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Metal-Catalyzed Vinyl Addition Polymers for 157 nm Resist Applications. 2. Fluorinated Norbornenes: Synthesis, Polymerization, and Initial Imaging Results

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ABSTRACT: Three metal-catalyzed vinyl addition copolymers derived from partially fluorinated norbornenes and tricyclononenes have been synthesized and evaluated for use in formulating photoresists for 157 nm lithography imaging. The transparency of these polymers at 157 nm, as measured by variable angle spectroscopic ellipsometry (VASE), is greatly improved over their nonfluorinated counterparts. The results of preliminary lithographic evaluations of resists formulated from these polymers alone and with the addition of several new fluorinated dissolution inhibitors are presented. Images as small as 70 nm have been printed in some formulations.

Introduction

Advances in microlithographic materials over the past 30 years have contributed significantly to the production of higher-performing semiconductor devices. Key to these advances is the design of polymers for use with each new imaging technology. Polymers tailored for 365, 248, and 193 nm optical lithography have all demonstrated high resolution in part because they are sufficiently transparent at their respective wavelengths. As the industry prepares for 157 nm imaging, new polymers will be needed. However, designing a single-layer, chemically amplified photoresist[1] that is capable of printing sub-100 nm lines at practical thickness (∼200−250 nm) using 157 nm radiation is a significant challenge since water, oxygen gas, and even simple hydrocarbons like polyethylene absorb very strongly in this spectral region. The difficulty lies in designing a polymer that not only is transparent at this very short wavelength but also possesses all of the characteristics required of a good resist such as resistance to plasma etching processes, adhesion to a wide range of substrates, and exceptional mechanical properties. It is therefore not surprising to many industry experts that the most challenging aspect of implementing 157 nm imaging is the development of a functional photoresist.

The photoresist can be divided into four functional modules[2] to simplify and better understand the design problem: a backbone that tethers the functional substituents and provides basic mechanical properties, an etch barrier that provides resistance to reactive ion etch (RIE), an acidic group that provides solubility in the industry standard tetramethylammonium hydroxide (TMAH) developer, and an acid-labile protecting group to enable chemical amplification.[3] Each module must be transparent to 157 nm radiation, and we have concentrated our efforts on the use of fluorinated compounds to realize this goal.[2,4,5] Hexafluoro-2-propanol and α-trifluoromethylcarboxylic acid groups have been identified as relatively transparent acidic group modules.[4] Both groups may be incorporated into a norbornane skeleton, which is advantageous for two reasons: the groups significantly lower the absorbance of the functionalized norbornanes compared to their nonfluorinated analogues, and carbon-rich alicyclic structures provide good etch resistance (as demonstrated in the 193 nm resists[6,7]). In addition, judicious introduction of fluorine onto norbornane can cause a very significant reduction in absorbance at 157 nm. Substitution of an electron-withdrawing group such as a fluorine or a trifluoromethyl group at the 2-position of norbornane enhances the transparency more efficiently than substitution at the 7-position (single carbon bridge).[8]

The knowledge gained from these preliminary investigations guided our design of functional polymers for imaging at 157 nm, inspiring the exploration of a wide variety of polymer platforms. These include metal-catalyzed vinyl addition polymers of fluorinated norbornenes and tricyclononenes, carbon monoxide copolymers of the same compounds, and free-radical copolymers of these compounds with other electron-deficient monomers. This paper reports our recent progress in developing 157 nm resist materials based on the first of these three polymer systems. Progress on the other two platforms and our work on silicon-based platforms will be discussed elsewhere.[9]

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Experimental Section

Materials. All starting materials were procured from Aldrich except 1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol (AZ Clariant), triphenylsulfonium nonaflate (AZ Clariant), 1,4-bis(2-hydroxyhexafluoroisopropyl)benzene (Oakwood), and 2-(trifluoromethyl)acrylic acid (Honeywell and Central Glass Co.) and used as received unless noted otherwise. All solvents were dried by the standard methods. All manipulations and polymerizations with air-sensitive materials were performed in a helium-filled drybox or using standard Schlenk vacuum line techniques under argon. All liquid reagents used for vacuum-UV measurements were distilled from appropriate drying agents, thoroughly degassed by freeze, pump, thaw cycles, and sealed in glass ampules under vacuum. Diazomethane was generated from Diazald by the standard procedure.[10]

Instruments and Equipment. Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300 or a Varian Unity Plus 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{19}F, 282 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, $CFCl_3$) or to the chemical shift of the solvent. Infrared spectra were recorded on a Nicolet Avatar *360* IR spectrometer. Melting points are uncorrected. Mass spectra were measured on a Finnigan MAT TSQ-700 spectrometer. Molecular weights (M_w) and polydispersity indices (PDI) were measured from THF solutions using a Viscotek GPC equipped with a set of two 5 mm cross-linked polystyrene columns (linear mix and 100 Å) from American Polymer Standards and are reported relative to polystyrene standards. Polymers containing acidic functional groups were pretreated with either diazomethane or iodomethane/DBU before GPC measurement, unless noted otherwise. Differential scanning calorimetry (DSC) measurements and thermal gravimetric analysis (TGA) were performed on a Perkin-Elmer Series-7 thermal analysis system. Gas chromatographs were recorded on a Hewlett-Packard 5890 Series II with an HP-5 (cross-linked 5% PH ME siloxane) capillary column and flame ionization detector (FID).

Vacuum-UV Spectroscopy. Gas-phase VUV measurements were made on an Acton CAMS-507 spectrophotometer fitted with a custom-made gas cell attachment. The details of the cell design and implementation have been described previously.[5] VUV spectra of polymer films were calculated from measurements made with a J.A. Woollam VU301 variable angle spectroscopic ellipsometer (VASE) and/or measured with the Acton CAMS-507 spectrophotometer. The films were cast on either silicon wafers (VASE) or calcium fluoride disks (Acton) from solutions in propylene glycol methyl ether acetate (PGMEA) or cyclohexanone and baked at 100−130 °C for at least 5 min prior to analysis. All absorbance data reported are in base 10.

Imaging. All imaging work was performed on an Exitech 157 nm small field (1.5 × 1.5 mm^2) mini-stepper (0.6 NA) using either a binary mask (σ 0.7) or phase-shift mask (σ 0.3) at International SEMATECH in Austin, TX. Scanning electron micrographs were collected on a JEOL JWS-7550, and cross-sectional data were collected on a Hitachi 4500 microscope. Coating, baking, and development of resist films were performed using an FSI Polaris 2000 track. Thickness measurements were made on a Prometrix interferometer. A typical resist formulation was prepared by mixing the polymer with 6 wt % (relative to polymer) photoacid generator (triphenylsulfonium nonaflate) and 0.3 wt % tetrabutylammonium hydroxide (TBAH) as the base to control acid diffusion and reduce T-topping. Dissolution inhibitors were mixed with the polymer to the desired ratio. The entire mixture was diluted in PGMEA to provide a viscosity that provides resist thicknesses of approximately 100−200 nm after spinning the resist at 2500 rpm onto a silicon wafer that had been previously coated with ~80 nm BARC (bottom antireflective coating, Shipley AR19). The postapply bake was 140 °C for 60 s, and the postexposure bake was 130 °C for 90 s, unless stated otherwise. The exposed resists were developed in the industry-standard 0.26 N tetramethylammonium hydroxide (TMAH) developer.

Synthesis. 3-(Bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol (NBHFA, 1). To a 1 L Parr pressure reactor containing a stir bar were added 1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol:ether complex (OH:ether = 10:1, 402 g, 1.93 mol), freshly cracked cyclopentadiene (51.0 g, 772 mmol), and hydroquinone (0.40 g, 3.63 mmol). The bomb was sealed and heated to 175 °C for 24 h and then cooled to room temperature. The unreacted ether complex was recovered by ambient pressure distillation. The product and cyclopentadiene were separated by vacuum distillation (30 mmHg, 85−94 °C) to yield 136 g (64%) of impure product. The product was dissolved in hexanes (400 mL) and extracted with 4 M NaOH (3 × 300 mL). The brown aqueous extract was reacidified with concentrated HCl until the aqueous phase was neutral. The product was extracted with hexanes (3 × 300 mL), dried over $MgSO_4$, and concentrated in vacuo to yield a slightly yellow viscous liquid that is a mixture of *endo* and *exo* (8:2 by NMR analysis) product (129 g, 61%). The product was redistilled under vacuum to remove the yellow color, but this did not appear to affect subsequent chemistry. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.63 (m, 1H), 1.22−1.50 (m, 3H), 1.61−2.12 (m, 3H), 2.37 (bs, 1H), 2.75−2.92 (m, 2H), 5.92−6.22 (m, 2H). ^{19}F NMR (DMSO-d_6, 282 MHz, ppm): δ −81.6 (q, J = 9.9 Hz, *endo* 3F), −82.1 (q, J = 7.9 Hz, *exo* 3F), −82.2 (q, J = 8.2 Hz, *exo* 3F), −82.6 (q, J = 9.9 Hz, *endo* 3F). IR (KBr, cm^{-1}): 3598, 3487, 3061, 2965, 2868, 1214, 1141, 716. HRMS−CI (*m*/*z*): $[M + H]^+$ calcd for $C_{11}H_{13}F_6O$, 275.087; found, 275.086.

