectroscopic analysis of these polymers by ^{1}H NMR and MALDI-TOF MS confirmed that the hydrogen chain transfer agent generated hydrogen-terminated vinyl addition homopolymers of 1. The optical density of these polymers is extremely low at 193 nm and is independent of molecular weight.
Keywords: Norbornene, transparency, 193 nm, hydrogen, chain transfer

1. Introduction

Semiconductor manufacturers use a process known as photolithography to transfer circuitry information inscribed on a mask onto the silicon substrate [1]. In this process, photoresist solutions are spun on silicon wafers to form photosensitive thin films. The major component in photoresist formulations (besides organic solvent) is the binder resin. Binder resins impact important photoresist film characteristics such as dissolution behavior in developer [2]. This characteristic is profoundly affected by molecular weight and molecular weight distribution of the binder resin. Another important characteristic of the film that is affected by the binder resin is transparency especially at imaging wavelengths [3]. Thus, it is desirable to provide binder resins with controlled molecular weight and molecular weight distributions that do not impact the optical transparency of the photoresist film at imaging wavelengths.

In the recent shift from 248 nm 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, norbornene/maleic anhydride copolymers, norbornene/maleic anhydride/acrylate polymers, and vinyl addition norbornene polymers. Unique among these polymers, vinyl addition norbornene polymers held the promise of both high transparency as well as excellent etch resistance [4]. Vinyl addition norbornene polymers are typically synthesized using late transition metal catalysts [5].

A few years ago, several publications appeared that discussed the incorporation of the bis-trifluorocarbinol substituted norbornene 1 (α,α-bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-ethanol or HFANB) into photoresist binder resins [6,7,8]. 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 using palladium catalysts could be achieved using olefinic chain transfer agents. Unfortunately, to obtain low optical densities (OD) for these polymers at 193 nm a post-polymerization end group modification step such as epoxidation or hydrogenation was required [9]. In this contribution, we investigated hydrogen as a molecular weight control agent for the homopolymerization of 1 using palladium

catalysts and report on the optical density at 193 nm of such homopolymers.

1   **2**
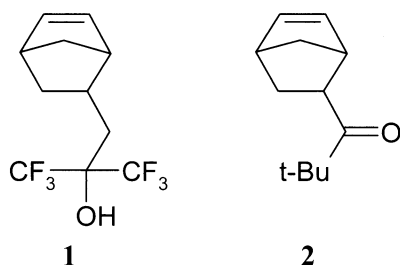
2. Experimental

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.

HFANB (**1**) was obtained from Promerus LLC and N,N-dimethylanilinium tetrakis(pentafluoro phenyl)borate (DANFABA) from Boulder Scientific. The synthesis of bis(di-*i*-propylphenylphosphine) palladium diacetate has been reported previously [9].

NMR, GPC, MALDI-TOF MS, and optical density (OD) were determined as previously reported [9].

2.2. Polymerization of **1** in the presence of hydrogen.

Monomer **1** (5.00 g, 0.0182 mol) was weighed into a glass vial and combined with 1.8 mL of a stock solution of DANFABA (0.0032 g, 0.0040 mmol in 2 mL of toluene). To this solution was added 7 mL of toluene. The mixture was added to a glass pressure vessel, charged with hydrogen gas to 20 psig and heated to 80 °C for one hour. To this mixture was added 0.7 mL of a stock solution of bis(di-*i*-propylphenylphosphine) palladium diacetate (0.0012 g, 0.0020 mmol in 2 mL of toluene). The mixture was stirred for 18 h. After cooling, the polymer was precipitated by pouring the reaction mixture into heptane. The precipitated polymer was filtered and dried at 100 °C in a vacuum oven. Yield 4.32 g (86%). ^{1}H NMR (CDCl$_3$): δ 0.5-2.6 (br m, aliphatic hydrogens, 11H), 2.6-3.3 (br s, O*H*, 1H). GPC: M_w = 22,900; M_n = 9900. The procedure was repeated, but under 30 psig hydrogen. The resulting yields and molecular weights are presented in Table 1.

