

Pd(II)-catalyzed addition polymerization and ring opening metathesis polymerization of alicyclic monomers: routes to new matrix resins for 193 nm photolithography

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Abstract

A series of alicyclic polymers designed for 193 nm photoresist applications have been synthesized and characterized. These polymers were synthesized by Pd(II)-catalyzed addition and ring opening metathesis polymerization techniques. Methods for removing residual metal complexes of Pd(II) and Ir(IV) from alicyclic polymers were developed. The low absorbance of these polymers at 193 nm and their high dry etch resistance make them attractive candidates for 193 nm lithography. When formulated with onium-type photoacid generators and plasticizers in propylene glycol monomethyl ether acetate, these photoresists have demonstrated high resolution and high sensitivity. © 1998 Elsevier Science B.V. All rights reserved.

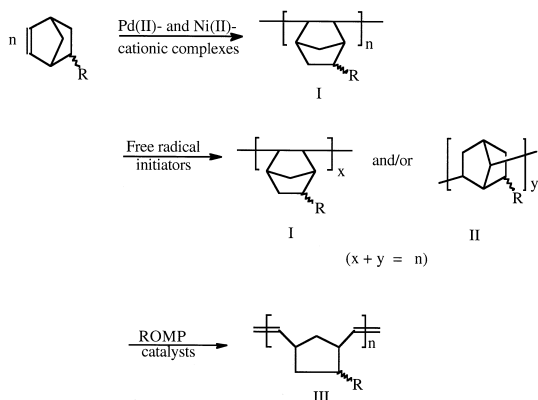
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1. Introduction

Cycloalkenes like norbornene and its derivatives can undergo addition polymerization reactions by three general synthetic pathways: free radical [1,2], ionic [3–6], and ring opening metathesis [7–14], as shown in Scheme 1. The route chosen and the structure obtained depends on the nature of the initiator or catalyst employed. Free radical polymerization of these

types of monomers is initiated by organic peroxides or hydroperoxides (di-*tert* butyl peroxide, *t*-butyl hydroperoxide, benzoyl peroxide) [1,2] and azo compounds (azobisisobutyronitrile (AIBN), azobiscyclohexylbutyronitrile); and produces saturated polymers that retain their cyclic units. Ionic polymerization of cycloalkenes like norbornene in the presence of $C_2H_5AlCl_2$, Pd(II) complexes, etc., [15] produce a saturated polymer that retains its cyclic unit with 2,3-enchainment [3–6]. The ring opening metathesis polymerization catalysts based on transition metal complexes of Cr, W, Ru,

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Scheme 1. Pathways for the polymerization of norbornene and its derivatives.

Mo, Os, or Ir [7–14] and some Ziegler–Natta type catalysts [16,17] produce unsaturated polymers that have one less ring than the starting monomer.

The use of alicyclic polymers as matrix resins in 193 nm lithography is not accidental, especially in light of the drive in the integrated circuit (IC) industry over the years to develop lithographic technologies using ever shorter and shorter wavelengths, so as to enable greater packing densities and higher device speeds. The industry has migrated from 436 nm (G-line) and 405 nm (H-line) to 365 nm (I-line), where most devices are produced today. The very latest generation of integrated circuits is printed in the deep UV region (248 nm). The resolution necessary for manufacturing future generations of ICs with feature sizes below 0.15 μm is beyond the current limits of 365 and even 248 nm UV lithography. According to The Semiconductor Industry Association's 'Technology Roadmap for Semiconductors' [18], 193 nm lithography is a promising candidate for achieving such high resolution.

Lithography at 193 nm opens up new possibilities, but also poses major technological challenges. Optical materials such as quartz that are nominally transparent at 248 nm have significant absorption and undergo laser-induced changes in index at 193 nm. Although excellent 193 nm lens systems have been constructed, the

damage threshold for these lenses limits the exposure power that can be delivered to the wafer [19–21]. Few organic polymers, on the other hand, are transparent enough to serve as resists at this wavelength. Consequently, new single layer resists with high-performance imaging characteristics (resolution, depth of focus, process latitude, adhesion, sensitivity), plasma etch resistance equivalent to or superior to conventional DUV resists, and compatibility with industry-standard processing chemicals (aqueous base developers) will be required for 193 nm imaging technology [22].

Transparency at 193 nm and etch resistance were once thought to be mutually exclusive. Conventional wisdom held that aromaticity was required for etch resistance, but aromatics have allowed $\pi - \pi^*$ transitions in the spectral region near 190 nm and therefore absorb at that wavelength strongly. Consequently, phenolic resins used for I-line and 248-nm photoresists, NovolacTM and polydroxystyrene, respectively, are far too opaque at 193 nm to be used in formulating single-layer resists for use at that wavelength. Fortunately, it turns out that it is not aromaticity that is required for plasma etch resistance; it is simply a high C:H ratio [23].

The use of terpolymers and tetrapolymers of acrylic and methacrylic acids and esters has provided good imaging properties at 193 nm, but with dry etch resistance that is less than that of I-line resists [24–26]. Attempts to improve dry etch resistance by incorporation of pendant cycloaliphatic groups [27,28] met with some success, but the acrylate backbone, which serves to tether all of these groups has poor intrinsic dry etch resistance and is known to depolymerize upon exposure to the radiation present during reactive ion etching and ion-implantation (R.R. Kunz, 1996, personal communication).

Our attempt to incorporate cyclic olefins into the photoresist polymer backbone is a radical departure from the conventional 193 nm photoresist design concept typified by acrylic polymers [24–26] or acrylic polymers with pendant cyclic olefins [27,28], or cyclic olefin/acrylic

hybrid polymers [29]. It is the unique architectures of the polymer backbones of our resist materials that impart properties that make them good candidates for 193 nm resist applications. Various aspects of this work have been published in part elsewhere [30–35].

The cycloaliphatic backbone of our polymers contributes to dry etch resistance and thermal stability as well as tethering the pendant functionalities required for imaging. The materials have a pendant acidcleavable group, a *tert*-butyl ester, that undergoes acid catalyzed thermolysis, which is accompanied by a large change in polarity. They have carboxylic acid or maleic anhydride units, which enhance the adhesion, wettability and solubility of the materials in aqueous base developing solvent. The resist design incorporates the concept of chemical amplification [36,37], a process that involves the photogeneration of species within the resist, which catalyze subsequent chemical events that in turn modify the solubility of the polymer in aqueous base. In this way, the overall quantum efficiency of the reactions responsible for modifying solubility is greatly enhanced. Thus, such systems have very high sensitivity. This chemical amplification concept has been exploited in many resist systems. A recent review of chemically amplified resist systems has been provided by Ito [38].

In considering materials for use in 193 nm photoresist applications, the choice of functionalized monomers (e.g., cyclic olefin derivatives with functional or reactive groups like esters, carboxylic acids and anhydride) is therefore critical, as it is the interactions of these groups that determine the physical and chemical properties of the polymers which allows one to tailor the materials to provide specific functions, such as differential solubility between the acidic group and its protected analog in the developing solvent, adhesion to silicon substrate, enhancement of mechanical properties, etc. The physical and chemical properties of these polymers are indeed modified by the incorporation of such functional or reactive groups, due principally to

intra- and inter-molecular polar, hydrogen-bonding, or ionic interactions. These types of interactions have been reported to modify specific properties of polymeric materials, such as the glass transition and melt temperatures, rubbery modulus above the glass transition, dynamic mechanical behavior, melt rheology, relaxation behavior, dielectric properties, solution behavior, permeability, compatibility, adhesion, solid-state morphology [39–41]. For instance, the presence of ionic functional groups in polymers usually leads to improved mechanical strength and increased glass transition temperatures. Also, functional groups can promote miscibility or compatibility of polymer blends [42]. In adhesion and coatings applications, functional groups have been reported to influence adhesive bonding of substrates such as inorganic solids, organic polymers, pigments, dyes, etc., to surfaces [43].

Numerous heterogeneous and homogenous catalytic systems are now known to initiate the ring-opening metathesis reaction of cycloolefins such as norbornene and its derivatives [7–11,14,44,45]. These catalyst systems are made up of one, two, or several components, the main one of which is a compound of a transition metal, especially those from groups 6, 7 or 8 of the periodic table—mostly Mo, W, Ru and Re; cocatalysts like organometallic compounds; and promoters, compounds containing oxygen, nitrogen, halogens, etc., which are sometimes incorporated into the catalyst system. Some of the catalyst systems are active only in non-polar solvents while others require polar solvents in order to be activated.

While a majority of known ROMP catalysts [14] can polymerize strained all-hydrocarbon cyclic monomers such as norbornene and dicyclopentadiene to very high extent, the rate of polymerization observed for cycloolefins containing functional groups, especially nucleophilic functionalities, are sometimes considerably slower due to interaction of the metathesis catalysts with the electrophilic center. However, catalyst systems based on Ru, Os, or Ir com-

pounds [46,47], however, are able to polymerize norbornene derivatives in common non-polar and weakly polar organic solvents and in ethanolic and aqueous solutions [13].

Certain palladium compounds like PdCl_2 and several Pd(II)-halide complexes catalyze the addition polymerization of norbornene derivatives with functional groups at reaction temperatures above 100°C . The molecular weights of the obtained polymers were reported to be generally low (below 10 000 Da) and the yields were also moderate [48]. High molecular weight addition polymers of norbornene derivatives with carboxylic ester groups were also reportedly made at ambient temperature with $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ [49], and palladium(II)-alkyl complexes [50–53], albeit in low yields. Polymer yields above 70%, were only obtained when the pure *exo* isomer was polymerized [49]. Recently, (η^3 -allyl)palladium(II) catalysts with weakly coordinating counterions were reported to catalyze the addition polymerization of norbornene derivatives with functional groups to very high yield and high molecular weight. These catalysts were also reported to have substantially increased activity for the polymerization of *endo* substituted norbornene derivatives [54].