***tert*-Butyl Bicyclo[2.2.1]hept-5-ene-2-carboxylate (NBTBE, 2).** To a three-neck flask equipped with a stir bar, addition funnel, and reflux condenser were added *tert*-butyl acrylate (237 g, 1.84 mol) and 4-*tert*-butylcatechol (1 g, 6.02 mmol). This mixture was warmed to 50 °C, and then freshly cracked cyclopentadiene (122 g, 1.84 mol) was added dropwise. The resulting solution was stirred for 1 h at 80 °C. The product was purified by vacuum distillation (78−80 °C/5 mmHg) to give a clear liquid that is a mixture of *endo*/*exo* (71/29 by GC) isomers (247 g, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.40 (s, 9H, *t*-Bu), 1.15−3.16 (m, 7H, aliphatic), 5.92−6.18, (m, 2H, CH═CH). IR (NaCl, cm^{-1}): 3062, 2975, 2943, 2869, 1727 (C═O), 1479, 1456, 1390, 1367, 1336, 1272, 1253, 1151, 1109, 1019, 852, 709. HRMS−CI (*m*/*z*): $[M + H]^+$ calcd for $C_{12}H_{19}O_2$, 195.1390; found, 195.1385.

Poly(NBHFA-*co*-NBTBE) (3). Typical Ni(II) procedure used to make a range of copolymers: To a 50 mL flask were added (η^6-toluene)bis(pentafluorophenyl)nickel(II) (49.0 mg, 0.103 mmol) and toluene (10 mL) in an inert atmosphere (argon). NBHFA (**1**, 2.12 g, 7.73 mmol) and NBTBE (**2**, 0.50 g, 2.58 mmol) were added to a 50 mL Schlenk tube and degassed by three freeze−pump−thaw cycles. The toluene solution containing the catalyst was transferred to the Schlenk tube via cannula, and the mixture was stirred at room temperature overnight. The dark orange solution was poured into 50 mL of methanol, and the white polymer was filtered and dried in vacuo to give desired product (1.45 g, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.21 (bs, *t*-Bu), 1.0−2.2 (bm, aliphatic), 3.0 (bs, OH). 19F NMR ($CDCl_3$, 282 MHz, ppm): δ −76.1. IR (KBr, cm^{-1}): 3600, 3431, 2955, 2883, 1711 (C═O), 1460, 1378, 1209, 1137, 1014, 840. GPC: M_n = 26 000; PDI = 1.71 (not treated with diazomethane). Composition as determined by TGA: NBHFA/ NBTBE = 58/42.

Poly(NBHFA-*co*-NBTBE) (3). A typical Pd(II) procedure used to make a range of copolymers: To a 50 mL round-bottom flask equipped with a stir bar were added allylpalladium chloride dimer (951 mg, 2.60 mmol) and silver hexafluoroantimonate (1.79 g, 5.20 mmol) in a drybox. Dichloromethane (25 mL) was added, and the mixture was stirred at room temperature for 20 min. The mixture was filtered through a 0.45 mm syringe filter into a 100 mL round-bottom flask containing a solution of NBHFA (**1**, 10.0 g, 36.4 mmol) and NBTBE (**2**, 3.03 g, 15.6 mmol) in dichloromethane (25 mL). The resulting solution was stirred for 4 h at room temperature and then transferred to a 100 mL round-bottom flask contain-

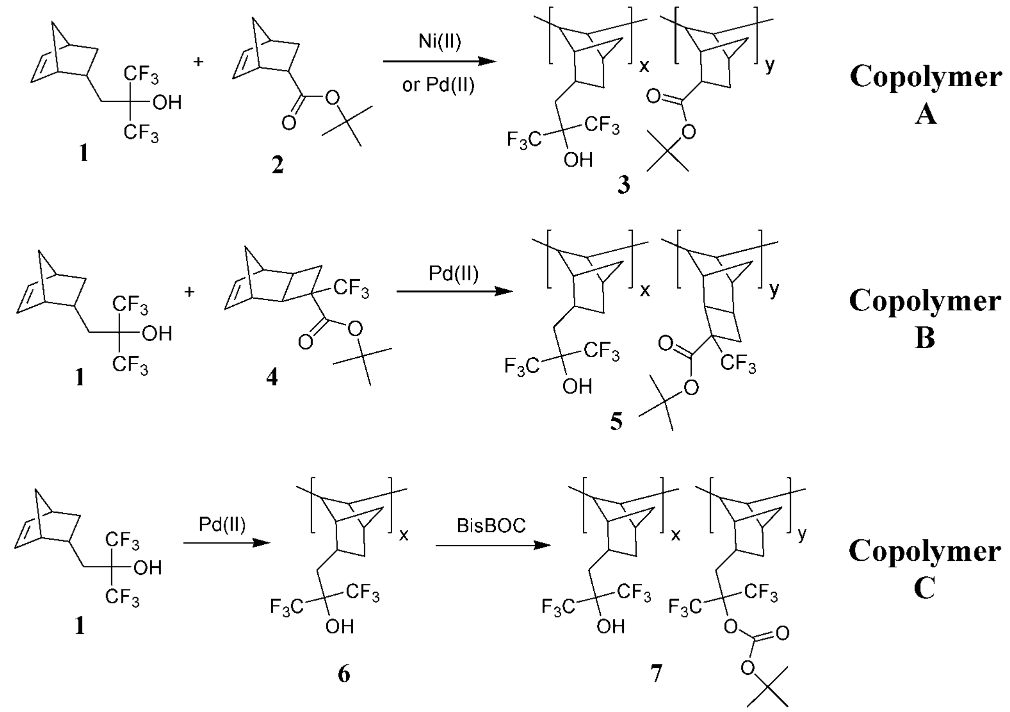


Figure 1. Three metal-catalyzed vinyl addition copolymers that have been made for 157 nm resist applications.

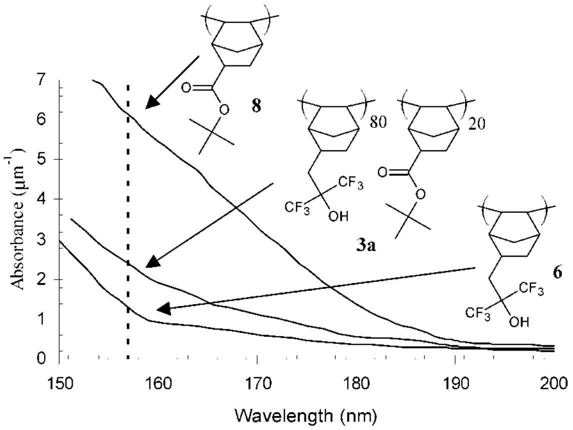


Figure 2. VASE spectrum of NBHFA/NBTBE copolymer (**3a**).

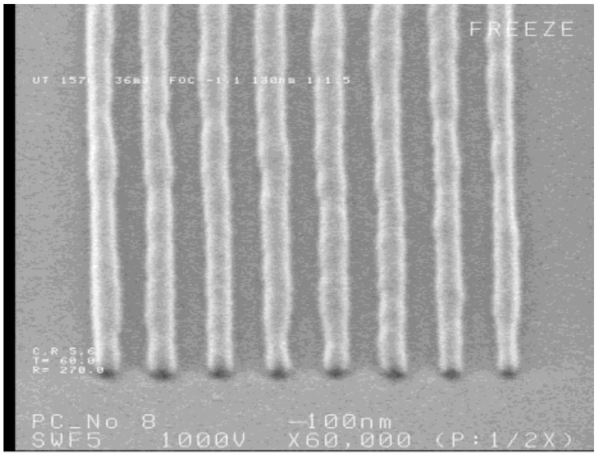


Figure 3. 130 nm lines in resist formulated from NBHFA/NBTBE copolymer **3a**. Note evidence of swelling.

ing polymer-bound 2,6-di-*tert*-butylpyridine (1.29 g). The reaction mixture was stirred at room temperature for 96 h, then filtered through Celite to remove the polymer-bound base, concentrated in vacuo, and precipitated into hexanes (800 mL).

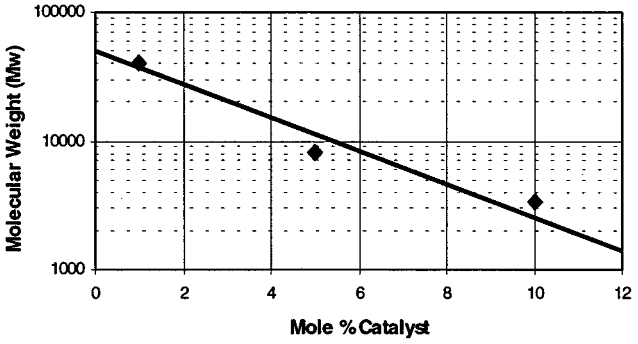


Figure 4. Effect of catalyst loading on the molecular weight of vinyl addition polymer (**6**).

