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Alicyclic Polymers for 193 nm Resist Applications: Synthesis and Characterization

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A series of new alicyclic polymers designed for use as 193 nm photoresist materials has been synthesized and characterized. These resins are based on cycloaliphatic co- and terpolymers of 2-methylpropylbicyclo[2.2.1]hept-5-ene-2-carboxylate (trivial name, carbo-*tert*-butoxy norbornene), bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (trivial name, norbornene carboxylic acid), 8-methyl-8-carboxytetracyclo[4,4,0.1,^{2,5}1^{7,10}]dodec-3-ene (trivial name, methyl tetracyclododecene carboxylic acid), 5-(hydroxymethyl)-2-norbornene-2-methanol, and maleic anhydride, which were synthesized by free radical, Pd(II)-catalyzed addition, and ring-opening metathesis polymerization techniques. The polymers derived from ring-opening metathesis polymerization were hydrogenated to provide another member of this group of materials. The polymers are soluble in common organic solvents and have glass transition temperatures ranging from less than 60 °C to higher than 250 °C depending on their specific structure and mode of polymerization. The low absorption of these polymers at 193 nm wavelength and their high resistance to reactive ion etching make these attractive candidates for 193 nm resist applications.

Introduction

In considering polymeric materials for use as matrix resins in 193 nm photoresist applications, factors such as sensitivity, transparency to 193 nm radiation, dry etch resistance, compatibility with the industry standard developer solutions (0.26 N tetramethylammonium hydroxide), ease of synthesis, and availability of monomers are very critical. Furthermore, the polymers must have acceptable mechanical properties and excellent adhesion to a variety of substrate materials and provide clear, glassy, and amorphous thin films by spin-coating from environmentally benign solvents. This combination of properties is achieved by careful design and choice of monomers. The design is guided by the rich literature that describes the influence of polymer structure on physical properties.[1]

While it appeared possible to achieve most of the design requirements, demands for 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 are, therefore, generally very strongly absorbing in that region. Consequently, the phenolic resins used for I-line and 248-nm photoresists, novolac and polyhydroxystyrene, respectively, are far too opaque at 193 nm to be used in formulating single-layer resists at that wavelength. Fortunately, it is not aromaticity that is required for plasma etch resistance, it is simply a high C/H ratio.[2]

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.[3] Attempts to improve the dry etch resistance by the incorporation of pendant cycloaliphatic groups[4] have met with some success, but the acrylate backbone, which serves to tether all of these groups, has poor dry etch resistance and is known to depolymerize upon exposure to radiation such as that generated during reactive ion etching and ion implantion.[5] This radiation response is the basis for the positive tone function of poly(methyl

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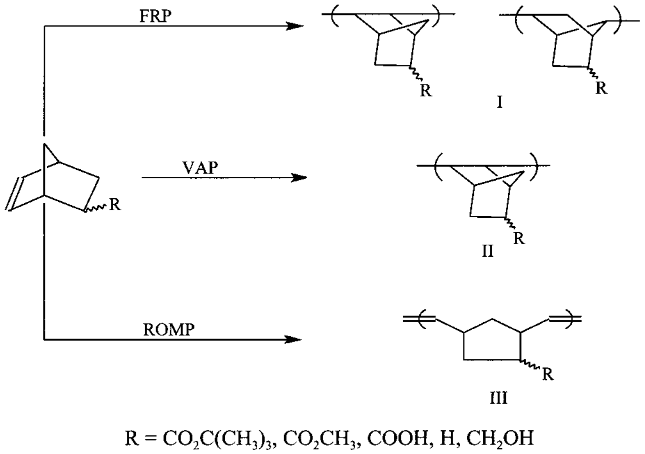
Scheme 1



methacrylate) upon exposure to high-energy electron beam and ion beam radiation.

The discovery of dry etch resistant, nonaromatic materials by Kaimoto et al.[6] in 1992 created a new perspective for the design of resist materials and has had a particularly important influence on the design of materials for 193 nm lithography. In this paper, we report our investigations on a series of new co- and terpolymers of cycloaliphatic olefins (e.g., norbornene derivatives) and maleic anhydride designed for 193 nm resist applications. These polymers were synthesized by free radical, Pd(II)-catalyzed addition and ring-opening metathesis polymerization techniques, utilizing azobisisobutyronitrile (AIBN) and di-*tert*-butyl peroxide initiators, Pd(II)- and Ir(IV)-based catalysts, respectively.

It must be noted that the incorporation of cyclic olefins into our photoresist polymer backbone represents a radical departure from the conventional 193 nm photoresist design concept, as typified by acrylic polymers[3] or acrylic polymers with pendant cyclic olefins,[4,6] or cyclic olefin/acrylic hybrid polymers.[7] It is the unique architectures of the alicylclic polymer backbones of these resist materials that impart the important properties (such as high etch resistance,[8,9] low UV absorption at 193 nm, etc.) that make them very good candidates for 193 nm resist applications. To our knowledge, this work represents the first attempt to employ alicyclic polymers for 193 nm resist applications. Aspects of this work have been published in part elsewhere.[8−10] A full and detailed account of this work can be found in ref 11.