In this paper, we present the results of the polymerizations of a series of cycloaliphatic olefins: norbornene and its derivatives, and methyl tetracyclododecene and its derivatives. These polymers were synthesized by ring opening metathesis polymerization (utilizing mostly Ir(IV)- and Ru(IV)-based catalysts) and Pd(II)-catalyzed addition polymerization techniques using Pd(II)-complexes of the type: $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ and (η^3 -allyl)palladium(X), where X = SbF_6 and BF_4 . We also present the results of the formulation, processing and characterization (in terms of their plasma etch resistance, optical properties, thermal, mechanical, and environmental stability, etc.) of alicyclic polymer photoresist materials using 248 nm KrF and 193 nm ArF exciplex laser exposure tools.

2. Experimental

2.1. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on QE-300 MHz and Varian 300 MHz spectrometers with the solvent proton and carbon signals, respectively, as standards. Infrared spectra were measured using a Nicolet Magna-IR™ FTIR/550 spectrometer. Mass spectral analyses were conducted using a Finnigan MAT TSQ-70 mass spectrometer. The purity of the monomer samples was determined with a Hewlett-Packard Series II 5890 gas chromatograph, equipped with a glass capillary column. Molecular weight determinations were made with size exclusion chromatography (SEC) using a viscotek chromatograph equipped with American Polymer Standards AM Gel 100/5, AM Gel 500/5 and AM Gel Linear/5 columns at 25°C , with tetrahydrofuran as eluent. Molecular weights are presented as polystyrene equivalents, unless noted otherwise. Thermal analyses were performed with a Perkin-Elmer Series-7 DSC Differential Scanning Calorimeter and a Perkin-Elmer Series-7 TGA7 Thermogravimetric Analyzer under a nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN.

2.2. ArF exciplex laser (193 nm) stepper

Fig. 1 is a schematic of a stepper with ArF or KrF exciplex laser illumination source used in exposing the photoresist films. In the stepper system, the image field is partitioned and refractive optics are employed to form the image on the wafer. Printing is done in the step-and-repeat projection mode, which involves carrying out a series of exposures on the wafer such that the mask image is stepped (by means of a precise mechanical stage) to a new position before each exposure. Such a mask is called a reticle. With reduction optics, it is possible for the size of a feature on the reticle to be greater

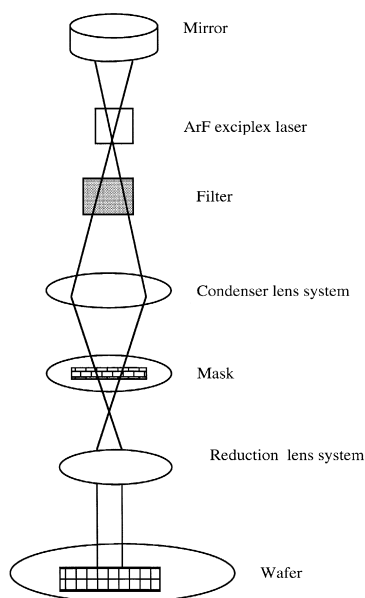


Fig. 1. Schematic of a stepper with ArF excimer laser illumination source. The only difference between this schematic and that of the KrF excimer laser is the illumination source.

than the size of the corresponding image projected on the wafer [55]. The ISI MicroStep ArF stepper has a variable NA lens and experiments were conducted at 0.6 NA, a field size diameter of 1.5×1.5 mm and partial coherence of 0.7.

2.3. Materials

All chemicals were purchased from Aldrich Chemical and used as received with the following exceptions. Norbornene carboxylic acid (NBCA) was purchased from Pfaltz and Bauer, and used as received. Cyclopentadiene was obtained by cracking dicyclopentadiene and used immediately. Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride was obtained from Strem Chemicals. 8-methyl-8-carboxy tetracyclo[4,4,0.1^{2,5},1^{7,10}]dodec-3-ene or Methyltetracyclododecene carboxylic acid (MTDCA) was obtained by the hydrolysis of 8-methyl-8-methoxycarbonyltetracyclo[4,4,0.1^{2,5},1^{7,10}]dodec-3-ene (obtained from Japan Synthetic Rubber). Methyltetracyclododecene and tetracy-

clododecene were obtained from B.F. Goodrich. Bistetrafluoroborate tetrakis(cyanomethane) palladium $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ was prepared using an adaptation of published procedures [56]. (η^3 -Allyl)palladium(II) complexes with tetrafluoroborate and hexafluoroantimonate counterions were prepared using an adaptation of published procedures [54]. Triphenylsulfonium hexafluoroantimonate was prepared according to a literature procedures [57]. CD11TM anti-reflective coating was obtained from Brewer Scientific. BARLTM antireflective coating was obtained from IBM. PD-523ADTM developer, 0.21 N aqueous tetramethylammonium hydroxide solution with surfactant was obtained from Japan Synthetic Rubber. LDD-26WTM developer, 0.26 N aqueous tetramethylammonium hydroxide was obtained from Shipley.

3. Synthesis of alicyclic monomers

3.1. General procedure for the synthesis of 2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (trivial name: carbo-*t*-butoxy norbornene (CBN))

Freshly cracked cyclopentadiene (CPD) (132.0 g, 2.0 mol) was added (dropwise) to a stirred solution of 256.0 g (2.0 mol) of *tert*-butyl acrylate and 2 g (9.6 mmol) of 3,5-di-*tert*-butyl phenol. The mixture was stirred for 6–8 h at 140°C, and the product isolated by vacuum distillation as a colorless oil (291 g, 75%): b. 100°C/20 mmHg; GC (99% purity, exo:endo = 30:70%); FTIR (cm^{-1}) 2950 (C–H), 2900 (C–H), 1730(C=O) 1140 (C–O–C); MS (CI⁺) m/z = 195 (M + 1); ¹H NMR (CDCl_3) δ 1.35 (s, 9H, =C(CH₃)₃), 1.8 (m, 1H), 2.1 (m, 1H), 2.85 (bm, 2H), 3.14 (2H, bridged-head protons), 5.9 (bm, 2H, endo-olefinic) 6.1 (m, 2H, exo-olefinic protons), 6.15 (bm, 2H, endo-olefinic protons). ¹³C-NMR (CDCl_3) δ 27.9 (C(CH₃)₃), 28.7, 30.0, 41.3, 42.4, 43.9, 44.0, 45.7, 46.0, 46.3, 49.4, (76.6, 77.0, 77.4, CDCl_3), 79.4, 131.9, 135.6, 137.2, (173.5, 175.5, carbonyl).

Anal. Calc. for $(C_{12}H_{18}O_2)_n$: C, 74.22; H, 9.28.
Found: C, 74.28; H, 9.55.

3.2. The synthesis of 2-methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (trivial name: carbomethoxy norbornene (CMN))

A 250-ml flask fitted with a reflux condenser, an addition funnel, and a magnetic stirrer was charged with 78 g of methyl acrylate and 10 g of hydroquinone. The mixture was stirred at 100°C. A 60-g solution of freshly cracked cyclopentadiene (CPD) that was maintained at ice-water temperature (to prevent it from dimerizing) was slowly added (dropwise) to the refluxing methyl acrylate solution. After the addition of CPD, the mixture was refluxed for 12 h. The product was purified by fractional distillation to afford a colorless oil in 80% yield. $b \sim 145^\circ\text{C}/1 \text{ atm}$. GC: 97% purity. $^1\text{H NMR}$ (CDCl_3) δ 6.5 (t, olefinic 1H), 6.2 (complex,), 3.8 (s, 3H, =OCH₃), 3.6 (d, 1H), 3.0 (s, 2H) 1.6 (s, 2H, bridge-head protons).

3.3. Synthesis of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (trivial name: norbornene carboxylic acid (NBCA))

Dicyclopentadiene (100 g, 0.758 mol) was cracked in a round bottom flask that was fitted with a vigereux column and a condenser. The cyclopentadiene (CPD) formed was allowed to drip into a round bottom flask that was charged with 109 g (1.52 mol) of acrylic acid and 5 g (0.024 mol) of 3,5-di-*tert*-butylphenol and maintained at room temperature. As the CPD dripped into the collection flask, the reaction between it and the dienophile (acrylic acid) was very exothermic, and the temperature increased to $> 80^\circ\text{C}$. Following the addition to the acrylic acid, the reaction vessel was fitted with a reflux condenser and heated to 100°C for 4 h. The product was purified by fractional distillation to afford the acid (70 g) as a foul-smelling colorless liquid, b . 143–145°C/1 atm. $^1\text{H NMR}$ (CDCl_3) δ 11.4 (s, 1H, =COOH), 6.0 (t, 2H), 3.0 (complex), 2.1 (s, 1H), 2.0 (s, 1H), 1.5 (t).

4. Synthesis of alicyclic polymers

4.1. General procedure for the synthesis of ring opening metathesis polymers

To a round bottom flask charged with 15 ml of the mixed solvent (water/ethanol/*p*-dioxane = 3/5/7 (v/v)) was added 50 mmol of the monomer, 0.5 mmol of dipotassium hexachloroiridate (K_2IrCl_6 (catalyst)), 5 mmol of Zn (reducing agent), 50 mmol of acetic acid, and 0.5 mmol of 1-decene (molecular weight regulator). The resulting mixture was stirred at 50°C for 24 h, after which it was diluted with THF and then filtered to remove the residual catalyst and zinc acetate. The filtrate was poured into methanol to precipitate the polymer. The recovered polymer was redissolved in THF, and reprecipitated in methanol. This procedure was repeated twice. The final product was dried in vacuo at 60°C.