The resulting gray powder was collected by vacuum filtration and dried in vacuo at 50 °C for 4 h. The crude polymer was dissolved in ethyl acetate (150 mL), and hydrogen gas was bubbled through the solution for 30 min. The solution was then stirred for another 2 h to allow the black solid (Pd) to coagulate and precipitate. The black solid was removed by filtration through Celite. The filtrate was treated with activated carbon and stirred for 3 h. The activated carbon was removed by filtration through Celite, and the resulting filtrate was washed with saturated $NaHCO_3$, water, and brine, dried with $MgSO_4$, filtered, concentrated in vacuo at 50 °C, and precipitated into hexanes. Filtration provided the product as a white powder (9.2 g, 70%), which was dried under a high vacuum (0.5 mmHg) at 150 °C. ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 1.40 (bs, *t*-Bu), 0.40−3.20 (bm, aliphatic), 7.68 (bs, OH). IR (KBr, cm^{-1}): 3600, 3421, 2955, 2873, 1700 (C═O), 1445, 1367, 1219, 1142, 1019. GPC: M_w = 3150; PDI = 3.38 (not treated with diazomethane). Composition as determined by TGA: NBHFA/NBTBE = 65/35. A_{157} = 2.78 μm^{-1}.

***tert*-Butyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (TCNCF$_3$TBE, 4).** To a 300 mL Parr pressure reactor equipped with a stir bar were added quadricyclane (20.0 g, 217 mmol) and *tert*-butyl 2-(trifluoromethyl)acrylate (**9**, 46.0 g, 238 mmol). The pressure reactor was sealed, and the reaction mixture was stirred overnight at 100 °C. The crude product was allowed to cool to room temperature and fractionally distilled under vacuum. The product was collected at 90−94 °C/6 mmHg as a clear oil (52.0 g, 83%). ^1H NMR

($CDCl_3$, 300 MHz, ppm): δ 1.50 (s, 9H, *t*-Bu), 1.25−3.02 (m, 8H, aliphatic), 5.95−6.05 (m, 2H, CH=CH). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −65.0, −74.0. IR (NaCl, cm^{-1}): 3050, 2975, 1736 (C=O), 1475, 1372, 1316, 1280 (C−F), 1255, 1157, 1127, 840. HRMS−CI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{17}F_3O_2$, 289.141; found, 289.142.

Poly(NBHFA-*co*-TCNCF$_3$TBE) (5, 23, 24). The procedure described above for poly(NBHFA-*co*-NBTBE) (**3**) was used here to make a wide range of copolymer ratios. Higher molecular weight polymers were obtained by using less Pd(II) catalyst, and lower molecular weight polymers were obtained by using more catalyst, as shown in Figure 4. Yields = 20−30%. For **23**, ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 1.40 (bs, *t*-Bu), 0.40−3.60 (bm, aliphatic), 7.67 (bs, OH). FT-IR (KBr, cm^{-1}): 3600, 3467, 2955, 2878, 1716 (C=O), 1613, 1460, 1371, 1219, 1137, 1014, 988, 707, 661. GPC: M_w = 13 800; PDI = 2.19 (not treated with diazomethane). Composition as determined by TGA: NBHFA/TCNCF$_3$TBE = 74/26. A_{157} = 1.97 μm^{-1}. For **24**, ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 1.41 (bs, *t*-Bu), 0.40−3.20 (bm, aliphatic), 7.67 (bs, OH). FT-IR (KBr, cm^{-1}): 3595, 3452, 2955, 2878, 1710 (C=O), 1613, 1454, 1372, 1214, 1142, 1024. GPC: M_w = 5200; PDI = 2.78 (not treated with diazomethane). Composition as determined by TGA: NBHFA/TCNCF$_3$TBE = 83/17. A_{157} = 1.67 μm^{-1}.

Poly(3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol) (Poly(NBHFA), 6). To a 100 mL round-bottom flask equipped with a stir bar were added allylpalladium chloride dimer (1.33 g, 3.65 mmol) and silver hexafluoroantimonate (2.51 g, 7.29 mmol) in a drybox. Dichloromethane (50 mL) was added, and the mixture was stirred at room temperature for 20 min. The mixture was filtered through a 0.45 mm syringe filter into a 100 mL round-bottom flask containing a solution of NBHFA (**1**, 20.0 g, 72.9 mmol) in dichloromethane (50 mL). The clear yellow solution was stirred overnight at room temperature and then precipitated into hexanes (2 L). The light yellow powder was collected by vacuum filtration and dried in vacuo overnight. The resulting polymer (20.0 g) was dissolved in ethyl acetate (250 mL), and hydrogen gas was bubbled through the solution for 30 min. The solution was stirred for another 2 h, and the black solid was removed by filtration through a bed of Celite. The filtrate was treated with activated carbon and stirred for 4 h. The activated carbon was removed by filtration through Celite, and the resulting filtrate was concentrated and precipitated into hexanes (2 L). Vacuum filtration afforded a white powder (11.0 g, 55%). ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 0.50−2.80 (bm, aliphatic), 7.6 (bs, OH). ^{19}F NMR (CD_3OD, 282 MHz, ppm): δ −75.0 to −77.0. IR (KBr, cm^{-1}): 3600, 3471, 2954, 2881, 1453, 1214, 1145, 1025, 714. GPC: M_w = 8150; PDI = 2.11. A_{157} = 1.15 μm^{-1}.

Poly(NBHFA-*co*-NBHFABOC) (7, 25). A typical procedure used to make a range of copolymer ratios: To a 100 mL round-bottom flask equipped with a stir bar were added poly(NBHFA) (**6**, 1.35 g, 4.92 mmol) and di-*tert*-butyl dicarbonate (480 mg, 2.22 mmol) in freshly distilled THF (13 mL). The solution was stirred for 5 min at room temperature, followed by the addition of 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 30 mg, 0.246 mmol). Upon addition of DMAP, the solution turned slightly brown, and a slow evolution of gas was observed. The reaction mixture was stirred at room temperature overnight. The polymer was precipitated into a mixture of water (100 mL) and methanol (30 mL), filtered, and dried in vacuo at 50 °C to yield a white powder (1.34 g, 88%). For **25**, ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 1.48 (bs, *t*-Bu), 0.60−3.00 (bm, aliphatic), 7.66 (bs, OH). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −72.7 (bs, $C(CF_3)_2OC$), −77.6 (bs, $C(CF_3)_2OH$). IR (KBr, cm^{-1}): 3598, 3465, 2953, 2880, 1771 (C=O), 1609, 1440, 1373, 1285 (C−F), 1250, 1215, 1134, 985, 871, 713. Composition as determined by TGA: NBHFA/NBHFABOC = 67/33. A_{157} = 2.17 μm^{-1}.

Poly(NBTBE) (8). This polymer was made by using a similar procedure to the one used for making **3** (allyl Pd catalyst with proton sponge). Yield = 60%. ^1H NMR (acetone-d_6, 300 MHz, ppm): δ 1.0−3.0 (m, aliphatic), 1.40 (bs, *tert*-butyl). IR (KBr, cm^{-1}): 2971, 2879, 2571, 1724 (C=O), 1455, 1392, 1367, 1290, 1151, 1049, 886, 846, 660. GPC: M_w = 5380; PDI = 1.79. A_{157} = 6.02 μm^{-1}.

***tert*-Butyl 2-(Trifluoromethyl)acrylate (9).** To a 300 mL Parr pressure reactor containing a stir bar was added 2-(trifluoromethyl)acrylic acid (15.0 g, 94.9 mmol) in diethyl ether (35 mL). This solution was cooled to −40 °C with a dry ice/2-propanol bath. Isobutene (35 mL) was condensed into the pressure reactor. To this solution was added concentrated H_2SO_4 (1 mL), and the bomb was securely sealed. The reaction was stirred at room temperature overnight, cooled to −40 °C, and poured into ice-cold 1 N NaOH (150 mL). The organic layer was separated, and the aqueous layer was extracted two times with diethyl ether (35 mL). The combined organic solutions were washed with water until neutral, dried over $MgSO_4$, and dried in vacuo to give a clear liquid (20.3 g, 99%). The product was further purified by vacuum distillation (73 °C/100 mmHg). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.50 (s, 9H, *t*-Bu), 6.30−6.31 (m, 1H, C*H*=CH_2), 6.57−6.59 (m, 2H, CH=CH_2). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −66.1. IR (NaCl, cm^{-1}): 2980, 2934, 1731 (C=O), 1405, 1365, 1348, 1268 (C−F), 1113, 849. HRMS−CI (*m/z*): $[M + H]^+$ calcd for $C_8H_{11}F_3O_2$, 195.063; found, 195.063.