The cycloaliphatic backbone of these polymers contributes to dry etch resistance and thermal stability and serves to tether the pendant functionalities required for imaging. The materials incorporate a pendant acid cleavable group such as a *tert*-butyl ester that undergoes acid-catalyzed thermolysis accompanied by a large change in polarity. They also incorporate a carboxylic acid group or maleic anhydride unit, which enhances the adhesion, wettability, and solubility of the material in aqueous base developing solvent. The resist design incorporates the concept of chemical amplification,[12] a process that involves the photogeneration of species within the resist that 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 greater than 1. Thus, such systems have very high sensitivity. This chemical amplification concept has been exploited in the design of a large number of new resist systems.[13−28]

Norbornene and its derivatives were polymerized by free radical polymerization (FRP), ring-opening metathesis polymerization (ROMP), and Pd(II)-catalyzed vinyl addition polymerization (VAP) techniques. Scheme 1 shows the synthetic pathways to these polymers. Polymers I, II, and III are isomers that differ in enchainment and in physical properties. Co- and terpolymerization

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of norbornene and derivatives of norbornene with other alicyclic monomers such as maleic anhydride (MAH), methyl tetracyclododecene carboxylic acid (MTDCA), etc., was also studied. [Note that 2, 3- and 2,7-enchainments of repeating units are reported in type I polymers.[29]]

Experimental Section

Instrumentation. ^{1}H 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. UV absorption spectra were recorded on a Hewlett-Packard 8450A diode array UV−vis spectrophotometer. Molecular weight determinations were made with size exclusion chromatography (SEC) using a Viscotek chromatograph equipped with a viscosity and a refractive index indicator, as well as American Polymer Standards Corporation 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 °C/min. Elemental analyses of samples were performed at Galbraith Laboratories, Inc., Knoxville, Tennessee.

Materials. All chemicals were purchased from Aldrich Chemical Company 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 was used immediately. Bis(tricyclohexylphosphine)benzylidineruthenium dichloride was obtained from Strem Chemicals Inc. 8-Methyl-8-carboxytetracyclo[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 Company). Bis-tetrafluoroborate tetrakis(cyanomethane)palladium $[Pd(CH_3CN)_4](BF_4)_2$ and bis-tetrafluoroborate tetrakis(cyanomethane)nickel $[Ni(CH_3CN)_4](BF_4)_2$ were prepared according to the literature procedures.[30] (η^3-Allyl)-palladium(II) complexes with tetrafluoroborate and hexafluoroantimonate counterions were prepared in situ according to literature procedures.[31] Di-μ-chlorobis-(6-methoxybicyclo[2.2.1]-hept-2-ene-endo-5σ,2π)dipalladium(II) was prepared according to literature procedures.[32] Tetrabutylammonium hexatungstate(VI), tetrabutylammonium hexamolybdate(VI), tetrabutylammonium octamolybdate(VI), and tetrabutylammonium trihydrogen decavanadate(V) were prepared using literature procedure.[33] Triphenylsulfonium hexafluoroantimonate was prepared according to a literature procedure.[34]

Monomer Synthesis. *2-Methylpropyl Bicyclo[2.2.1]hept-5-ene-2-carboxylate (Trivial Name, Carbo-tert-butoxynorbornene [CBN]).* Freshly cracked cyclopentadiene (CPD) 132.0 g, 2.0 mol) was added (dropwise) to a stirred solution of *tert*-butyl acrylate (256.0 g, 2.0 mol) and 3,5-di-*tert*-butylphenol (2 g, 9.6 mmol). The mixture was stirred for 6−8 h at 140 °C, and the product was isolated by vacuum distillation as a colorless oil (291 g, 75%): bp 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); ^{1}H NMR (CDCl$_3$, δ) 1.35 (s, 9H, = C(CH$_3$)$_3$), 1.8 (m, 1H), 2.1 (m, 1H), 2.85 (bm, 2H), 3.14 (2H, bridgedhead protons), 5.9 (bm, 2H, endo-olefinic), 6.1 (m, 2H, exo-olefinic protons), 6.15 (bm, 2H, endo-olefinic protons); ^{13}C NMR (CDCl$_3$, δ) 27.9 (C(CH$_3$)$_3$), 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. Calcd for $(C_{12}H_{18}O_2)_n$: C, 74.22; H, 9.28. Found: C, 74.28; H, 9.55.

Synthesis of Polymers. *General Procedure for the Synthesis of Pd(II)-Catalyzed Addition Polymers.* A three-neck flask fitted with a reflux condenser and two septum caps was charged with a solution of 51.5 mmol of the monomer in 20 mL of nitromethane and a magnetic stirrer. The solution was degassed, and the vessel was back-filled with N$_2$. A solution of 0.2 mmol of $[Pd(MeCN)_4](BF_4)_2$ in acetonitrile was then introduced by means of a syringe. The mixture was left to react for 72 h at room temperature under a steady stream of dry N$_2$, after which it was poured into acetonitrile. The precipitated polymer was filtered, dissolved in tetrahydrofuran, reprecipitated in acetonitrile and filtered. This precipitation procedure was repeated as necessary to produce a white polymer, which was then dried in vacuo at 60 °C.