4.2. Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (trivial name: poly(carbo-*t*-butoxy norbornene) (Poly(CBN)))

Poly(CBN) was isolated as light yellow solid in 89% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 (–C(CH₃)₃), 1.6–3.2 (–CH₂, –CH [bridge-head, main chain]), 5.21–5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}) ν : 1740 (C=O), 1120 (C–O–C), 990 (C=C–H, *trans*), 740 (C=C–H, *cis*). GPC: $M_w = 43\,000$, $M_n = 19\,000$. DSC: $T_g = 85^\circ\text{C}$. TGA: $T_d = 250^\circ\text{C}$.

4.3. Poly(2-methyl propyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-2-methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) (trivial name: poly(carbo-*t*-butoxy norbornene-co-carbomethoxy norbornene) (Poly(CBN-co-CMN)))

Poly(CBN-co-CMN) was synthesized from a charge of CBN:CMN = 80:20 mol% ratio. The

product and was isolated as a lightly yellow-colored solid in 66% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 1.6–3.2 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]), 3.65 ($-\text{OCH}_3$) 5.21–5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}) ν : 1740 ($\text{C}=\text{O}$), 1120 ($\text{C}-\text{O}-\text{C}$), 990 ($\text{C}=\text{C}-\text{H}$, *trans*), 740 ($\text{C}=\text{C}-\text{H}$, *cis*). GPC: $M_w = 101\,000$, $M_n = 54\,000$. DSC: $T_g = 85^\circ\text{C}$. TGA: $T_d = 250^\circ\text{C}$. Composition: CBN:CMN = 81:19 (mol%, by $^1\text{H NMR}$).

4.4. *Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-8-methyl-8-carboxy-tetracyclo[4,4,0,1^{2,5},1^{7,10}]dodec-3-ene (trivial name: poly(carbo-t-butoxy norbornene-co-methyltetracyclododecene carboxylic acid) (Poly(CBN-co-MTDCA)))*

Poly(CBN-co-MTDCA) was synthesized from a charge of CBN:MTDCA = 80:20 mol%, and was isolated as a lightly yellow-colored solid in 75% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 2.0–2.8 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]), 5.2–5.4 (vinyl proton). FTIR (film on NaCl plate, cm^{-1}) ν : 3600 (OH), 1729 ($\text{C}=\text{O}$), 1120 ($\text{C}-\text{O}-\text{C}$), 970 ($\text{C}=\text{C}-\text{H}$, *trans*), 848 ($\text{C}=\text{C}-\text{H}$, *cis*). GPC: $M_w = 59\,000$, $M_n = 16\,000$. DSC: $T_g = 122^\circ\text{C}$. TGA: $T_d = 250^\circ\text{C}$.

5. General procedure for the hydrogenation of ROMP-derived polymers

5.1. Method A

To a stirred solution of (2.0 g, 10 mmol) of the ROMP-derived polymer in 40 ml of propyleneglycol monomethyl ether (PGME) and 20 ml of THF, was added hydrazine monohydrate (40 mmol), *tert*-butyl peroxide (40 mmol) and acetic acid (40 mmol). The reaction mixture was stirred at 50°C for 72 h, after which it was poured into 500 ml of methanol. The recovered polymer was purified by repeated precipitation from THF into methanol and was dried in vacuo at 60°C .

5.1.1. Hydrogenated poly(CBN) made by method A

Hydrogenated poly(CBN) was obtained as a white solid in 87% yield, with 84% hydrogenation (determined by $^1\text{H NMR}$ analysis). $^1\text{H NMR}$ (CDCl_3) δ 1.2–1.9 ($-\text{CH}_2-\text{CH}_2-$ main chain), 1.3 ($-\text{C}(\text{CH}_3)_3$), 2.0–3.2 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]), 5.2–5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}) ν : 2941 ($\text{C}-\text{H}$), 1727 ($\text{C}=\text{O}$), 1155 ($\text{C}-\text{O}-\text{C}$) GPC: $M_w = 28\,900$, $M_n = 15\,000$. DSC: $T_g = 57^\circ\text{C}$. TGA: $T_d = 252^\circ\text{C}$.

5.1.2. Hydrogenated poly(CBN-co-MTDCA)

Hydrogenated poly(CBN-co-MTDCA) was obtained as a white solid in 75% yield, with 82% degree of hydrogenation (determined by $^1\text{H NMR}$ analysis). $^1\text{H NMR}$ (CDCl_3) δ 1.16–1.91 ($-\text{CH}_2-\text{CH}_2-$ main chain), 1.3 ($-\text{C}(\text{CH}_3)_3$), 2.0–2.8 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]), 5.21–5.4 (vinyl proton). FTIR (film on NaCl plate, cm^{-1}) ν : 3600 ($-\text{OH}$), 2941 ($\text{C}-\text{H}$), 1727 ($\text{C}=\text{O}$), 1155 ($\text{C}-\text{O}-\text{C}$). DSC: $T_g = 107^\circ\text{C}$. TGA: $T_d = 252^\circ\text{C}$.

5.2. Method B

To a stirred solution (2.0 g, 10 mmol) of the ROMP-derived polymer in 50 ml of 1,4-dioxane was added *p*-toluenesulfone hydrazide (4.7 g, 25 mmol) and tripropylamine (4.3 g, 30 mmol). The reaction mixture was stirred and refluxed for 4 h under dry N_2 and then passed through a 1/2-in. layer of celite on a glass filter to remove residual catalyst. The solution was poured into a 1:1 mixture of water and acidified to pH 2 with conc. HCl. The precipitated polymer was purified and dried in the same manner as in method A.

5.2.1. Hydrogenated poly(CBN) made by method B

Yield: 1.5 g (75%); degree of hydrogenation: $> 99\%$; IR and NMR were same as that of polymer obtained with method A. GPC: $M_n = 10,200$. DSC: $T_g = 70^\circ\text{C}$. TGA: $T_d = 252^\circ\text{C}$.

Anal. Calcd. for $(C_{12}H_{18}O_2)_{0.77}/(C_8H_{10}O_2)_{0.23}$: C, 74.75; H, 9.24. Found: C, 73.94, H, 9.99 (trace elements: Ir, 0.04%, Zn, 0.03%, N, < 0.5%, Cl, 0.012%). The feed composition was $(C_{12}H_{18}O_2)_{0.8}/(C_8H_{10}O_2)_{0.2}$.

5.3. General procedure for the hydrolysis of ROMP polymers

To a stirred solution of 4.9 g of a typical ROMP polymer (poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-2-methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate)), (CBN:CMN = 81:19%) in 50 ml of PGME was added KOH (0.66 g, 10 mmol) and tetrabutyl ammonium bromide (0.32 g, 1 mmol). The mixture was stirred at 60°C for 24 h, after which it was poured into 1 liter of 2% HCl. The precipitated polymer was purified by reprecipitation from THF into water. The isolated white polymer was dried in vacuo at 60°C. Yield: 84%. 1H NMR ($CDCl_3$) δ 1.2–1.9 ($-CH_2-CH_2-$ main chain), 1.3 ($-C(CH_3)_3$), 1.8–3.2 ($-CH_2, -CH$ [bridge-head, main chain]), 5.2–5.4 (vinyl proton). FTIR (film on NaCl plate, cm^{-1}) ν : 3600 ($-OH$), 1732, ($C=O$), 1705($C=O$), 1149 ($C-O-C$). GPC: $M_w = 93\,300$, $M_n = 51\,000$. DSC: $T_g = 100^\circ C$. TGA: $T_d = 252^\circ C$. Composition: CBN:COOH = 74:26 (mol%) (determined by 1H NMR analysis).

5.4. General procedure for the tetrakis(acetonitrile)palladium(II)-bis(tetra-fluoroborate)-catalyzed addition polymerization of alicyclic monomers

The polymers were made by using a modification of the procedure developed by Breunig and Risse [49]. A serum bottle was charged with a solution of 51.5 mmol of the monomer in 20 ml of nitromethane and a magnetic stir bar and was then sealed with a Teflon-lined rubber septum. The solution was degassed and the vessel back-filled with N_2 . A solution of 0.2 mmol of $[Pd(MeCN)_4](BF_4)_2$ in 5 ml of nitromethane

was then introduced by means of a syringe. The reacting mixture was then stirred for 72 h at room temperature, after which it was poured into acetonitrile. The precipitated polymer was filtered, dissolved in tetrahydrofuran, reprecipitated in acetonitrile and filtered again. This precipitation procedure was repeated as necessary to produce a white polymer, which was then dried in vacuo at 60°C.

5.5. PolyCBN

PolyCBN was isolated as a white solid in 30% yield. 1H NMR ($CDCl_3$) δ 1.4 ($-C(CH_3)_3$), 2.0–3.0 ($-CH_2, -CH$ [bridge-head, main chain]). FTIR (film on NaCl plate, cm^{-1}) 2900–3000 ($C-H$), 1720 ($C=O$), 1150 ($C-O-C$). GPC: $M_w = 10\,000$, $M_n = 6000$. TGA: decomposition temperature (T_d): 250°C. Anal. Calcd. for $(C_{12}H_{18}O_2)$: C, 74.00; H, 9.00. Found: C, 73.58, H, 8.83, N, < 0.5 (trace elements: Pd, 130 ppm, F, < 64 ppm, B, 30 ppm).