***tert*-Butyl 2-(Trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (NBCF$_3$TBE, 10).** To a 100 mL three-neck flask equipped with a stir bar, addition funnel, and reflux condenser was added *tert*-butyl 2-(trifluoromethyl)acrylate (**9**, 11.7 g, 59.8 mmol) in THF (50 mL). Freshly cracked cyclopentadiene (11.9 g, 89.7 mmol) was added dropwise, and the resulting solution was stirred at room temperature overnight. The product was purified by vacuum distillation (75−77 °C/10 mmHg) to yield a colorless liquid (13.5 g, 84%) that is a mixture *endo* and *exo* product (1:1). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.41−1.54 (9H, *endo*/*exo t*-Bu), 1.28−3.38 (m, 6H, aliphatic), 6.01−6.03 (m, 1H, CH=CH), 6.25−6.28 (m, 1H, CH=CH). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −64.7, −67.2. IR (NaCl, cm^{-1}): 3071, 2979, 2887, 1731 (C=O), 1476, 1459, 1394, 1370, 1336, 1283 (C−F), 1225, 1155, 1120, 1100, 1072, 1047, 1038, 1015, 958, 931, 909, 857, 844, 822, 800, 787, 733, 717, 696, 666. HRMS−CI (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{18}F_3O_2$, 263.126; found, 263.126.

***tert*-Butyl 3-(Bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propyl carbonate (NBHFABOC, 12).** To a 250 mL three-neck flask containing a stir bar and thermometer were added NBHFA (**1**, 15.5 g, 56.5 mmol), dry THF (150 mL), and di-*tert*-butyl dicarbonate (13.6 g, 62.2 mmol). The solution was stirred at room temperature for 5 min, and then 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 0.69 g, 5.65 mmol) was added. Upon addition of DMAP, the solution turned slightly brown, and a slow evolution of gas (CO_2) was observed. No elevation of temperature was seen. After the evolution of gas had ceased (10 min), the solution was stirred at room temperature overnight. The solvent was removed in vacuo, and the residue was dissolved in diethyl ether (200 mL) and washed with 2 wt % HCl. The resulting solution was washed with saturated $NaHCO_3$ (200 mL) and brine (200 mL). After drying over $MgSO_4$, the product was purified by column chromatography using silica gel and hexanes as the eluent to give the title compound as a colorless liquid (21.1 g, 93%). A sample of the product was further purified by vacuum distillation (115−120 °C/6 mmHg). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.64 (m), 1.23−1.45 (m), 1.50 (d, *J* = 1.2 Hz, *t*-Bu), 1.52 (d, *J* = 1.2 Hz, *t*-Bu), 1.56 (s), 1.92−2.06 (m), 2.25 (bs), 2.43 (m), 2.48 (m), 2.63 (bs), 2.79 (bs), 2.85 (bs), 5.98 (m), 6.07 (m), 6.21 (m). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −72.4 (q, *J* = 7.9 Hz, *endo* 3F), −72.5 (q, *J* = 7.9 Hz, *endo* 3F), −72.7 (q, *J* = 10.2 Hz, *exo* 3F), −72.9 (q, *J* = 10.2 Hz, *exo* 3F). IR (NaCl, cm^{-1}): 3061, 2974, 2873, 1773 (C=O), 1477, 1440, 1373, 1330, 1287 (C−F), 1249, 1218, 1132, 1092, 981, 873, 781, 710. HRMS−CI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{21}F_6O_3$, 375.1395; found, 375.1398.

Poly(NBHFA-*co*-carbon monoxide). To a 300 mL Parr pressure reactor were added NBHFA (**1**, 4.00 g, 14.6 mmol), palladium(II) acetate (3.3 mg, 0.015 mmol), copper(II) tosylate (0.060 g, 0.15 mmol), 2,2′-bipyridine (0.069 g, 0.44 mmol), benzoquinone (0.318 g, 2.94 mmol), and methanol (15 mL). The reactor was sealed and pressurized with carbon monoxide to 440 psi. The reaction mixture was stirred at 90 °C overnight, and then excess carbon monoxide was vented. Diethyl ether (150 mL) was added to produce a red solution, which was washed with a solution of 5 wt % Na_2CO_3 (5 × 100 mL) and then saturated sodium chloride (2 × 100 mL). The organic solution was stirred for ca. 15 min with activated carbon (ca. 2 g). Magnesium sulfate was added, and the resulting mixture was filtered through filter paper, condensed to ca. 20 mL by rotary evaporation, filtered through a 0.2 μm PTFE membrane, concentrated, and dried in vacuo overnight at 50 °C to yield a white powder (3.76 g, 85%). Further purification of the polymer (precipitation) was not necessary because ^{1}H NMR analysis proved that all the monomer had been consumed during polymerization. ^{1}H NMR (acetone-d_6, 300 MHz, ppm): δ 0.40−3.00 (bm, aliphatic), 3.60 (bs, aliphatic), 6.60 (bs, OH). IR (KBr, cm^{-1}): 3400, 2968, 2879, 1752 (C=O end group), 1718, 1629, 1215, 1144. GPC: $M_w = 1940$; PDI = 1.43. $A_{157} = 2.64\ \mu m^{-1}$.

Poly(NBCF$_3$TBE-*co*-carbon monoxide) (11). This polymer was made by a procedure (above) similar to the one used for making poly(NBHFA-*co*-carbon monoxide). Yield = 90%. IR (KBr, cm^{-1}): 2982, 1795, 1739, 1372, 1295, 1171. GPC: $M_w = 1590$; PDI = 1.45. $A_{157} = 3.62\ \mu m^{-1}$.

Poly(NBHFA-*co*-NBHFABOC-*co*-carbon monoxide). To a 100 mL round-bottom flask equipped with a stir bar were added poly(NBHFA-*co*-carbon monoxide) (3.78 g, 12.5 mmol as an alcohol), freshly distilled THF (38 mL), di-*tert*-butyl dicarbonate (0.824 g, 3.78 mmol), and 4-(*N*,*N*-dimethylamino)-pyridine (0.05 g, 0.40 mmol). The resulting solution was stirred overnight at room temperature. The THF was evaporated, and ether (50 mL) was added. The resulting solution was washed with 5 wt % Na_2CO_3 (50 mL), 0.05 N HCl (50 mL), and brine (2 × 50 mL), dried over $MgSO_4$, filtered, concentrated, and dried in vacuo overnight at 50 °C to yield a pale yellow solid (3.58 g, 88%). Protection ratio = 24% (by TGA). GPC: $M_w = 1830$; PDI = 1.53. $A_{157} = 2.78\ \mu m^{-1}$.

Poly(NBHFABOC-*co*-carbon monoxide) (13). To a 100 mL round-bottom flask equipped with a stir bar and reflux condenser were added poly(NBHFA-*co*-NBHFABOC-*co*-carbon monoxide) (ca. 6 g, ca. 0.022 mol based on monomers), freshly distilled THF (80 mL), di-*tert*-butyl dicarbonate (6 g, 0.028 mol), and 4-(*N*,*N*-dimethylamino)pyridine (0.36 g, 3.0 mmol). The solution was stirred overnight at room temperature, and then a solution of 5 wt % Na_2CO_3 (ca. 2 mL) was added. The resulting mixture was heated to 60 °C and stirred at that temperature for 2 h, cooled to room temperature, and concentrated in vacuo. Diethyl ether (100 mL) was added to dissolve the residue. The ether solution was washed with 0.05 N HCl (3 × 100 mL) and brine (2 × 100 mL), dried over $MgSO_4$, filtered, concentrated, and dried in vacuo overnight at 50 °C to yield a pale yellow solid (7.79 g). Protection ratio = 92.5% (by TGA). IR (KBr, cm^{-1}): 2983, 2879, 1774 (C=O), 1737 (C=O end group), 1374, 1247, 1133. GPC: $M_w = 2890$; PDI = 1.68. $A_{157} = 2.90\ \mu m^{-1}$.

1,4-Di[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)-ethyl]cyclohexane (1,4-HFAC, 15). A slightly modified literature preparation[11] was used. Under a nitrogen atmosphere, 1,4-bis(2-hydroxyhexafluoroisopropyl)benzene (**14,** 15.0 g, 37.0 mmol), rhodium catalyst (5 wt % on carbon, 2.0 g), and 2-propanol (30 mL) were added to a 300 mL Parr pressure reactor equipped with a stir bar. The reactor was sealed and charged with hydrogen gas (ca. 600 psi at room temperature). The reaction mixture was stirred overnight at 135 °C (ca. 650 psi). The resulting mixture was filtered to remove the catalyst, and the 2-propanol solution was concentrated in vacuo. The product was purified by fractional distillation (48−52 °C/0.15 mmHg) to give a clear oil that is a mixture of cis/trans isomers (13.0 g, 84%) that are presumably 10% cis and 90% trans (by GC analysis). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.30−2.28 (m, cyclohexyl-H), 2.91 (s, OH). ^{13}C NMR ($CDCl_3$, 75.4 MHz, ppm): δ 23.4 (s, alicyclic), 26.6 (s, alicyclic), 36.3 (s, alicyclic), 41.6 (s, alicyclic), 77.8−79.9 (m, C−CF_3), 123.4 (q, CF_3). IR (KBr, cm^{-1}): 3600, 3482, 2983, 2896, 1464, 1363, 1207, 1141, 1078, 969, 897.