Removal of Palladium Catalyst from Polymers. One-hundred milliliters 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 3−6 h. The resulting dark precipitate was allowed to stand overnight to aggregate and settle on the bottom of the flask. The black residue was removed by filtration through a Celite pad, and the clean, colorless filterate was concentrated to approximately 10 mL and then added 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.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) (Trivial Name, Poly(carbo-tert-butoxynorbornene) [Poly(CBN)]). Poly(CBN) was isolated as a white solid in 30% yield. ^{1}H NMR (CDCl$_3$) δ 1.4 (−C(CH$_3$)$_3$), 2.0−3.0 (−CH$_2$, −CH [bridgehead, 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)).

Poly(bicyclo[2.2.1]hept-5-ene-2-carboxylic acid). (Trivial Name, Poly(2-norbornene carboxylic acid) [Poly(NBCA)]). Poly(NBCA) was isolated as a white solid in 55% yield. ^{1}H NMR (DMSO-d_6) (= 1.0−3 (br, CH$_2$, −CH [bridgehead, 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 = 9,000, M_n = 6000. TGA: T_d = 250 °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).

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-2-norbornene carboxylic acid) [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. ^{1}H NMR (CDCl$_3$) δ 1.4 (−C(CH$_3$)$_3$), 2−3.0 (−CH$_2$, −CH [bridgehead, 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: M_w = 9000, M_n = 6000. TGA: T_d = 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 $(C_{12}H_{18}O_2)_{0.7}/(C_8H_{10}O_2)_{0.3}$.

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Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-bicyclo[2.2.1]hept-5-ene-2-methanol) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-5-norbornene-2-methanol) [Poly(CBN-co-NME]). Poly(CBN-*co*-NME) was synthesized from a charge of CBN/NBCA = 70/30 mol % ratio and isolated as a white solid in 45% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2−3.0 ($-CH_2$, −CH [bridgehead, 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: M_w = 4100, M_n = 2500. TGA: T_d = 250 °C.

General Procedure for the Synthesis of Free Radical Polymers Using Di-tert-butyl Peroxide (DTBP). These materials were prepared by an adaptation of the procedure published by Gaylord et al.[29] A three-neck flask fitted with a reflux condenser, with the other two ports capped with rubber septa, was charged with 51.5 mmol of the monomer in 20 mL of propylene glycol methyl ether acetate (PGMEA) and 84.7 mmol of di-*tert*-butyl peroxide. The mixture was degassed and the vessel back-filled with nitrogen. It was then stirred and heated at 130 °C for 24 h under a steady stream of dry N_2, after which it was poured into hexanes to precipitate the polymer. The precipitated polymer was filtered, dissolved in THF, reprecipitated in hexanes, and filtered. This precipitation procedure was repeated as necessary, and finally, the resulting polymer was dried in vacuo at 60 °C.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) (Trivial Name, Poly(carbo-tert-butoxynorbornene) [Poly(CBN)]). Poly(CBN) was isolated as a white solid with a tinge of yellow color in 50% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2.0−2.8 ($-CH_2$, −CH [bridgehead, main chain]). FTIR (film on NaCl plate, cm^{-1}): 2900−3000 (C−H), 1720 (C=O), 1150 (C−O−C). GPC: M_w = 13 000, M_n = 8000. TGA: T_d = 250 °C. Anal. Calcd. for ($C_{12}H_{18}O_2$): C, 74.22; H, 9.28. Found: C, 74.16; H, 9.08

Poly(bicyclo[2.2.1]hept-5-ene-2-carboxylic acid) (Trivial Name, Poly(2-norbornene carboxylic acid) [Poly(NBCA)]). Poly(NBCA) was isolated as a white solid in 50% yield. ^{1}H NMR (DMSO-d_6): δ 1.0−3 (br, CH_2, −CH [bridgehead, 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 = 1500, M_n = 1100. TGA: T_d = 250 °C. Anal. Calcd for ($C_8H_{12}O_2$): C, 69.56; H, 7.25. Found: C, 67.87; H, 6.91.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-bicyclo[2.2.1]-hept-5-ene-2-carboxylic acid) or Poly(carbo-tert-butoxynorbornene-co-2-norbornene carboxylic acid) [Poly(CBN-co-NBCA)]. Poly(CBN-*co*-NBCA) was synthesized from a charge of CBN/NBCA = 80/20 mol % and isolated as a white solid with a tinge of yellow color in 59.3% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2−3.0 ($-CH_2$, −CH [bridgehead, 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). GPC: M_w = 30 000, M_n = 12 000. TGA: T_d = 250 °C. Anal. Calcd. for $(C_{12}H_{18}O_2)_{0.78}/(C_8H_{10}O_2)_{0.22}$: C, 73.44; H, 8.93. Found: C, 72.85; H, 9.45. The feed composition was $(C_{12}H_{18}O_2)_{0.8}/(C_8H_{10}O_2)_{0.2}$.

Poly(bicyclo[2.2.1]hept-5-ene) (Trivial Name, Poly(norbornene) [Poly(NBE)]). Poly(NBE) was isolated as a white solid in 60% yield. ^{1}H NMR (C_6D_6): δ 1.0−2 (br, CH_2, −CH [bridgehead, main chain]). FTIR (film on NaCl plate, cm^{-1}): 3100−2900 ($-CH_2$), 1900 (C−H). GPC: M_w = 1300, M_n = 900. TGA: T_d = 400 °C.