5.6. PolyNBCA

Poly(NBCA) was isolated as a white solid in 55% yield. 1H NMR ($DMSO-d_6$) δ 1.0–3 (br, $CH_2, -CH$ [bridge-head, main chain]), 7.4 (s). FTIR (film on NaCl plate, cm^{-1}) 3500–3000 (OH), 2900–3000 ($C-H$), 1708 ($C=O$, carboxylic acid). GPC: $M_w = 9000$, $M_n = 6000$. TGA: $T_d = 250^\circ C$. Anal. Calcd. for $(C_8H_{10}O_2)$: C, 69.56; H, 7.25. Found C, 65.68, H, 7.72, N, < 0.5 (trace elements: Pd, 121 ppm, F, < 64 ppm, B, 20 ppm).

5.7. Poly(CBN-co-NBCA)

Poly(CBN-co-NBCA) was synthesized from a charge of CBN:NBCA = 70:30 mol% ratio, and isolated as a white solid in 35% yield. 1H NMR ($CDCl_3$) δ 1.4 ($-C(CH_3)_3$), 2–3.0 ($-CH_2, -CH$ [bridge-head, main chain]). FTIR (film on NaCl plate, cm^{-1}) 3400–3200 (OH), 2900–3000 ($C-H$), 1720 ($C=O$, ester), 1705 ($C=O$, carboxylic acid), 1150 ($C-O-C$, ester).

Gpc: Mw = 9000, Mn = 6000. Tga: Td = 250°C. Anal. Calcd. for $(C_{12}H_{18}O_2)_{0.66}/(C_8H_{10}O_2)_{0.34}$: C, 72.05; H, 8.62. Found: C, 71.67, H, 8.89, N, < 0.5 (trace elements: Pd, 339 ppm, F, < 290 ppm, B, < 50 ppm). The feed composition was $(C_{12}H_{18}O_2)_{0.7}/(C_8H_{10}O_2)_{0.3}$.

5.8. Poly(carbo-*t*-butoxy norbornene-co-5-norbornene methanol) (Poly(CBN-co-NME))

Poly(CBN-co-NME) was synthesized from a charge of CBN:NBCA = 70:30 mole ratio, and isolated as a white solid in 45% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 2–3.0 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (film on NaCl plate, cm^{-1}) 3600–3200 (OH), 2900–3050 (C–H), 1720 (C=O, ester), 1705 (C=O, carboxylic acid), 1150 (C–O–C, ester). GPC: Mw = 4100, Mn = 2500. TGA: Td = 250°C.

5.9. General procedure for (η^3 -allyl)-palladium(II) hexafluoroantimonate-catalyzed addition polymerization of alicyclic monomers

Inside a dry box flushed with argon, allyl palladium chloride dimer [$(\eta^3\text{-allyl})\text{PdCl}_2$] (9.44 mg, 0.026 mmol) and silver hexafluoroantimonate (AgSbF_6) (24.8 mg, 0.073 mmol) were stirred in 5 ml of dichloromethane. After 10 min at 25°C, the yellow mixture was filtered through a 0.45- μm pore filter to remove AgCl. The filtrate ($(\eta^3\text{-allyl})\text{palladium(II)}$ hexafluoroantimonate catalyst) was added to a serum bottle charged with a solution of 10.3 mmol of the monomer in 10 ml of dichloromethane and a magnetic stir bar. The bottle was then capped with a Teflon-lined rubber septum, taken outside the dry box and left to react under vigorous stirring for 36 h. The resulting viscous solution was poured into methanol. The precipitated polymer was filtered, dissolved in THF and reprecipitated in methanol and filtered. The polymer was dried in vacuo at 60°C.

5.10. PolyCBN

PolyCBN was synthesized from a charge of CBN (exo:endo = 44:56) (10.3 mmol) and a monomer:catalyst ratio ca. 400 and isolated as a solid in 50% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 2–3.0 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (cm^{-1}) 2900–3000 (C–H), 1720 (C=O, ester), 1150 (C–O–C, ester). GPC: Mw = 30 000, Mn = 20 000.

5.11. PolyNBCA

PolyNBCA was synthesized from a charge of NBCA (100% exo isomer) (14.5 mmol) with a monomer:catalyst ratio of ca. 880 and isolated as a solid in 60% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.6–3.0 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (cm^{-1}) 3400–3100 (carboxylic OH), 2900–3000 (C–H), 1720 (C=O, ester), 1150 (C–O–C, ester). GPC: Mw = 20 000, Mn = 3424.

5.12. Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-bicyclo-[2.2.1]hept-2-ene) (trivial name: poly(carbo-*t*-butoxy norbornene-co-norbornene) (poly(CBN-co-NB)))

Poly(CBN-co-NB) was synthesized from a charge of CBN (26 mmol) and NB (26 mmol) and a monomer:catalyst ratio of ca. 240 and isolated as a solid in 71% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 2–3 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (cm^{-1}) 2900–3000 (C–H), 1720 (C=O, ester), 1150 (C–O–C, ester). GPC: Mw = 37 000, Mn = 8600.

5.13. Poly(2-methyl propylbicyclo[2.2.1]hept-5-ene-2-carboxylate-co-8-methyltetracyclo[4,4,0,1^{2,5},1^{7,10}]dodec-3-ene) (trivial name: poly(carbo-*t*-butoxy norbornene-co-methyltetracyclododecene) (poly(CBN-co-MTDCA)))

Poly(CBN-co-MTD) was synthesized from a charge of CBN (26 mmol) and MTD (26 mmol) and a monomer:catalyst ratio of ca. 210 and

isolated as a solid in 90% yield. $^1\text{H NMR}$ (CDCl_3) δ 1.4 ($-\text{C}(\text{CH}_3)_3$), 2–3 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (cm^{-1}) (C–H), 1720 (C=O, ester), 1150 (C–O–C, ester). GPC: $M_w = 16\,500$, $M_n = 6600$.

5.14. General procedure for (η^3 -allyl)palladium(II) tetrafluoroborate-catalyzed addition polymerization of alicyclic monomers

Inside a dry box flushed with argon, allyl palladium chloride dimer [$(\eta^3\text{-allyl})\text{PdCl}_2$] (27 mg, 0.074 mmol) and silver tetrafluoroborate (AgBF_4) (60.6 mg, 0.311 mmol) were stirred in 5 ml of dichloromethane. After 10 min at 25°C, the yellow mixture was filtered through a 0.45- μm pore filter to remove AgCl . The filtrate ($(\eta^3\text{-allyl})\text{palladium(II)}$ tetrafluoroborate catalyst) was added to a serum bottle charged with a solution of 14.5 mmol of the monomer in 10 ml of dichloromethane and a magnetic stir bar. The bottle was then capped with a Teflon-lined rubber septum and taken outside the dry box, where the reaction mixture was vigorously stirred for 36 h. The resulting viscous solution was poured into methanol. The precipitated polymer was filtered and dissolved in THF and reprecipitated in methanol and filtered. The recovered polymer was dried in vacuo at 60°C.

5.15. PolyCBN

PolyCBN was synthesized from a charge of CBN (exo:endo = 44:56) (10.3 mmol) and a monomer:catalyst ratio ca. 100 isolated as a solid in 60% yield. $^1\text{H NMR}$ (CDCl_3) = 1.4 ($-\text{C}(\text{CH}_3)_3$), 2–3.0 ($-\text{CH}_2$, $-\text{CH}$ [bridge-head, main chain]). FTIR (cm^{-1}) 2900–3000 (C–H), 1720 (C=O, ester), 1150 (C–O–C, ester). GPC: $M_w = 14\,000$, $M_n = 9000$.

5.16. Process for removing Pd(II) complexes from polymers

A total of 100 ml of a 5% solution of the polymer in THF was placed in a 250 ml three-

neck round bottom flask fitted with a dispersion tube that was inserted below the surface of the solution. Hydrogen gas was bubbled through the solution at a slow rate for 1–4 h. The resulting dark precipitate was allowed to stand overnight to aggregate. It settled on the bottom of the flask. The black residue was removed by filtration through a celite pad and the clean, colorless filtrate was concentrated to approximately 10 ml and then paired to a solution of 200 ml of acetonitrile to precipitate the polymer. The sample was isolated by filtration and dried in vacuo at 60°C. The procedure routinely provides polymers with less than 130 ppm of Pd by trace metal analysis, if done for only 2 h. Polymers with significantly less Pd can be isolated, if the reaction is run for much longer time.

5.17. Optical measurements on alicyclic polymer films

A Hewlett-Packard 8450A diode array UV–visible spectrophotometer was used to obtain ultraviolet spectra as follows: resist polymer, co and terpolymer solutions were dissolved in propylene glycol monomethyl ether acetate at 16% by weight relative to solvent and spin coated at 2500 rpm on 1-in. quartz wafers and then baked at 150°C for 60 s, after which, the thickness of the film and the UV absorbance were recorded. Thickness was determined by an average of at least three values obtained at different positions along a scratch using the Alpha Step profilometer.

A Woolam Variable Angle Scanning Ellipsometer (VASE) was used to measure the Cauchy coefficients of the photoresist compositions as follows: the photoresist solution comprising 15% by weight of polymer relative to solvent and 3 wt.% of triphenylsulfonium hexafluoroantimonate (relative to polymer weight) in propylene glycol monomethyl ether acetate was filtered through a 0.45 μm Teflon filter. The resist was spin coated at 2500 rpm to ~ 0.4 μm thickness on silicon wafers. The post-apply-bake process was 150°C for 60 s in hard

contact with the bake plate. Post-exposure bake of the wafer was conducted with minimal delay (< 5 min) for 60 s at 140°C, after which the wafer was placed in the VASE and scanned to determine its Cauchy coefficients. These Cauchy coefficients were used to determine the film thickness of the resist films by means of a Prometrix SM-200 film thickness probe.