1,4-Di[1-*tert*-butoxycarbonyloxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (1,4-HFACBOC, 16). To a 100 mL round-bottom flask equipped with a stir bar were added 1,4-HFAC (**15**, 2.00 g, 4.80 mmol) and di-*tert*-butyl dicarbonate (2.62 g, 12.0 mmol) in freshly distilled THF (20 mL). The resulting mixture was stirred for 5 min before the addition of 4-(*N*,*N*-dimethylamino)pyridine (117 mg, 0.960 mmol). Gas evolution was observed after a few minutes and lasted about 5 min. The resulting mixture was stirred overnight at room temperature and then concentrated in vacuo. The resulting white solid was dissolved in chloroform (30 mL) and washed with 1 M HCl (2 × 30 mL), saturated sodium bicarbonate (2 × 30 mL), and brine (30 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated in vacuo, and dried under reduced pressure to yield a white solid (2.88 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.40 (s, 18H, *t*-Bu), 1.60 (m, 4H, aliphatic), 1.90 (m, 4H, aliphatic), 3.10 (m, 2H, aliphatic). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −68.3, −74.2. IR (KBr, cm^{-1}): 2986, 2893, 1771 (C=O), 1604, 1484, 1464, 1402, 1371, 1274, 1216, 1165, 1142, 1115, 1006, 959, 862, 769, 715.

Triethylaminoboron Trifluoride. To a cooled (dry ice/acetonitrile) 250 mL round-bottom flask equipped with a stir bar and addition funnel was added boron trifluoride diethyl etherate (30 g, 211 mmol). Triethylamine (60 mL) was added dropwise to the flask via the addition funnel. The formation of white precipitate was immediately observed. After the addition of triethylamine, the reaction was allowed to warm to room temperature, and excess triethylamine was removed in vacuo. The white residue was purified by vacuum fractional distillation (85 °C/3 mmHg) to give a white solid (32.0 g, 91%), which melted at approximately 25 °C. The compound was kept in the refrigerator and used in the next step without further purification.

Methyl 3,3-Difluoro-2-(trifluoromethyl)acrylate (19). A slight modification of the literature procedure[12] was used: To a 100 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser were added triethylaminoboron trifluoride (32.0 g, 189 mmol) and methyl 2-(trifluoromethyl)-3,3,3-trifluoropropanoate (30.5 g, 145 mmol). The reaction mixture was refluxed for 3 h and then cooled to room temperature. The residue was purified by vacuum transfer (bulb to bulb distillation) to give a clear oil (19.8 g, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.84 (s, 3H, methyl). ^{19}F NMR (CD_3OD, 282 MHz, ppm): δ −59.5 (m, 1F, RC=CF_2), −59.1 (m, 3F, CF_3), −58.5 (m, 1F, RC=CF$_2$). IR (NaCl, cm^{-1}): 2960, 1767 (C=O), 1710, 1439, 1372, 1152, 1081, 1040, 1024. HRMS−CI (*m*/*z*): $[M + H]^+$ calcd for $C_5H_3F_5O_2$, 191.0131; found, 191.014.

Methyl4,4-Difluoro-3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]-non-7-ene-3-carboxylate (TCNF$_2$CF$_3$ME, 20). To a 300 mL Parr pressure reactor equipped with a magnetic stir bar were added quadricyclane (1.5 g, 16.3 mmol) and methyl 3,3-difluoro-2-(trifluoromethyl)acrylate (**19**, 3.9 g, 20.4 mmol). The pressure vessel was sealed, and the reaction mixture was stirred at 100 °C for 72 h. After cooling to room temperature, the residue was purified by fractional vacuum distillation (39−40 °C/0.30 mmHg) to yield a clear oil (1.0 g, 22%) that is a mixture of *syn* and *anti* product (1:1). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.28−1.45 (m), 2.00−2.10 (d), 2.30−2.33 (m), 2.60−80 (m), 3.10 (s), 3.19 (s), 3.49 (s), 3.82 (s, CH_3), 3.83 (s, CH_3), 6.08−6.16 (m, CH=CH), 6.21−6.25 (m, CH=CH). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ −62.4 (s, 3F, CF_3), −69.2 (s, 3F, CF_3), −86.4 (d, 1F, CF_2), −98.4 (d, 1F, CF_2), −107.7 (d, 1F, CF_2), −114.8 (d, 1F, CF_2). IR (NaCl, cm^{-1}): 3058, 2991, 2909, 1752 (C=O), 1429, 1317, 1219, 1045, 897, 794, 697.

Poly(NBHFABOC) (26). This polymer was made by using the same procedure (but with higher di-*tert*-butyl dicarbonate loading, 1.1 equiv to monomer unit) as the one used above for poly(NBHFA-*co*-NBHFABOC) (**7**). Yield = 90%. IR (KBr, cm^{-1}): 2985, 2882, 1772 (C=O), 1478, 1458, 1439, 1373, 1287, 1249, 1218, 1133, 983, 870, 781, 757. GPC: $M_w = 46\,900$; PDI = 1.89. $A_{157} = 2.44\ \mu m^{-1}$.

Table 1. Absorbance and Molecular Weights of Polymers Studied

polymer	copolymer type	*x*	*y*	M_w	PDI	A_{157} (μm^{-1})
3	A	65	35	3150	3.38	2.78
3a		80	20	*b*		2.28
6				8150	2.11	1.15
8				5380	1.79	6.02
11				1590	1.45	3.62
13				2890	1.68	2.9
23	B	74	26	13800	2.19	1.97
24		83	17	5200	2.78	1.67
25	C	67	33	8150[a]	2.11[a]	2.17
26				46900	1.89	2.44

[a] Assumed to be the same as polymer **6**. [b] No data.

Results and Discussion

The addition polymerization of functional norbornene derivatives using late-transition-metal catalysts is important because it provides a route to many polymers with good mechanical properties. The focus of current research in this area is the design of catalysts that efficiently polymerize norbornenes with either *endo*- or *exo*-pendant oxygen functionalities.[13] These polymerizations have proved to be difficult mainly because of catalyst inhibition due to coordination of the functionality to the metal center. Our studies with fluorinated norbornenes having pendant oxygen functionalities showed that some of these compounds do polymerize while others do not polymerize readily.

We have utilized both Ni(II)[14–16] and Pd(II)[17,18] catalysts in our polymerizations and were able to make several fluorinated, functional polymers for 157 nm lithography applications.[8,19] What follows is a discussion of the synthesis and evaluation of three copolymers based on NBHFA, as shown in Figure 1. Each system has its own weaknesses and strengths, and these will be discussed in turn. Table 1 lists the absorbance at 157 nm and relevant data for all the polymers made.

Copolymer A. NBHFA/NBTBE Copolymers. Nickel(II) Addition Polymerization. NBHFA (**1**) and NBTBE (**2**) were copolymerized using (η^6-toluene)bis(pentafluorophenyl)nickel(II) as the catalyst to produce a range of copolymers with molecular weights in excess of 20 000 (Figure 1, **A**).

The absorbance of one of these copolymers, poly(NBHFA-*co*-NBTBE) (**3a**, $x = 80$, $y = 20$), is 2.30 μm^{-1} at 157 nm (Figure 2). This absorbance is much lower than that of poly(NBTBE) (**8**, 6 μm^{-1}) but higher than that of poly(NBHFA) (**6**, 1.15 μm^{-1}). In essence, we have diluted the absorbance of poly(NBHFA) by incorporating the much more transparent monomer, NBHFA.

Preliminary lithographic evaluation of resists formulated with these polymers showed excessive swelling (Figure 3). The molecular weights of the norbornene–maleic anhydride alternating copolymers we developed for 193 nm imaging ranged from 3000 to 8000; therefore, we reasoned that the molecular weights of these addition polymers must be decreased significantly to control the swelling problem.

Efforts to reduce the molecular weight of the Ni(II)-catalyzed polymers have been unsuccessful. No significant change in molecular weight was observed with increased catalyst loadings up to 10 mol %. The use of chain termination or transfer agents such as 1-hexene to promote β-hydride elimination[20] has been met with little success.[19] Therefore, our focus shifted toward polymers made using Pd(II) catalysts.

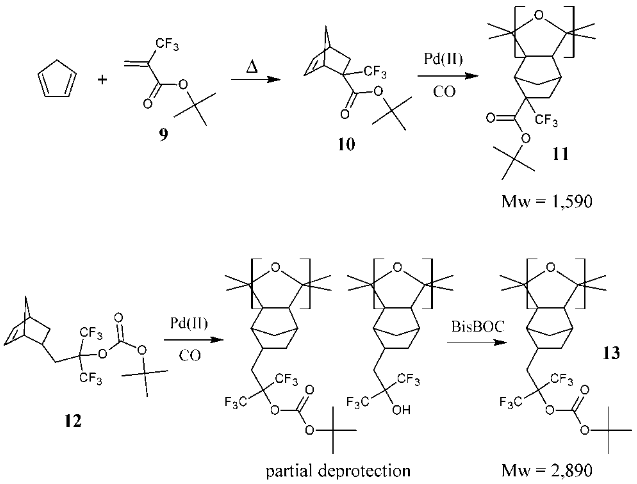


Figure 5. Synthesis of low molecular weight carbon monoxide copolymers for use as dissolution inhibitors.