General Procedure for the Synthesis of Free Radical Polymers Using Azobisisobutyronitrile (AIBN). A three-neck flask was fitted with a reflux condenser. The other two necks were sealed with rubber septa, and the flask was charged with 310 mmol of the monomer and 31 mmol of AIBN in 60 mL of dry THF. This mixture was purged with dry nitrogen for 30 min. It was then stirred and heated at 65 °C for 24 h under a steady stream of dry N_2, after which it was poured into hexanes to precipitate the polymer. The precipitated polymer was filtered, dissolved in THF, reprecipitated in hexanes, and refiltered. The polymer was redissolved in THF, precipitated in water, left stirring in the water for at least 6 h to remove unreacted maleic anhydride, and then filtered. This precipitation procedure was repeated at least three more times to ensure the complete removal of unreacted maleic anhydride. Finally, the filtered polymer was dried in in vacuo at 80 °C.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-alt-maleic anhydride) (Trivial Name, Poly(carbo-tert-butoxynorbornene-alt-maleic anhydride) [Poly(CBN-alt-MAH)]). [Poly(CBN-*alt*-MAH)] was synthesized from a charge of 155 mmol of CBN, 155 mmol of MAH, and 31 mmol of AIBN and isolated as a white solid in 80% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2−3.0 ($-CH_2$, −CH [bridgehead, main chain]). FTIR (film on NaCl plate, cm^{-1}): 2977−2890 (C−H), 1867−1786 (C=O, cyclic anhydride), 1729 (C=O, ester), 1158−1059 (C−O−C, aliphatic ester), 930−850 (C−O−C, cyclic anhydride). GPC: M_w = 7000, M_n = 5000. TGA: T_d = 250 °C. Anal. Calcd. for $(C_{12}H_{18}O_2)_{0.5}/(C_4H_2O_3)_{0.5}$: C, 65.75; H, 6.85. Found: C, 64.91; H, 6.81.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-alt-maleicanhydride-alt-8-methyl-8-carboxytetracyclo[4,4,0.1^{2,5},1^{7,10}]-dodec-3-ene) (Trivial Name, Poly(carbo-tert-butoxynorbornene-alt-maleic anhydride-alt-methyltetracyclododec-3-ene carboxylic acid) [Poly(CBN-alt-MAH-alt-MTDCA)]). [Poly(CBN-*alt*-MAH-*alt*-MTDCA)] was synthesized from a charge of CBN/MAH/MTDCA = 40/50/10 mol % and isolated as a white solid in 40% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2−3.0 ($-CH_2$, −CH [bridgehead, main chain]). FTIR (film on NaCl plate, cm^{-1}): 3500−3100 (OH, carboxylic acid), 2977−2890 (C−H), 1867−1786 (C=O, cyclic anhydride), 1724 (C=O, ester), 1158−1059 (C−O−C, aliphatic ester), 930−850(C−O−C, cyclic anhydride). GPC: M_w = 4000, M_n = 2000. TGA: T_d = 250 °C.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-alt-maleic anhydride-alt-bicylo[2.2.1]hept-5-ene (Trivial Name, Poly(carbo-tert-butoxynorbornene-alt-maleic anhydride-alt-norbornene) [Poly(CBN-alt-MAH-alt-NBE)]). [Poly(CBN-*alt*-MAH-*alt-NBE*)] was synthesized from a charge of CBN/MAH/NBE = 40/50/10 (molar ratio) and isolated as a white solid in 55% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2−3.0 ($-CH_2$, −CH [bridgehead, main chain]). FTIR (film on NaCl plate, cm^{-1}): 3500−3100 (OH, carboxylic acid), 2980−2890 (C−H), 1867−1786 (C=O, cyclic anhydride), 1724 (C=O, ester), 1158−1059 (C−O−C, aliphatic ester), 930−850 (C−O−C, cyclic anhydride). GPC: M_w = 6000, M_n = 4000. TGA: T_d = 250 °C.