The experiment above was repeated at larger scale (80 g of **1**) in a total of 200 mL of toluene but under 50 and 90 psig hydrogen and with a

monomer to Pd to DANFABA molar ratio of 25000:1:5. The resulting yields and molecular weights are summarized in Table 1.

3. Results and Discussion

A series of homopolymerizations of **1** were carried out using bis(di-*i*-propyl phenylphosphine)palladium diacetate and DANFABA in the presence of hydrogen to control molecular weight. The molar ratio of **1** to Pd required was quite low and the molar ratio of Pd to DANFABA employed was 1 to 5. The polymerizations were run at two different scales: 5 g and 80 g of monomer. The results of these polymerizations are presented in Table 1.

Table 1. Polymerization of **1** using bis(di-*i*-propylphenylphosphine)palladium diacetate and DANFABA in the presence of increasing hydrogen pressure.

Run	H$_2$ (psig)	Yield (%)	Mw	Mn	OD (193)
1	20	89	22900	9900	0.04
2	30	86	18100	8450	0.03
3	50	76	13500	5700	0.03
4	90	70	12200	6630	0.02

The isolated yields of polymer were good ranging from 70 to about 90%. As the pressure of hydrogen was increased from 20 to 90 psig, the M_w of the homopolymer of **1** decreased from 22900 to 12200. Higher hydrogen pressure results in lower molecular weight polymer.

The polymers were characterized by both ^{1}H NMR and MALDI-TOF MS techniques. The ^{1}H NMR spectrum shows that a vinyl addition polymer was produced; no resonances due to olefinic moieties are observed. The MALDI-TOF MS trace of the homopolymer (negative ion mode) is shown in Figure 1. Only one significant polymer series is observed and it is consistent with a hydrogen-terminated poly(**1**). Since in the negative ion mode, loss of H$^+$ from the polymer chain occurs, an HFANB polymer chain with a degree of polymerization of 10 and two hydrogen end groups would exhibit a molecular ion of 2741 as is observed in the mass spectrum. (A much less intense polymer series is observed due to loss of CF$_3$H (70 Daltons) from the polymer chain.)

End group determination for poly(**1**) and the inverse molecular weight dependence of poly(**1**) on hydrogen pressure indicate that hydrogen is involved in the chain transfer step and that a phosphine-stabilized (presumably cationic) Pd-H

species is the active catalyst. See Scheme 1. Insertion of norbornene into the Pd-H bond yields a cationic Pd-C bonded intermediate. A hydrogen-terminated poly(norbornene) and regeneration of the cationic Pd-H catalyst results from a σ-bond metathesis reaction between this Pd-C intermediate and hydrogen [10]. See Scheme 2.
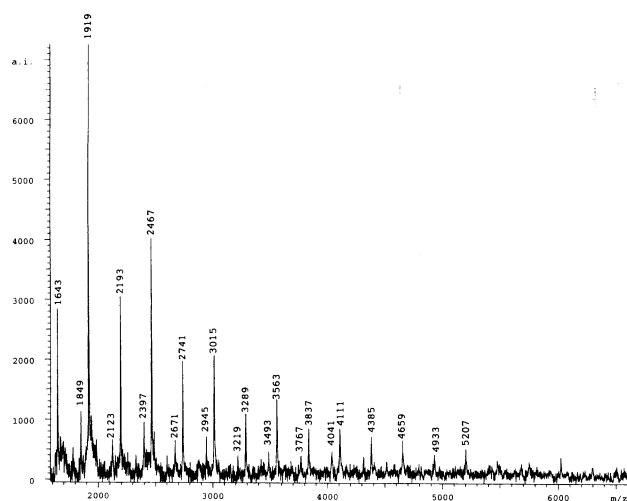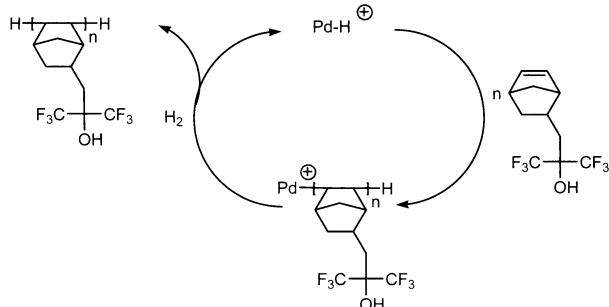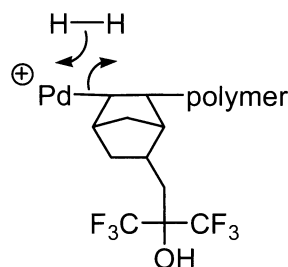