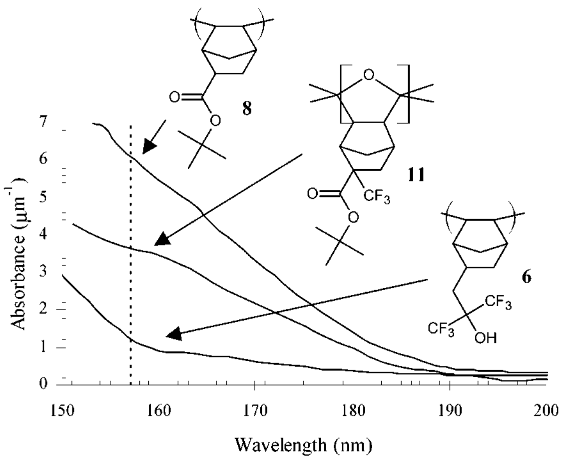
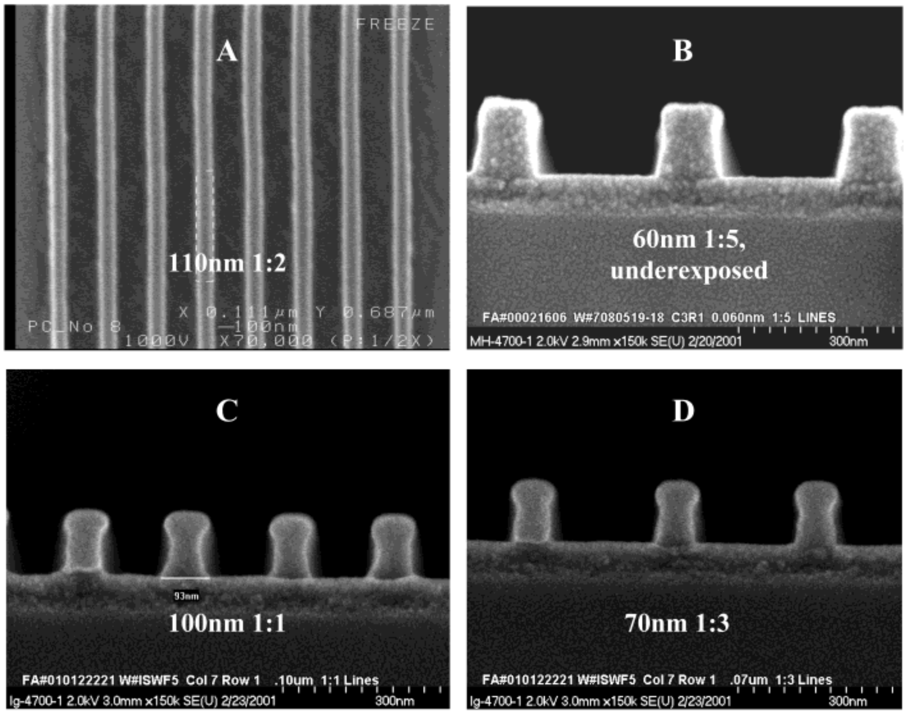


Figure 6. VASE spectrum of carbon monoxide dissolution inhibitor **11**.

Palladium(II) Addition Polymerization. Initially, polymers made from Risse's allyl palladium catalyst, (η^3-allyl)Pd(II)(SbF_6),[17,18] also had very high molecular weights. Employing less active catalysts to achieve lower molecular weights was considered. This would lower the yield of the polymer obtained, but because of the limited quantities of the monomers available, this route was postponed. The addition of 1-hexene did not significantly reduce the molecular weight of the Pd(II)-catalyzed polymers either. In addition, unlike the Ni(II) system, this catalyst cleaved any *tert*-butyl esters present on the norbornene monomers. Apparently, some acid is formed during polymerization. The only anion available is $^-SbF_6$, and the formation of $HSbF_6$, a very strong acid, is disastrous. This presented a large problem because the end use demands incorporation of some norbornene monomers with acid-labile functionalities. This problem was solved through the introduction of sterically hindered, polymer-bound pyridines as "proton sponges" to neutralize any acid that is produced. These hindered amines do not effectively bind to the active catalyst, so the rate of polymerization was not significantly affected. In addition, the proton sponge beads can be easily filtered away from the reaction media, providing a convenient way to eliminate any residual highly absorbing, basic pyridine species which could interfere with resist performance.



A, B: 50/50 blend of 80/20 **3** with **11** (DI)
C, D: 70/30 blend of 66/34 **3** with **11** (DI)

Conditions: 157 nm exposure (0.6NA-0.3σ, 50 mJ/cm^2), phase shift mask, 148 nm thick resist on 70 nm anti-reflective layer (AR19), 140°C-60s PAB, 130°C-90s PEB, 20 sec 0.26N TMAH development.

Figure 7. Scanning electron micrograph images of NBHFA/NBTBE copolymers with carbon monoxide dissolution inhibitor **11**.

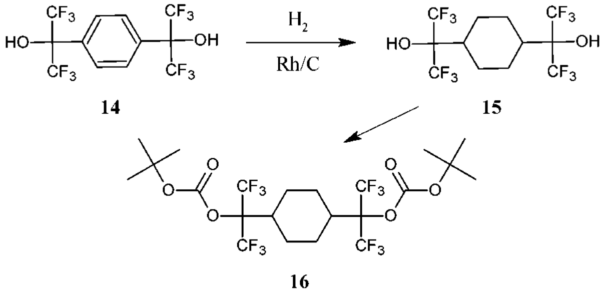


Figure 8. Synthesis of 1,4-HFACBOC (**16**) for use as a dissolution inhibitor.

In contrast to the Ni(II) polymerizations discussed above, lower molecular weight polymers were successfully obtained by increasing the loading of palladium catalyst. As shown in Figure 4, vinyl addition polymers with molecular weights below 9000 were obtained by using ≥5 mol % catalyst. Using large amounts of catalyst is expensive and not ideal for photoresist applications because of the cost related to removal of metal contamination. Therefore, this is not a fully satisfying solution, but is a workable one, and it provides resist material while the search for more effective chain transfer agents continues. Most of the catalyst was removed from the final polymers by precipitation and filtration. This has provided polymers that are acceptable for initial lithographic testing purposes, although reduction of residual metallic impurities to less than 20 ppb levels will be necessary for commercial resist applications.

In summary, using hindered, polymer-bound amines and higher catalyst loadings allow the synthesis of useful polymers by the palladium addition polymerization route. All the polymers discussed from this point forward were made with the allyl palladium catalyst using the new procedure.

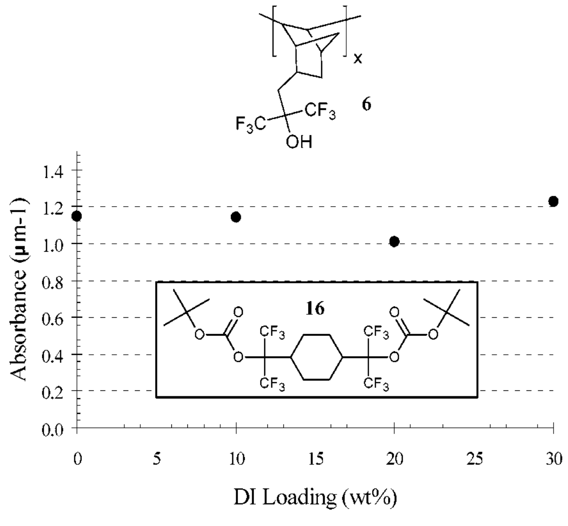


Figure 9. VUV absorbance of 1,4-HFACBOC (**16**) blended with polymer **6** at several concentrations.