5.18. Plasma etch rate measurements on alicyclic polymer films

The dry etch resistance of the resist polymers was determined using a Lam Research Model Rainbow Plasma Etcher under the Cl₂/HBr plasma conditions that are used at SEMATECH to etch polysilicon. The resist was coated on 8 in. silicon wafers to a thickness of 0.6–0.7 μm, baked at 150 for 60 s, and then etched under Cl₂/HBr plasma. The Cl₂ and HBr flow rates were 280 and 125 sccm, respectively. The top and bottom electrodes were maintained at 60°C. The electrodes were supplied with 500 W power. The magnetic field applied to the plasma was 30 Gauss. Two samples of each resist polymer were etched for 60 s. The film thickness was measured before and after etching. The etch rate for each run was calculated by dividing the decrease in thickness of the resist film by the etching time, and the etch rate for each polymer was taken as the average of the two runs for each polymer sample.

5.19. Photoresist formulation and processing

The photoresist solutions were prepared as follows: the resist polymer (13–16 wt.% relative to solvent) and triphenylsulfonium hexafluoroantimonate (3 wt.% relative to polymer weight) were dissolved in propylene glycol monomethyl ether acetate and filtered through a 0.45 μm Teflon filter. Several wafer surface preparation methods were studied. These included hexamthylidisilazane (HMDS) prime, CD-11™, DUV-18™ anti-reflection coatings and IBM-BARL™ antireflective coatings. The resists were spin coated at 2500 rpm to give

~ 0.4–0.7 μm thick films on silicon wafers, or on the antireflection coatings. The post-apply-bake process was 150°C for 60 s (unless otherwise stated) in hard contact with the bake plate. Post-exposure bake of the wafer was conducted with minimal delay (< 5 min) for 60 s at 140°C. The development processes employed consisted of either two 15-s puddles with either 0.065 N, 0.13 N, or 0.26 N tetramethylammonium hydroxide (TMAH) developer solution with surfactant (LDD-26W™ or JSR PD-523AD™ developer) followed by de-ionized water rinse.

5.20. Imaging experiments

Exposures were made using either a 193 nm ISI stepper with ArF exciplex laser illumination source or a 248 nm GCA-XLS stepper with KrF exciplex laser illumination source. The 193 nm stepper has a variable NA lens and experiments were conducted at 0.6 NA, a field size diameter of 1.5 × 1.5 mm and partial coherence of 0.7. The 248 nm stepper has a 0.53 NA lens and experiments were conducted using annular illumination with 0.5 and 0.73 inner and outer sigma. Scanning electron micrographs were recorded on an AMRAY Instruments Scanning Electron Microscope.

6. Results and discussion

6.1. Synthesis of alicyclic monomers

CBN, CMN, and NBCA were synthesized by the Diels–Alder reaction technique between cyclopentadiene and the corresponding acrylic or acrylate dienophile. This technique gave a mixture of endo- and exo-isomers with the endo-isomers predominating.

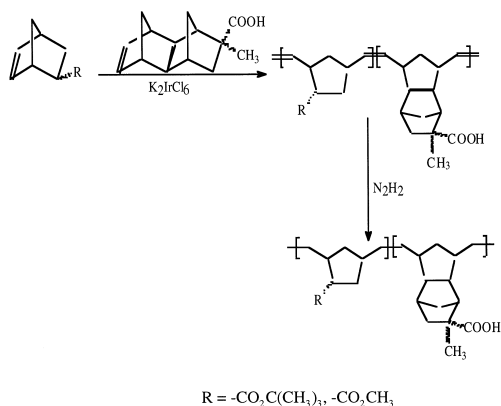
6.2. Polymerization of alicyclic monomers

It has been known for some time that norbornene undergoes ring opening metathesis polymerization in the presence of Ziegler–Natta catalysts [14,58–60]; reduced oxides of Cr, Mo

and W [61,62]; and hydrated halides of Ru, Os, and Ir [13,47], resulting in an unsaturated polymer, poly(1,3-cyclopentylenevinylene). Norbornene also undergoes cationic polymerization in the presence of $C_2H_5AlCl_2$ [63], and free radical polymerization in the presence of di-*tert*-butyl peroxide [1,2] to reportedly yield poly(2,7-bicyclo[2.2.1]hept-2-ene), a saturated polymer, in both cases. Gaylord et al. [2] attributed the unusual 2,7-enchainment of the polymer derived from free radical initiation to skeletal structural rearrangements of the bicyclic monomeric unit that take place during the propagation reaction. Norbornene also undergoes addition polymerization in the presence of compounds of Pd(II) [3,4,17,48,49,64] and Ti(IV) [47], resulting in poly(2,3-bicyclo[2.2.1]hept-2-ene), a saturated polymer with 2,3-enchainment. Breunig and Risse [49] and Mathew et al. [54] have recently reported Pd(II)-catalyzed addition polymerization of norbornene derivatives bearing a variety of functional groups including esters. Part of the present study involved attempts to employ some of the above chemistries to synthesize cycloaliphatic polymers with pendant free carboxylic acid groups and carboxylic acids protected with acid-cleavable groups such as *tert*-butyl esters, tailored for 193 nm resist use.

6.3. Ring opening metathesis polymerization of alicyclic monomers

The synthesis of the ROMP polymers is illustrated in Scheme 2. The yield of the ROMP polymerizations was high as were the molecular weights of the products. The molecular weights of these polymers were controlled by addition of alpha-olefins such as 1-decene to the feed. Under these conditions, there is a trade off between yield and molecular weight as shown in Fig. 2. Photoresist formulations are generally prepared from polymers with low molecular weights so that solutions with higher solid content and lower viscosity can be prepared. There-



Scheme 2. R = $-CO_2C(CH_3)_3$, $-CO_2CH_3$. Ring opening metathesis polymerization of various alicyclic monomers using K_2IrCl_6 . Following polymerization, the polymer was hydrogenated with diimide produced in situ.

fore, the ability to control molecular weight by this means and other means is desirable.

Of all our attempts to polymerize CBN with various ROMP catalysts, K_2IrCl_6 in the presence of acetic acid and zinc (reducing agent) in a mixed solvent of water/ethanol/*p*-dioxane = 3/5/7 (v/v) gave the best yield (28.3%). However, with the use of molecular weight regulators like alpha olefins (1-decene), the polymer yield increases significantly, reaching 90% (see Fig. 2) in some cases. It was also possible to copolymerize CBN with CMN and MTDCA under these conditions. However, this

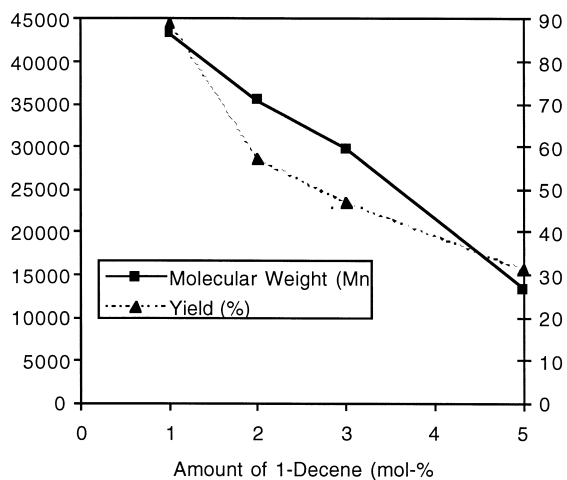


Fig. 2. Control of ROMP polymer molecular weight with 1-decene.

Table 1
The results of the hydrogenation reaction of poly(CBN)^a

| Oxidant (mol%) | Solvent | Mn ^b ($\times 10^4$) | Temp (°C) | Time (h) | Conversion ^c (mol%) |
|-------------------------------|-------------|-----------------------------------|-----------|----------|--------------------------------|
| Air | PGME/THF | 4.33 | 25 | 24 | 76 |
| Air | PGME/THF | 3.5 | 25 | 24 | 13 |
| Air | PGME/THF | 2.97 | 25 | 24 | 15 |
| Air | PGME/THF | 3.54 | 25 | 48 | 13 |
| Air | PGME/THF | 2.97 | 25 | 48 | 42 |
| Air | Toluene | 4.33 | 25 | 24 | 37 |
| H ₂ O ₂ | PGME/THF | 4.33 | 50 | 72 | 49 |
| TBPO ^d | PGME/THF | 4.33 | 50 | 72 | 84 |
| TBPO ^d | PGME/THF | 3.54 | 50 | 72 | 92 |
| TBPO ^d | PGME/THF | 2.97 | 50 | 72 | 94 |
| TBPO ^d | PGME/THF | 4.33 | 80 | 72 | 37 |
| TBPO ^e | 1,4-dioxane | 4 | | | 100 |

^aHydrogenation was carried out using 10 mmol of PCBN, 50 mmol of hydrazine monohydrate, 50 mmol of acetic acid, and 50 mmol of oxidant in 50 ml of solvent.

^bDetermined by GPC.

^cDetermined by ¹HNMR.

^dTBPO: *tert*-butyl peroxide.

^eHydrogenation was carried out using 10 mmol of PCBN, *p*-toluenesulfone hydrazide (25 ml) and tripropylamine in 50 ml of 1,4-dioxane.

catalyst system did not effectively homopolymerize norbornene carboxylic acid. This may be due to the formation of a complex between Ir⁴⁺ and the carboxylic acid group.

It should also be mentioned that RuCl₃ · 3H₂O also initiates polymerization in these monomers: norbornene and carbomethoxy norbornene.