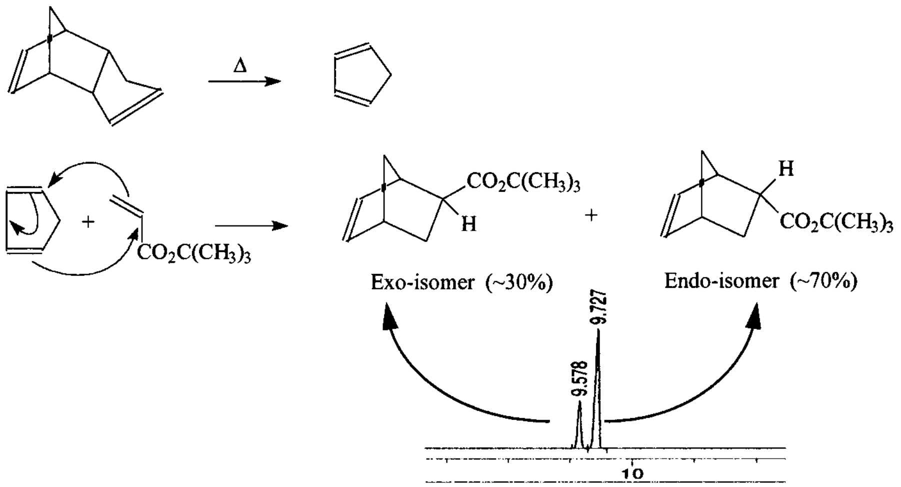
Poly(bicyclo[2.2.1]hept-5-ene-2-carboxylic acid) (Trivial Name, Poly(2-norbornene carboxylic acid) [Poly(NBCA)]). Poly(NBCA) was isolated as a white solid in 25% yield. ^{1}H NMR (DMSO-d_6) (= 1.0−3 (br, CH_2, −CH [bridge-head, main chain]), 7.4 (s). FTIR (film on NaCl plate, cm^{-1}) 3500−3000 (OH), 2900−3000 (C−H), 1708 (C=O, carboxylic acid). GPC: M_w = 1,500, M_n = 1,100.

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 hexacholoroiridate (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 filterate 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.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) (Trivial Name, Poly(carbo-tert-butoxynorbornene) [Poly(CBN)]). Poly(CBN) was isolated as light yellow solid in 89% yield. ^{1}H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 1.6−3.2 ($-CH_2$, −CH [bridgehead, main chain]), 5.21−5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}): 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 °C. TGA: T_d = 250 °C.

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-2-methylbi-cyclo[2.2.1] hept-5-ene-2-carboxylate) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-carbomethoxynorbornene) [Poly(CBN-co-CMN)]). Poly(CBN-*co*-CMN) was

Scheme 2



synthesized from a charge of CBN/CMN = 80/20 mol % ratio and was isolated a light yellow solid in 66% yield. ^1H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 1.6−3.2 ($-CH_2$, $-CH$ [bridgehead, main chain]), 3.65 ($-OCH_3$), 5.21−5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}): 1740 (C=O), 1120 (C−O−C), 990 (C=C−H, trans), 740 (C=C−H, cis). GPC: M_w = 101 000, M_n = 54 000. DSC: T_g = 85 °C. TGA: T_d = 250 °C. Composition: CBN/CMN = 81/19 (mol %, by ^1H NMR).

Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-8-methyl-8-carboxytetracyclo[4,4,0.1^{2,5},1^{7,10}]dodec-3-ene) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-methyltetracyclododecene carboxylic acid) [Poly(CBN-co-MTDCA)]). Poly(CBN-*co*-MTCDCA) was synthesized from a charge of CBN/MTDCA = 80/20 mol %) and was isolated as a lightly yellow-colored solid in 75% yield. ^1H NMR ($CDCl_3$): δ 1.4 ($-C(CH_3)_3$), 2.0−2.8 ($-CH_2$, $-CH$ [bridgehead, main chain]), 5.2−5.4 (vinyl proton). FTIR (film on NaCl plate, cm^{-1}): 3600 (OH), 1729 (C=O), 1120 (C−O−C), 970 (C=C−H, trans), 848 (C=C−H, cis). GPC: M_w = 59 000, M_n = 16 000. DSC: T_g = 122 °C. TGA: T_d = 250 °C.

General Procedure for the Hydrogenation of the ROMP-Derived Polymers. Method A. To a stirred solution of (2.0 g, 10 mmol) of the ROMP-derived polymer in 40 mL of propylene glycol monomethyl ether (PGME) and 20 mL of THF were 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. It was dried in vacuo at 60 °C.

Method B. To a stirred solution of (2.0 g, 10 mmol) of the ROMP-derived polymer in 50 mL of 1,4-dioxane were added toluenesulfone hydrazine (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 passed through a 1/2-in. layer of Celite on a glass filter to remove residual catalyst. The solution was poured into 1 L of water and acidified to pH 2 with concentrated HCl. The precipitated polymer was purified and dried in the same manner as in method A above.

Hydrogenated Poly(CBN) Made by Method A. Hydrogenated poly(CBN) was obtained as a white solid with 84% hydrogenation (determined by ^1H NMR analysis). ^1H NMR ($CDCl_3$): δ 1.2−1.9 ($-CH_2-CH_2^-$, main chain), 1.3 ($-C(CH_3)_3$), 2.0−3.2 ($-CH_2$, $-CH$ [bridgehead, main chain]), 5.2−5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}): 2941 (C−H), 1727 (C=O), 1155 (C−O−C). GPC: M_w = 28 900, M_n =15 000. DSC: T_g = 57 °C. TGA: T_d = 252 °C.

Hydrogenated Poly(2-methylpropyl bicyclo[2.2.1]hept-2-carboxylate-co-8-methyl-8-carboxytetracyclo[4,4,0.1^{2,5},1^{7,10}]dodec-3-ene) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-methyltetracyclododecene carboxylic acid) [Poly(CBN-co-MTCDCA)]) Made by Method A. Hydrogenated poly(CBN-*co*-MTCDCA) was obtained as 2.74 g of a white solid with 82% degree of hydrogenation (determined by ^1H NMR analysis). ^1H NMR ($CDCl_3$): δ 1.16−1.91 ($-CH_2-CH_2-$, main chain), 1.3 ($-C(CH_3)_3$), 2.0−2.8 ($-CH_2$, $-CH$ [bridgehead, main chain]), 5.21−5.4 (vinyl proton). FTIR (film on NaCl plate, cm^{-1}): 3600 (−OH), 2941 (C−H), 1727 (C=O), 1155 (C−O−C). GPC: M_w = 60 000, M_n = 30 000. DSC: T_g =107 °C. TGA: T_d = 252 °C.