Dissolution Inhibitors. Several copolymers with varying ratios of NBHFA (**1**) and NBTBE (**2**) were successfully prepared (Figure 1, **A**). Some of these cycloolefin polymers have been imaged, and from those studies it was clear that addition of a dissolution inhibitor is an effective method for controlling their dissolution rate and eliminating swelling behavior in aqueous base.[21]

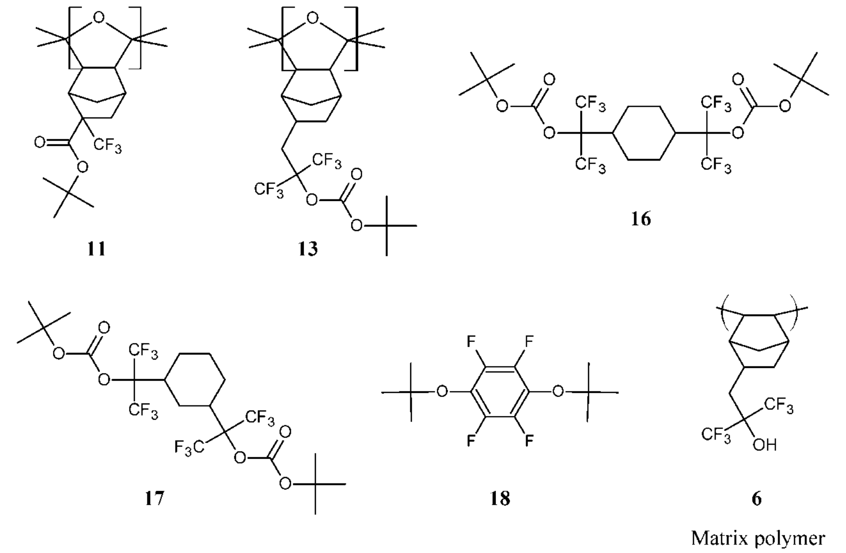


Figure 10. Dissolution inhibitors studied with matrix polymer **6**.

Table 2. Dissolution Rate of Five Dissolution Inhibitors (DI) at 10 wt % Showing Dissolution Efficiency in Matrix Polymer 6 (Refer to Figure 10)

	dissolution rate (nm/s)
base polymer (**6**[a])	165
DI **11**	14
DI **13**	13
DI **16**	<5
DI **17**	<5
DI **18**	42

[a] M_w of the polymer used is 3000.

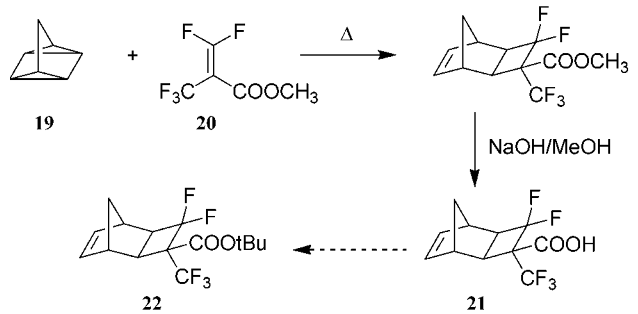


Figure 11. Syntheses of TCN compounds.

From studies of other 157 nm polymer platforms,[8,9] we discovered that the low molecular weight ketal carbon monoxide copolymers (**11** and **13**, Figure 5) derived from two fluorinated norbornenes are effective dissolution inhibitors. The absorbance of one of these polymers, **11**, as shown in Figure 6, is 3.6 μm^{-1} at 157 nm. Polymer **13** has an absorbance of 2.90 μm^{-1}. Both oligomers have better transparency than poly(NBTBE) (**8**). When these dissolution inhibitors are blended with poly(NBHFA-*co*-NBTBE) (**3**, $x = 66$, $y = 34$, $M_w = 3150$, $A_{157} = 2.73\ \mu m^{-1}$), they do not significantly increase the absorbance of the final resist formulation.

Polymer **3** was imaged with poly(NBCF$_3$TBE-*co*-carbon monoxide) (**11**) as the dissolution inhibitor (Figure 7). These images were much improved (there was significantly less swelling) over the images that were generated with the same polymers without dissolution inhibitor.

Several other dissolution inhibitors were auditioned. A promising one is 1,4-di[1-*tert*-butoxycarbonyloxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (1,4-HFACBOC, **16**), made from the reduction of 1,4-HFAB (**14**) followed by protection of the reduced alcohol (1,4-HFAC, **15**), as shown in Figure 8.

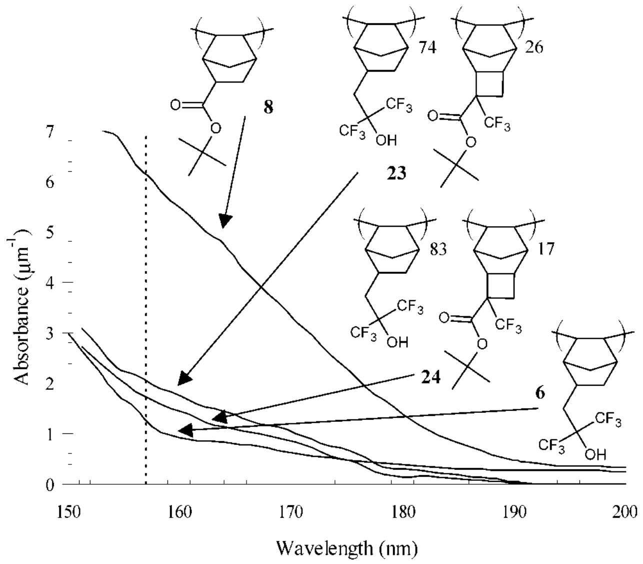
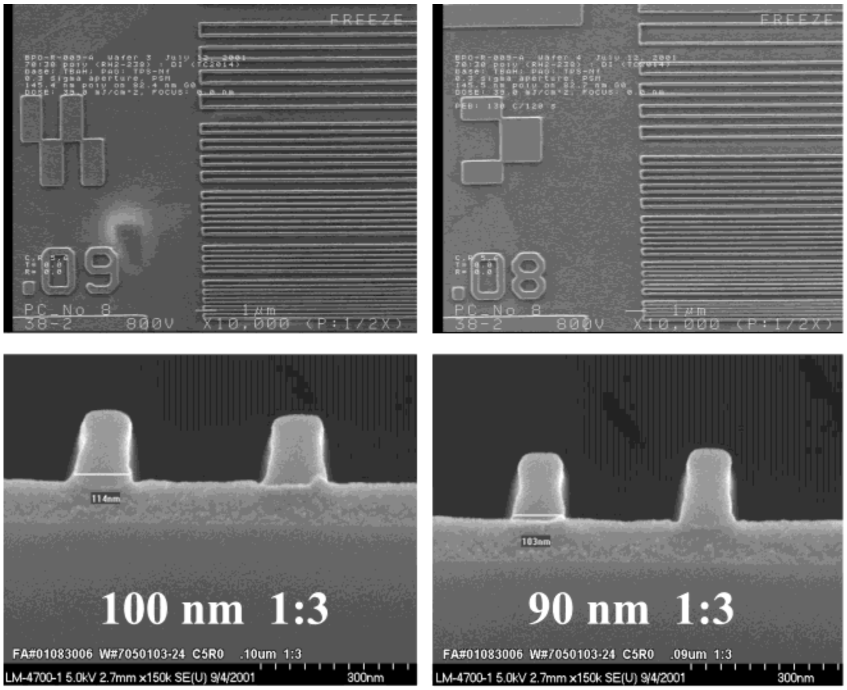


Figure 12. VASE spectra of TCN copolymers (**23** and **24**).

Various loadings of this dissolution inhibitor were mixed with the very transparent homopolymer, poly(NBHFA) (**6**). The absorbance of these blends, which contained amounts of dissolution inhibitor normally used in resist formulations, were measured by VASE in the thin film form. From these results it is clear that the dissolution inhibitor (**16**) does not add much to the absorbance of the matrix polymer (Figure 9). This dissolution inhibitor is quite transparent and can be expected to dilute the absorbance of matrix polymers having higher absorbance.

All three dissolution inhibitors (**11**, **13**, **16**), along with two other dissolution inhibitors (**17**, **18**), were tested for their inhibition efficiency by mixing them (10 wt %) with poly(NBHFA) (**6**) (Figure 10). As shown in Table 2, all compounds significantly inhibited the dissolution of the matrix polymer at 10 wt % loading. Compound **18** did not inhibit dissolution of the matrix polymer as well as the others, while compounds **16** and **17** are very effective. We are currently testing the lithographic perfor-



Formulation: 70/30 blend of **24** with **11** (DI), 6 wt% TPS-Nf, 0.3 wt% TBAH in PGMEA

Conditions: 157 nm exposure (0.6NA-0.3σ, 39.0 mJ/cm^2), phase shift mask, 146 nm thick resist on 82 nm anti-reflective layer (AR19), 140°C-60s PAB, 130°C-120s PEB, 20 sec 0.26N TMAH development.

Figure 13. Scanning electron micrographs of images in resist formulated from NBHFA/TCNCF$_3$TBE copolymer (**24**).

mance of these two dissolution inhibitors in combination with the existing NBHFA-*co*-NBTBE polymers (**3**).