Olefinic unsaturation (as occurs in the backbone of ROMP-derived polymers) in general

has appreciable absorption at 193 nm. In the presence of oxygen, these materials can potentially undergo radical-mediated crosslinking, essentially making them unusable in 193 nm resist applications. To investigate this phenomenon, we exposed some representative ROMP polymers to atmospheric oxygen over a span of 1 year, and at regular intervals, we evaluated the physical and chemical properties of small portions of these samples, to monitor any change

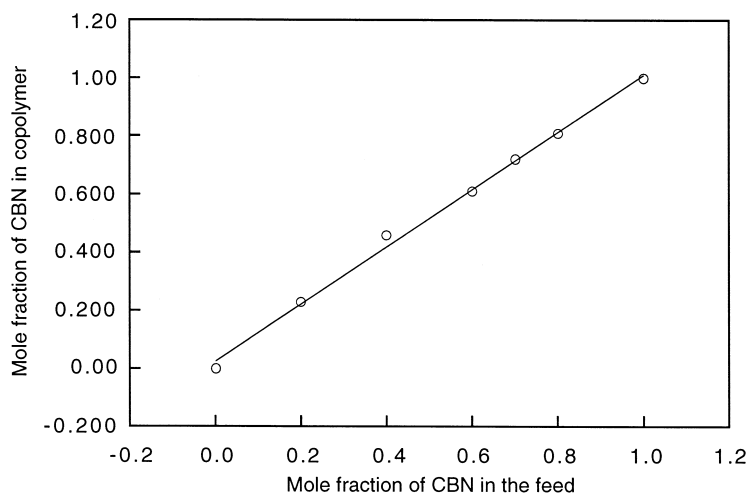


Fig. 3. Incorporation of CBN into copolymer poly(CBN-*co*- MTCDCA) (made by ring opening metathesis polymerization).

from the original samples. To our surprise, we observed no significant change in the color, solubility in common solvents, or the molecular weight of these samples over a span of 1 year.

We hydrogenated the ROMP-derived polymers, using literature procedures [65–67]. The results of our attempts to hydrogenate poly(CBN), a typical ROMP polymer are summarized in Table 1. We were able to achieve nearly 100% hydrogenation yield for the ROMP polymers, using the procedure developed by Hahn [68]. This procedure also cleaves the residual metal catalyst bound to the polymer, making it possible to remove the reduced catalyst by Celite filtration. Removing the catalyst provided polymers with excellent transparency at 193 nm and very low residual metal content (Ir: 0.04, Zn: 0.03%) as determined by trace metal analysis.

The results of the incorporation of CBN into copolymers of poly(CBN-co-MTDCA) for the ROMP techniques is shown in Fig. 3. The incorporation of CBN into the poly(CBN-co-MTDCA) made by ROMP is linearly dependent on its mole fraction in the feed.

6.4. Pd(II)-catalyzed polymerization of alicyclic monomers

Alicyclic monomers were polymerized with Pd(II) nitrile complex (as illustrated in Scheme 3 for CBN) and with (η^3 -allyl)Pd(II) complexes. Nitromethane and ethyl lactate were the two solvents best able to sustain the Pd(II)-initiated polymerization of the alicyclic monomers investigated. With ethyl lactate as the solvent, the polymerization remained homogenous throughout the entire duration, leading to higher yields than the polymerizations carried out in

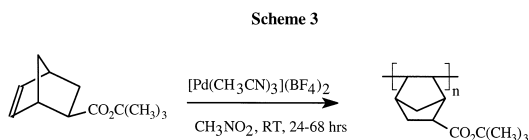
nitromethane. In polymerizations carried out in nitromethane, the polymer tended to precipitate out of solution after a critical molecular weight is reached, ca. Mw = 5000. Dichloroethane and chlorobenzene were the two solvents best able to sustain (allyl)Pd(II)-complexes initiated polymerization of the alicyclic monomers investigated in this study. On the average, (η^3 -allyl)Pd(II)-complexes gave consistently higher polymer molecular weights and higher yields than those obtained from the Pd(II) nitrile complex (see Tables 2 and 3). The polymers all show broad molecular weight distributions. The molecular weights of both type of polymers fall within the range of a few thousands to tens of thousands, which are suitable, in general for resist applications. They are in the same molecular weight regime as, for example, the novolacs used to formulate current I-line resists.

6.5. Polymer characterization

The thermogravimetric analysis profile of a typical resist copolymer, poly(CBN-co-NBCA) is shown in Fig. 4. All of the resist polymers, co- and terpolymers show similar TGA profiles. The deprotection temperature and decomposition temperature for the polymers are roughly 250°C and 400°C, respectively. The glass transition temperature (Tg) of the ROMP derived poly(CBN) is 90°C; the vinyl addition derived poly(CBN) is above the decomposition temperature, 250°C.

Fig. 5 is the IR spectrum of a typical alicyclic polymer (polyCBN). The spectrum shows evidence of *t*-butyl absorption at 1390–1370 cm⁻¹; the ester carbonyl stretch at 1730 and 1150 cm⁻¹; and the unique norbornene absorptions at 3060, 1575, 1340, and 720 cm⁻¹.

Representative ¹H NMR spectra of various alicyclic polymers made by the ROMP and Pd(II)-catalyzed polymerization techniques explored in this study are shown in Figs. 6 and 7. Characteristically, the polyCBN made by ROMP shows olefinic unsaturation around 5–6 ppm,



Scheme 3. Ethyl lactate can be used in place of nitromethane.

Table 2
 $(\eta^3\text{-Allyl})\text{Pd(II)}$ -catalyzed polymerization of alicyclic monomers

| M ^a | Pd(II) cat. ^b | [M]/[Pd(II)] ^c | Solv ^d | <i>t</i> (h) ^e | Mw ^f | Mw/Mn ^f | Yield (%) |
|-------------------|--------------------------|---------------------------|-------------------|---------------------------|-----------------|--------------------|-----------|
| CBN | Ia | 100 | CB | 36 | 22 400 | 4.51 | 75 |
| CBN | Ia | 400 | DCE | 36 | 30 400 | 1.48 | 50 |
| CBN | Ia | 400 | DCE | 18 | 7 300 | 2.14 | 80 |
| CBN | Ia | 168 | DCE | 18 | 9 600 | 2.66 | 50 |
| CBN | Ia | 943 | DCE | 48 | 17 500 | 1.72 | 25 |
| CBN | Ia | 1984 | DCE | 48 | 26 300 | 1.5 | 10 |
| NBCA ^g | Ia | 883 | DCE | 16 | 20 000 | 5.84 | 60 |
| MTD | Ia | 221 | DCE | 16 | 27 500 | 3.36 | 100 |
| TD | Ia | 232 | DCE | 18 | 11 100 | 6.04 | 100 |
| DNB | Ia | 156 | DCE | 18 | 422 400 | 5.45 | 90 |
| CBN/NB | Ia | 243 | DCE | 16 | 44 400 | 5.2 | 79 |
| CBN/NB | Ia | 300 | DCE | 16 | 49 300 | 9.00 | 76 |
| CBN/MTD | Ia | 221 | DCE | 18 | 16 500 | 2.51 | 90 |
| CBN/NB | Ia | 243 | DCE | 18 | 36 800 | 4.32 | 71 |
| CBN | Ib | 100 | CB | 36 | 13 900 | 1.51 | 60 |
| CBN ^h | Ib | 100 | – | 36 | 54 100 | 3.64 | 64 |
| CBN | Ib | 300 | DCE | 36 | 31 000 | 1.85 | 23 |
| CBN | Ib | 600 | DCE | 36 | 30 422 | 1.48 | 50 |
| CBN | Ib | 900 | DCE | 36 | 34 300 | 5.74 | 14 |
| CBN | Ic | 100 | DCE | 36 | | | 0 |
| CMN | Ic | 130 | CB | 36 | 12 800 | 1.52 | 25 |

^aAlicyclic monomer used in the addition polymerization. CBN, carbo-*t*-butoxy norbornene; CMN, carbomethoxynorbornene; NB, norbornene; NBCA, norbornene carboxylic acid; MTD, methyl tetracyclododecene; TD, tetracyclododecene.

^bPalladium catalyst. Catalyst Ia, $(\eta^3\text{-allyl})\text{Pd}(\text{SbF}_6)$; catalyst Ib, $(\eta^3\text{-allyl})\text{Pd}(\text{AgBF}_4)$; catalyst Ic, palladium tetrakis bis[fluoro-3-5-trifluoromethyl]phenyl borate.

^cMonomer to catalyst mole ratio.

^dSolvent. CB, chlorobenzene; DCE, dichloroethane; –, bulk polymerization.

^eReaction time at 25°C.

^fMw and Mw/Mn are the relative weight average molecular weight and the polydispersity index, respectively, determined by GPC, using polystyrene standards.

Table 3
 Addition polymerization of alicyclic monomers by Pd(II) nitrile catalysts^a

| Cat. | M | M/Cat. | <i>t</i> (h) | <i>T</i> (°C) | Mw | Mn | Yield (%) |
|------|------------------|--------|--------------|---------------|--------------------|-------------------|-----------|
| I | CBN | 300 | 72 | 25 | 10 000 | 6000 | 20 |
| I | CBN ^b | 300 | 168 | 25 | 2 500 | 1500 | 60 |
| I | CBN | 200 | 72 | 25 | 9 800 | 6000 | 30 |
| I | CBN | 160 | 96 | 25 | 6 700 | 4800 | 30 |
| I | CBN | 100 | 72 | 25 | 6 500 | 4500 | 32 |
| I | CBN | 80 | 24 | 25 | 3 500 | 2500 | 33 |
| I | CBN:NBCA = 80:20 | 200 | 72 | 25 | 10 000 | 6000 | 35 |
| I | CBN:NBCA = 75:25 | 200 | 96 | 25 | 9 000 ^c | 3000 ^c | 30 |
| I | CBN:NBCA = 90:10 | 100 | 68 | 25 | 9 000 | 6000 | 35 |
| I | CBN:NBCA = 80:20 | 100 | 150 | 25 | 10 000 | 6000 | 55 |
| I | CBN:NBCA = 70:30 | 100 | 65 | 25 | 9 300 | 5000 | 41 |
| I | CBN:NBCA = 80:20 | 50 | 72 | 25 | 5 000 | 4000 | 60 |
| I | NBCA | 100 | 150 | 25 | 10 000 | 6000 | 55 |

^aAll polymerizations were carried out with 52 mmol of monomer (exo:endo = 30:70) in 20 ml of nitromethane, except otherwise stated.