Made by Method B. Yield: 1.5 g. Degree of hydrogenation: 100%. IR and NMR were the same as that of the polymer obtained with method A. GPC: M_n = 10 200. DSC: T_g = 70 °C. TGA: T_d = 252 °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 $(C_{12}H_{18}O_2)_{0.8}/(C_8H_{10}O_2)_{0.2.}$

Hydrolysis of Poly(2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate-co-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate) (Trivial Name, Poly(carbo-tert-butoxynorbornene-co-carbomethoxynorbornene) [Poly(CBN-co-CMN)]). To a stirred solution of 4.9 g of poly(CBN-*co*-CMN) (CBN/CMN = 81/19%) in 50 mL of PGME were added KOH (0.66 g, 10 mmol) and tetrabutylammonium bromide (0.32 g, 1 mmol). The mixture was stirred at 60 °C for 24 h, after which it was poured into 1 L 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 ($-CH_2$, $-CH$ [bridgehead, main chain]), 5.2−5.4 (vinyl). FTIR (film on NaCl plate, cm^{-1}): 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 °C. TGA: T_d = 252 °C. Composition: CBN/COOH = 74/26 (mol %) (determined by ^1H NMR analysis).

Results and Discussion

Homo-, co-, and terpolymers of cycloaliphatic monomers such as CBN, NBCA, MTDCA, maleic anhydride, etc., offer great promise as resist materials for 193 nm lithography. The polymers are highly etch resistant[6] and are at least as transparent as the corresponding acrylic polymers.

Synthesis of Monomer. CBN (endo/exo ratio 70/30) was synthesized by the Diels−Alder reaction between cyclopentadiene and *tert*-butyl acrylate as shown in Scheme 2. The chromatogram in Scheme 2 shows the resolved isomers exo:endo ≈ 30/70%). CMN was synthesized by the same scheme.

Synthesis of Polymers. It has been known for some time that norbornene undergoes ring-opening metathesis polymerization in the presence of Ziegler−Natta

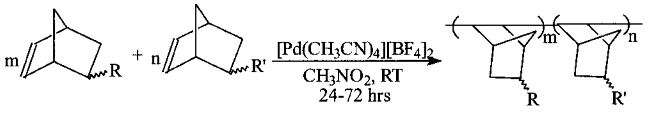
Table 1. Pd(II)-Catalyzed Addition Polymerization[a]

catalyst[g]	monomer[g]	monomer/catalyst	time (h)	temp. (°C)	M_w	M_n	yield (%)
$[Pd(CH_3CN)_4](BF_4)_2$	CBN	300	72	25	10000	6000	20
$[Pd(CH_3CN)_4](BF_4)_2$	CBN	200	72	25	9800	6000	30
$[Pd(CH_3CN)_4](BF_4)_2$	CBN	160	96	25	6700	4800	30
$[Pd(CH_3CN)_4](BF_4)_2$	CBN	100	72	25	6500	4500	32
$[Pd(CH_3CN)_4][BF_4]_2$	CBN	80	24	25	3500	2500	33
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 80/20	200	72	25	10000	6000	35
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 75/25	200	96	25	9000[b]	3000[b]	30
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 90/10	100	68	25	9000	6000	35
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 80/20	100	150	25	10000	6000	55
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 70/30	100	65	25	9300	5000	41
$[Pd(CH_3CN)_4][(BF_4]_2$c	CBN/NBCA = 80/20	300	100	25	3000	2000	65
$[Pd(CH_3CN)_4][(BF_4]_2$	CBN/NBCA = 80/20	50	72	25	5000	4000	60
$[Pd(CH_3CN)_4][(BF_4]_2$	NBCA	100	150	25	10000	6000	55
$[Ni(CH_3CN)_4][BF_4]_2$	CBN	100	48	25			0
$[Ni(CH_3CN)_4][BF_4]_2$	CBN	100	48	25			0
$PdCl_2$	CBN	100	96	25			0
CMNDP[de]	CBN	100	96	25			0
CMNDP[d,f]	CBN	100	96	25			0

[a] All polymerizations were carried out with 52 mmol of monomer (exo/endo = 30/70) in 20 mL of nitromethane, except otherwise stated. [b] Molecular weight was determined by light scattering. [c] Polymerization was carried out in ethyl lactate. [d] The catalysts were prepared using a procedure adapted from the literature.[32] [e] Polymerization was carried out in 20 mL of tetramethyl urea. [f] Polymerization was carried out in 20 mL of THF. [g] $[Pd(CH_3CN)_4](BF_4)_2$: bis-tetrafluoroborate tetrakis(cyanomethane)palladium. $[Ni(CH_3CN)_4](BF_4)_2$: bis-tetrafluoroborate tetrakis(cyanomethane)nickel. CMNDP: di-μ-chlorobis-(6-methoxybicyclo[2.2.1]hept-2-ene-*endo*-5σ,2π)dipalladium(II).