Figure 1. MALDI-TOF MS of hydrogen-terminated homopolymer of **1**. (* = loss of CF_3H)

Scheme 1. Proposed initiation and chain transfer steps.

Scheme 2. Chain transfer reaction.

While this catalytic cycle is supported by elucidation of the hydrogen poly(norbornene) end groups, it not clear at this juncture how the $Pd(OAc)_2(PR_3)_2$ derived catalyst enters the

polymerization cycle. However, recent studies have shown that Pd(II) complexes can form Pd-C bonds by metallation of the *i*-propyl substituents of phosphine ligands bonded to Pd [11].

In early transition metal Ziegler-Natta poly(olefin) technology, polymer molecular weight can be controlled by addition of hydrogen [12]. We are aware of only a few examples of molecular weight control of poly(olefins) using late transition metal olefin polymerization catalysts and hydrogen [13]. None of these references exemplify hydrogen as a chain transfer agent in homopolymerization of norbornene-type monomers.

The optical density (OD) of poly(**1**) made in the presence of hydrogen was measured at 193 nm. The results as a function of M_n are presented in Figure 2. Note that the ODs are very low (< 0.05 micron^{-1}) and that the values observed are independent of molecular weight. Contrast this behavior with that observed for the same polymer composition containing olefinic end groups (made using ethylene and 1-hexene chain transfer agents to control molecular weight) also presented in Figure 2. In the latter case, the olefinic end groups in poly(**1**) contribute to an increase in OD as the molecular weight decreases [9]. The saturated, hydrogen-terminated poly(**1**) do not contain unsaturated end groups and therefore exhibit very low ODs even at low molecular weight.
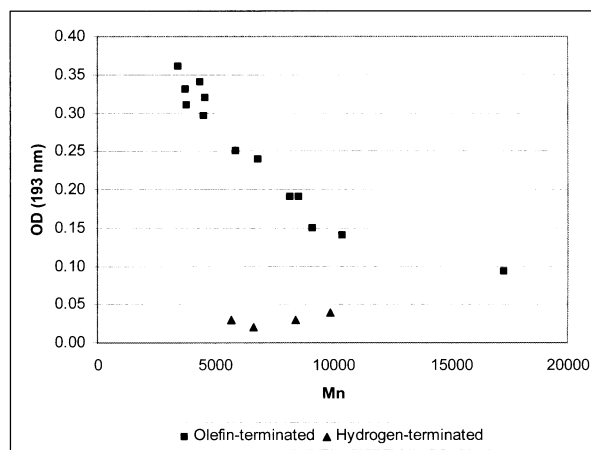

Figure 2. Plot of optical density (OD, at 193 nm) vs. M_n for both olefin-terminated poly(**1**) (squares) and hydrogen-terminated poly(**1**) (triangles).

In conclusion, hydrogen controls the molecular weight of poly(norbornene) made using palladium catalysts. In this process, hydrogen-terminated poly(norbornene) is synthesized that is extremely

transparent at 193 nm and therefore can serve as the basis for improved photoresist binder resins.

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3. See, for example, reference 2b, p190.

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