Copolymer B. NBHFA/TCNCF$_3$TBE Copolymers. The NBHFA/NBTBE copolymers (**3**) are all imageable, but they may incorporate as much as 34 mol % of the highly absorbing NBTBE (**2**) monomer. We would like to replace this monomer with much more transparent analogue NBCF$_3$TBE (**10**), but unfortunately this compound does not undergo vinyl addition polymerization using either our Ni(II) or Pd(II) catalytic procedure. The reason for this failure may be due to the reduced electron density of the double bond resulting from the close proximity of the strongly electron-withdrawing trifluoromethyl group, from steric inhibition, or both. We have therefore explored several alternative approaches to incorporating this monomer into a polymer system. One such approach involves the use of tricyclononene (TCN) analogues. Other approaches to incorporation will be covered elsewhere.[8,9]

The tricyclononene structure is advantageous for several reasons. Tricyclononenes can be easily synthesized from a wide range of alkene and alkyne starting materials. In addition, they behave much like norbornenes toward polymerization. The fused cyclobutane ring allows the electron-withdrawing trifluoromethyl and/or fluorine substituents to be positioned further away from the double bond, reducing the steric and electronic effects of these groups on the double bond. A partially fluorinated TCN monomer bearing a methyl ester functionality (**20**) has been synthesized as shown in Figure 11. The *tert*-butyl analogue (**22**) can be made by base-catalyzed hydrolysis of **20** followed by protection.

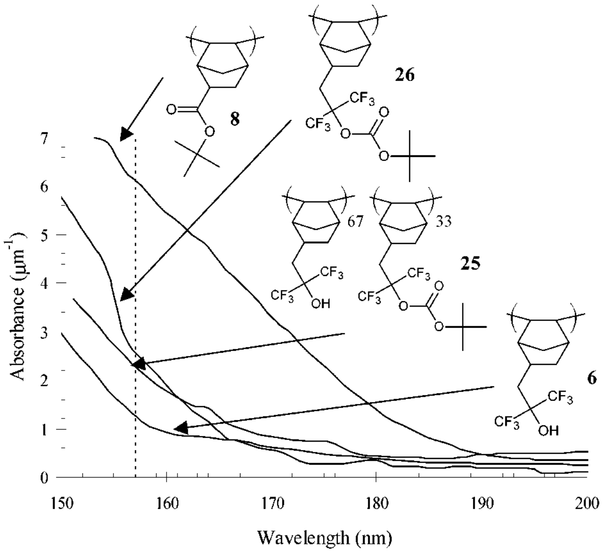
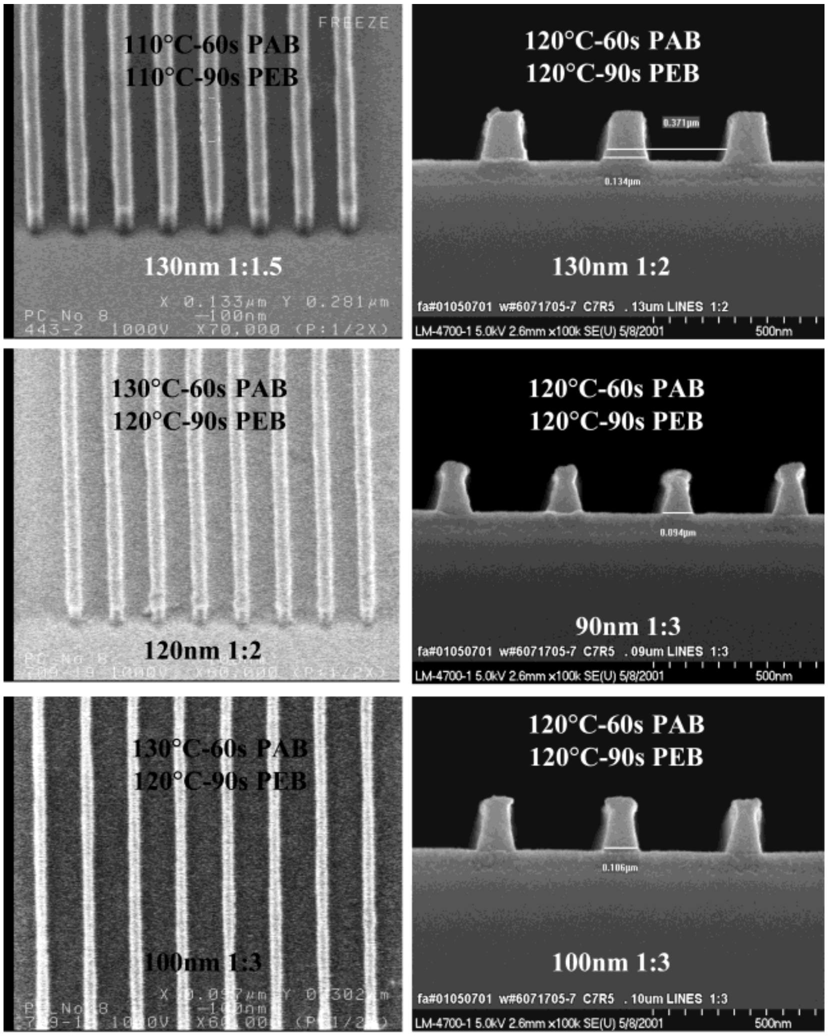


Figure 14. VASE spectra of NBHFA/NBHFABOC copolymer (**25**) and NBHFABOC homopolymer (**26**).

Fluorinated TCN compounds like these have been shown to undergo facile metal-catalyzed vinyl addition polymerization, unlike the analogous fluorinated norbornenes.[22] A model TCN monomer was prepared by reduction of **20** and was shown to be much more transparent than the parent norbornane hydrocarbon.[8] The homopolymers of the methyl ester of monomer **4** and monomer **20** have been shown to have absorbances of 3.79 and 2.86 μm^{-1}, respectively.[22] These TCN polymers are significantly less absorbing than the corresponding NBTBE homopolymer (**8**), which has an absorbance of 6 μm^{-1}. Thus, the TCN monomers appear



Formulation: Polymer **25**, 6 wt% TPS-Nf, 0.3 wt% TBAH in PGMEA
Conditions: 157 nm exposure (0.6NA-0.7σ, 17.3 mJ/cm^2), binary mask, 160 nm thick resist on 82 nm anti-reflective layer (AR19), 20 sec 0.26N TMAH development

Figure 15. Scanning electron micrographs of images in resist formulated from NBHFA/NBHFABOC copolymer (**25**).

to provide a promising route to incorporation of highly transparent ester functionalities into photoresist polymers. Initially, we have focused on polymers made from the more readily accessible monomer **4** for early imaging studies. Efforts are now underway that are directed toward making the more transparent and lithographically useful TCN monomer **22** (Figure 11).

Copolymers (**23** and **24**) from monomers **4** and **1** were made for initial imaging studies. The incorporation of monomer **4** into the polymer structure is close to the feed ratio of the monomer, so the ratio of the final copolymer can be easily controlled. The copolymers' absorbance spectra are shown in Figure 12. A significant reduction in absorbance is obtained by substituting the more transparent TCN monomer for the highly absorbing NBTBE monomer (**2**) in copolymer **3**. Preliminary tests using these polymers showed that this system, with the addition of a dissolution modifying agent such as those reported earlier in this paper (**11**, **13**, **16**, or **17**), is capable of high-resolution imaging (Figure 13). Studies directed toward optimizing the imaging performance of this TCN/dissolution inhibitor system are currently underway.

Copolymer C. NBHFA/NBHFABOC Copolymers. We have been able to make low molecular weight homopolymers (**6**) of NBHFA (**1**) using appropriate loadings of allyl palladium catalyst (Figure 4) in good yield (55%). Reported yields from polymerizations of functionalized monomers, especially those containing carbonyl groups, using this catalyst are generally lower. We believe the higher yields that have been obtained are due to the inability of the hexafluoro alcohol functionality to strongly chelate to the active catalyst due to steric hindrance and electron deficiency.

Partial protection of the homopolymer with di-*tert*-butyl dicarbonate provides a facile route to transparent copolymers that are functional analogues of the hydroxystyrene and *tert*-butyloxycarbonyloxystyrene copolymers (APEX-E[1]) that work so well for 248 nm imaging. The absorbance spectrum of one of these copolymers (**25**) and the completely protected homopolymer (**26**) are shown in Figure 14.

Resists formulated from these copolymers performed quite well in initial imaging tests. As shown in Figure 15, 100 nm 1:3 lines were resolved using polymer **25** ($M_w = 8150$, $A_{157} = 2.17\ \mu m^{-1}$), without the use of any dissolution inhibitor with a simple, binary mask. These copolymers showed high-resolution capability, and further lithographic evaluations of formulations based on them are underway.

Conclusion

Three vinyl addition copolymers that incorporate NBHFA (**1**) have been made and evaluated for 157 nm lithography. Initial imaging experiments with each system show great promise. Formulations based on the NBHFA/NBTBE (**3**) system and the carbon monoxide copolymer dissolution inhibitors image well. The inability to polymerize 2-trifluoromethyl-substituted norbornenes was overcome by making the corresponding tricyclononene derivatives. Quite transparent polymers (NBHFA/TCNCF$_3$TBE system, **5**) were made by incorporation of fluorinated tricyclononenes. Three new, relatively transparent dissolution inhibitors have been synthesized and evaluated. Resists formulated from these components are orders of magnitude more transparent than either the 248 nm resists or 193 nm resists and show great progress toward the development of useful imaging materials for 157 nm photolithography.

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