catalysts;[35−38] reduced oxides of Cr, Mo, and W;[39] and hydrated halides of Ru, Os, and Ir,[40,41] resulting in an unsaturated polymer, poly(1,3-cyclopentylenevinylene). Norbornene also undergoes cationic polymerization in the presence of $C_2H_5AlCl_2$[42] and free radical polymerization in the presence of di-*tert*-butyl peroxide[29] to reportedly yield poly(2,7-bicyclo[2.2.1]hept-2-ene), a saturated polymer, in both cases. Gaylord et al.[29] 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 vinyl addition polymerization in the presence of compounds of Pd(II)[43−46] and Ti(IV),[41] resulting in poly(2,3-bicyclo[2.2.1]hept-2-ene), a saturated polymer with 2,3-enchainment. Risse and co-workers[31,43] have more recently reported Pd(II)-catalyzed vinyl addition polymerization of norbornene derivatives bearing a variety of functional groups including esters.

Scheme 3



R = -H, $-CO_2C(CH_3)_3$ R' = COOH, CO_2CH_3, CH_2OH

Part of the present study was an attempt to employ the above chemistries to synthesize cycloaliphatic polymers with pendant free carboxylic acid groups and carboxylic acids protected with acid-labile groups such as *tert*-butyl esters tailored for 193 nm resist use. Norbornyl derivatives such as CBN and analogues were polymerized by (1) vinyl addition polymerization (VAP) with bis-tetrafluoroboratetetrakis(cyanomethane)palladium ($[Pd(CH_3CN)_4][BF_4]_2$), in nitromethane at room temperature (see Scheme 3), (2) free radical polymerization (FRP) with di-*tert*-butyl peroxide at 118−130 °C; and AIBN at 65 °C in THF (see Scheme 4), and (3) ring-opening metathesis polymerization (ROMP) with dipotassium hexachloroiridate (K_2IrCl_6) in a mixture of water, acetic acid and zinc at 50 °C (see Scheme 5). The ROMP polymers were then hydrogenated, using diimide, produced in situ from hydrazine (see Scheme 5).

Vinyl addition copolymerization of various norbornene derivatives using ($[Pd(CH_3CN)_4](BF_4)_2$) in nitromethane or ethyl lactate at room temperature was based on a procedure adapted from Risse and co-workers.[31,43,44]

Note that although only 2,3-enchainment of the cyclic olefins is shown in Scheme 4 above, 2,7-enchainment is also possible, as reported by Gaylord and co-workers.[29]

The yields of the polymers made by $[Pd(CH_3CN)_4][BF_4]_2$-catalyzed vinyl addition polymerization of CBN with an exo/endo mole ratio ca. 30/70 were relatively low. A GC analysis of the unreacted monomer after the reaction revealed that a disproportionate fraction of the exo isomer polymerized versus the endo isomer. Risse and co-workers[31] have observed similar phenomena and have speculated on the cause of the difference in reactivity between the two isomers. The reaction conditions, yields, and molecular weights of these polymers are summarized in Table 1.

Reduction of the Pd(II)-catalyzed addition polymers by simply bubbling H_2 gas through the solution reduces the Pd^{2+} attached to the chain end to Pd(0), which was easily removed by Celite filtration.