^bPolymerization was carried out in ethyl lactate.

^cMolecular weight was determined by light scattering. I: $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$; Bistetrafluoroborate tetrakis(cyanomethane) palladium.

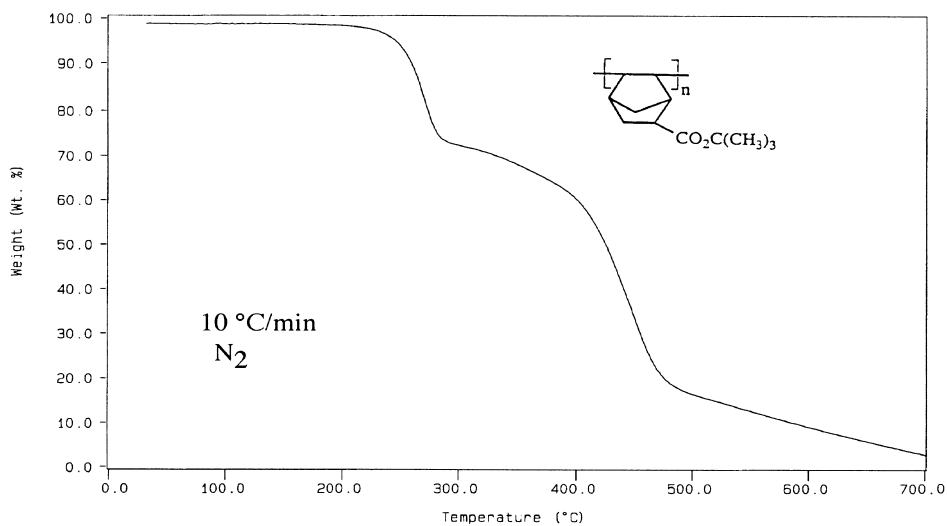


Fig. 4. TGA curve of a typical resist polymer, polyCBN. The other resist polymers, poly(CBN-co-NBCA), poly(CBN-co-MTDCA) show similar TGA profiles. Their decomposition temperatures are all in excess of 240°C.

which is assigned to the excluded double bonds in the polymer. The polyCBN made by Pd(II) complex catalyzed addition polymerization shows no such unsaturation. Rather, all the proton resonances in this polymer occur around the aliphatic region (1.5 to 4 ppm).

6.6. Process for removal of Pd(II)-complex from alicyclic polymers

Removal of metal catalysts from polymers continues to pose a major problem limiting the use of synthetic polymers in impurity-sensitive

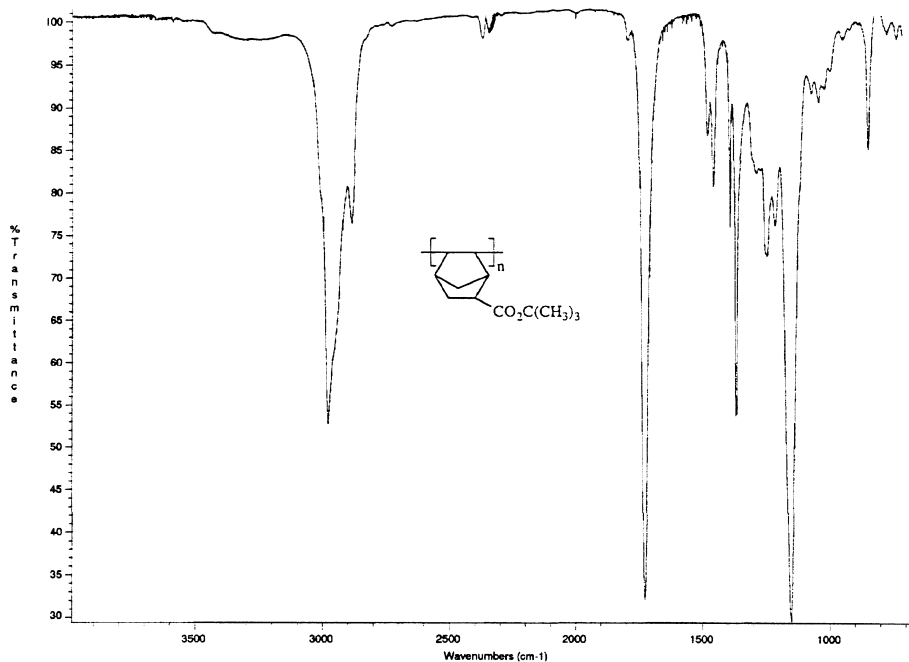


Fig. 5. IR spectra of polyCBN made with Pd(II) nitrile catalyst.

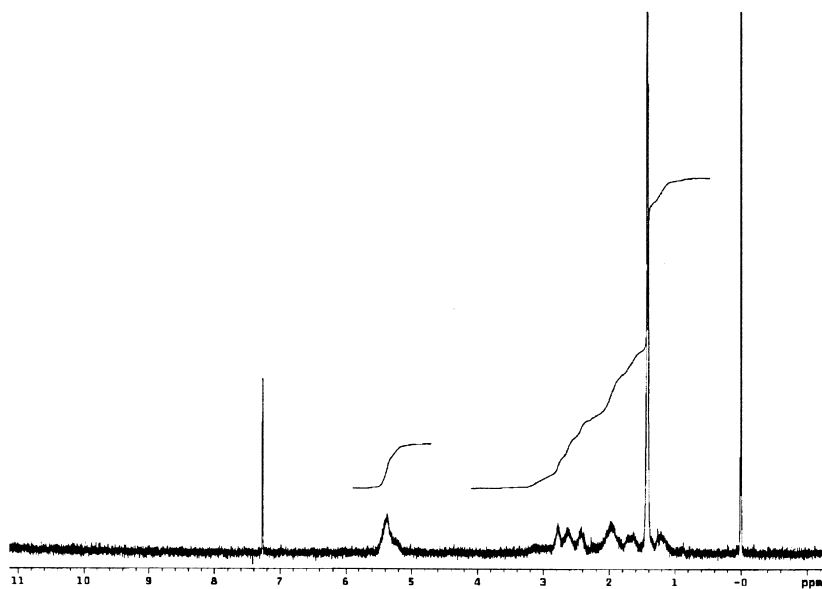


Fig. 6. ^1H NMR of poly(CBN) made by ring opening metathesis polymerization technique.

applications such as in the fabrication of semiconductor devices. To avoid this problem, researchers in the field have focused their attention on free radical polymerization systems. Unfortunately, many interesting monomers do not undergo free radical polymerization. The yields and molecular weights of some of those that do, especially the alicyclic monomers, tend to be very low. On the other hand, many transition

metal catalysts polymerize these monomers to very high yield and high molecular weight. Unfortunately, there does not exist a reliable process for removing the metal from the polymer once the polymerization is completed. Breunig and Risse [49] and Mathew et al. [54] pioneered the use of NaBH_4 in the demetallation of polymers made with Pd(II)-complexes. Unfortunately, this procedure is not efficient in

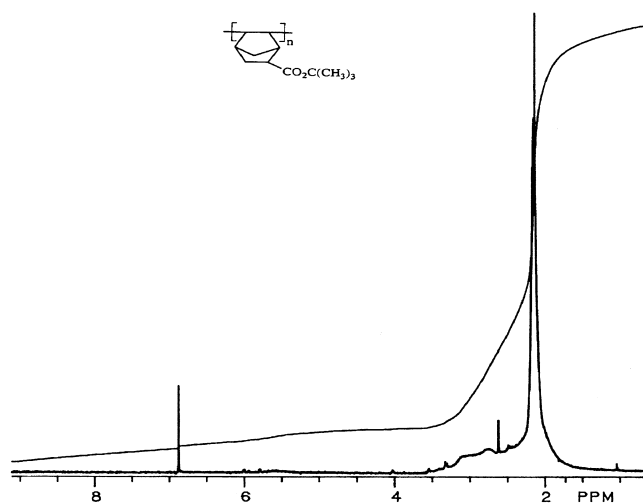


Fig. 7. ^1H NMR of poly(CBN) made by Pd(II) nitrile complex-initiated ionic polymerization technique.

removing the Pd(II)-metal complexes from the polymers studied in this project. Besides, the treatment of polymers bearing ester functional groups like the ones investigated in this study with NaBH_4 invariably reduces them to some extent to the corresponding alcohols, thereby altering the polymer. However, applying the hydrogenation process described above solves the above mentioned problems associated with NaBH_4 . By slowly bubbling H_2 gas through a solution of the polymer in any common solvent like THF, the Pd(II) metal catalyst is reduced to Pd(0), which agglomerates and can be easily filtered off, leaving a clean polymer. Trace metal analysis of a sample subjected to the procedure for only 1–2 h shows the following result: Pd, 130 ppm; B, 30 ppm. Treatment of the polymer for a much longer time results in significantly lower metal content.

6.7. Lithographic evaluation of alicyclic polymer photoresist systems

Our resists materials designed for 193 nm exposure have not only very high sensitivity, they have high transparency at the exposure wavelength and high stability to reactive ion etching conditions.

The new resists are formulated by dissolving the alicyclic polymer and a photoacid generator (PAG) such as triphenylsulfonium hexafluoroantimonate in an appropriate solvent such as propyleneglycol monomethylether acetate. Upon irradiation, the PAG in the resist film generates a latent image of strong acid, which upon baking, catalyzes the thermolysis reaction of the *t*-butyl ester pendant group, leading to the formation of isobutylene and a polymer with a norbornene carboxylic acid unit, which has a higher solubility in basic developing solvent

Table 4
Optical properties of typical photoresists

| Photoresist polymer | A | B (Å^2) | C (Å^4) |
|----------------------------|--------|----------------------|-------------------------|
| Poly(CBN- <i>co</i> -NBCA) | 1.4818 | 4.0083×10^5 | 1.5346×10^{11} |

Table 5

Absorption of a 1.0 μm thick film of resist polymers coated on quartz

| Polymer | UV absorbance/micron at 193 nm |
|-----------------------------|--------------------------------|
| PolyCBN | 0.4 |
| PolyCBN- <i>co</i> -NBCA | 0.37 |
| Poly(CBN- <i>co</i> -MTDCA) | 0.43 |
| Poly(CBN- <i>co</i> -NME) | 0.5 |

than its masked precursor. Development of the exposed and baked film in aqueous base generates a positive tone image of the mask.

6.8. Optical study of alicyclic polymer photoresist systems


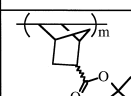
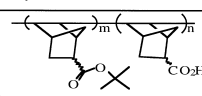
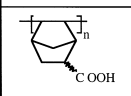
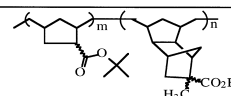
Over a limited wavelength range, the function relating the index of refraction of the photoresist to the incident wavelength of the incident light (the dispersion curve) can be adequately described by the following Cauchy empirical relation:

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4$$

where *A*, *B*, and *C* are the Cauchy coefficients. The Cauchy coefficients of a typical alicyclic polymer photoresist are summarized in Table 4.

Table 6

Etch rate data of representative resist polymers

| Resist Material | Etch Rate | Resist Material | Etch Rate |
|---|-----------|---|-----------|
| APEX-E | 1.00 |  Poly(NBE) | 0.31 |
|  Poly(CBN) | 0.85 |  Poly(CBN- <i>co</i> -NBCA) | 0.90 |
|  Poly(NBCA) | 0.75 |  Poly(CBN- <i>co</i> -MTDCA) | 0.80 |

Measurements were made relative to APEX-E DUV resist.

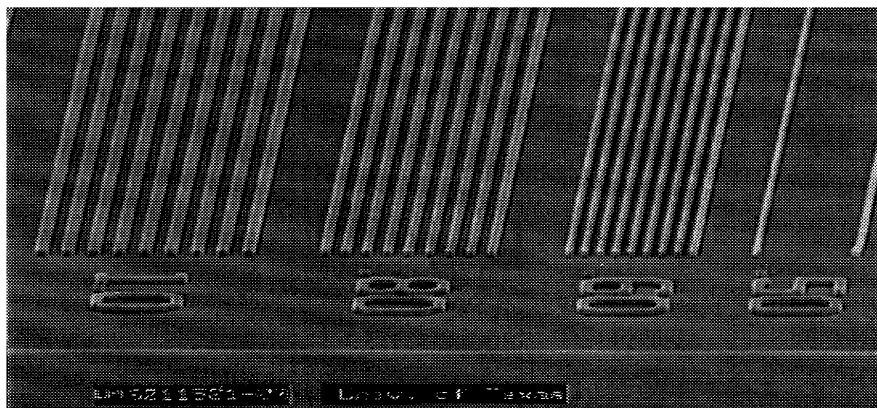


Fig. 8. Scanning electron micrograph image of 0.4–1.0 μm lines and spaces printed in resist formulated with poly(CBN-*co*-NBCA) made by Pd(II) nitrile complex-initiated addition polymerization. Image was printed with a 248 nm GCA-XLS Stepper with KrF exciplex laser illumination source.

These coefficients were used in the calculation of the resist film thickness. The UV absorption spectra of typical resist polymers are shown in Table 5.

6.9. Plasma etch resistance of the resist polymers

The dry etch resistance of a representative set of the polymers is shown in Table 6. These polymers etch at about the same rate or slower than APEX-E™ resist under Cl_2/HBr etching conditions.

6.10. Lithographic evaluation of photoresist compositions comprising alicyclic polymers

Preliminary evaluations of the resists formulated with poly(CBN-*co*-NBCA) and poly(CBN-*co*-MTDCA) using KrF (248 nm) and ArF exciplex (193 nm) laser exposure tools resulted in good performance with dose to clear (E_0) in the range of 5–25 mJ/cm^2 . Resists formulated with poly(CBN-*co*-NBCA) had cracking and adhesion problems. A scanning electron microscope (SEM) image showing 0.4–1.0 μm lines and spaces printed at 248 nm

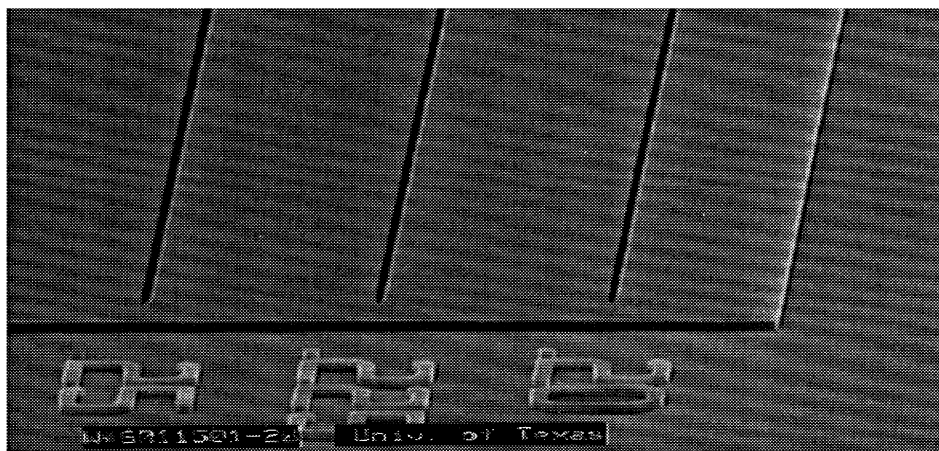


Fig. 9. Scanning electron micrograph image of 0.2, 0.225, and 0.25 μm trenches printed in resist formulated with poly(CBN-*co*-NBCA) made by vinyl addition copolymer.

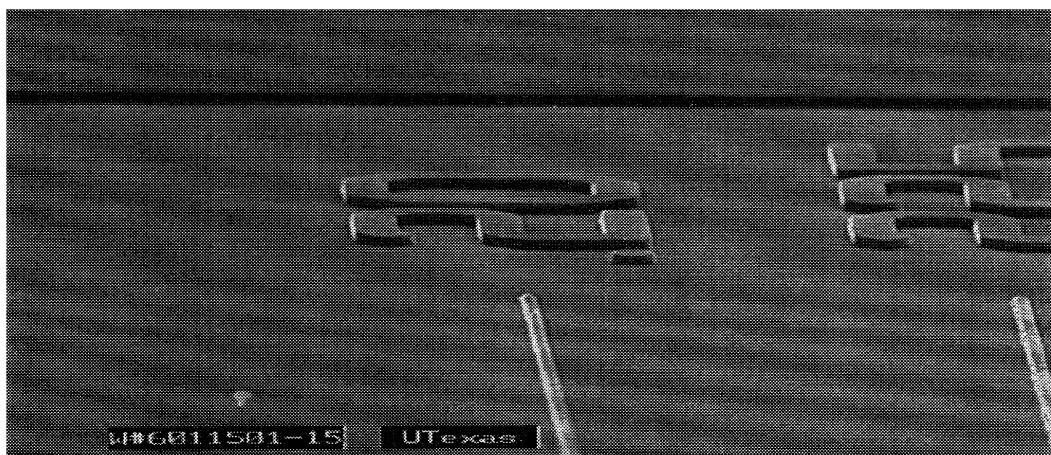


Fig. 10. Scanning electron micrograph image of 0.2 and 0.25 μm isolated lines printed with resist formulated with poly(CBN-*co*-MTDCA) made by ROMP. Image quality is excellent, with no lift-off of small features smaller as is in the case in Fig. 4. Image was printed with a 248 nm GCA-XLS Stepper with KrF exciplex laser illumination source.

in a typical poly(CBN-*co*-NBCA) (made by Pd(II)-catalyzed addition polymerization) resist formulation is shown in Fig. 8. Note that the image quality is excellent, but features with dimensions below 0.5 μm have lost adhesion to the substrate. Fig. 9 is a SEM image of 0.2–0.25 μm trenches printed with the same resist. Clearly, this resist is not resolution limited, but adhesion limited. Fig. 10 is a SEM of 0.2 and 0.25 μm isolated lines printed in resist formulated with unhydrogenated poly(CBN-*co*-MTDCA) made by ROMP. Image quality is good, with no lift-off of small features smaller as is the case in Fig. 8. However, resists formulated with hydrogenated poly(CBN-*co*-MTDCA) have serious adhesion problems.

7. Conclusions

We have synthesized and characterized a series of alicyclic polymers designed for use as matrix resins for 193-nm lithography. These polymers were synthesized by Pd(II)-catalyzed addition and ring opening metathesis polymerization techniques. The polymers derived from ring opening metathesis polymerization were hydrogenated to provide another class of

this kind of materials. Methods for removing residual metal complexes like Pd(II)- and Ir(IV)-complexes from these types of polymers were developed. The low absorbance of these polymers at 193 nm and their high dry etch resistance make them attractive candidates for 193 nm imaging. When formulated with onium-type photoacid generators in propylene glycol monomethyl ether acetate, these photoresists have demonstrated high resolution and high sensitivity.

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