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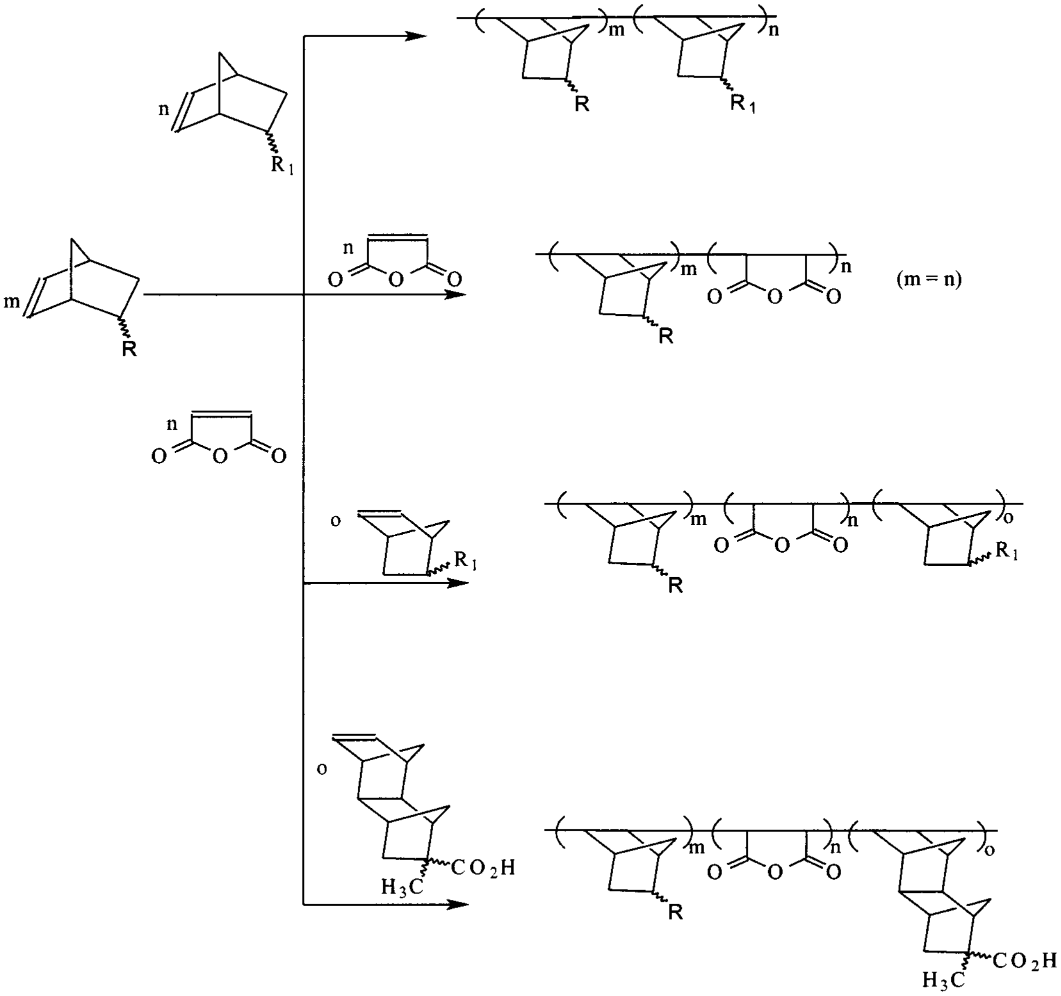
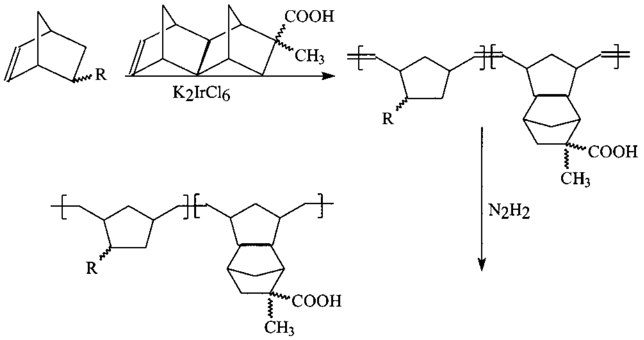
Scheme 4



Scheme 5



R = $-CO_2C(CH_3)_3$, $-CO_2CH_3$

The yields of the free radical polymerization were moderate and depend on the temperature and length of time of the reaction, the nature of initiator used, and the presence or absence of solvent (see Tables 2 and 3 for data on free radical polymerization initiated with DTBP and AIBN, respectively). Bulk polymerization afforded higher yields than solution polymerization. Only traces of polymer were obtained with DTBP when the reaction was carried out at 105 °C, a temperature lower than the boiling point (109 °C) of di-*tert*-butyl peroxide.

The molecular weights of the polymers obtained with DTBP initiator by the Gaylord procedure[29] were modest, and the polymers were typically light yellow. When dilute THF solutions of these polymers were poured into methanol followed by the addition of water and a few drops of HCl to break the resulting emulsion, white polymers were obtained. Excellent results were obtained by co- and terpolymerizing CBN with maleic anhydride, NBCA, and MTDCA at 65 °C, using azobisisobutyronitrile (AIBN) in appropriate solvents; the resulting polymers are predominantly of alternating copolymer architecture. We continue to study these interesting co-and terpolymerization reactions.

Elemental analyses of representative polymer samples were close to the estimated values of the various constituent elements of these polymers except for one sample, the homopolymer of nobornene carboxylic acid [polyNBCA], that was made by both free radical and Pd(II)-catalyzed vinyl addition polymerization. Elemental analysis shows the following result for polyNBCA: 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)). This polymer is very hygroscopic. Thus, the significant disparity between the calculated values and those derived from elemental analyses could be due to absorbed moisture in this polymer.

The yield of the ROMP polymerizations was high as were the molecular weights of the products. The molecular weights of these polymers can be controlled by addition of α-olefins such as 1-decene to the feed.

Table 2. Free Radical Polymerization Using DTBP Initiator

monomer, M	initiator, I	M/I	temp. (°C)	time (h)	M_w	M_n	yield (%)
CBN[a]	DTBP	1.36	118	30	7000	5000	25
CBN[a]	DTBP	1	118	30	10000	6400	40
CBN[a]	DTBP	0.63	118	30	12000	7000	40
CBN[a,c]	DTBP	3.7	130	48	38000	9000	40
CBN[a]	DTBP	1	105	48			trace
CBN/NBCA[b] = 80/20	DTBP	1	130	1.5	1400	700	30
CBN/NBCA[b] = 90/10	DTBP	0.7	130	18	3000	1400	50
CBN/NBCA[b] = 70/30	DTBP	1.8	130	18	5000	400	50
NBCA[a]	DTBP	1	118	18	1500	1000	50
NBE[b]	DTBP	2	115	24	1400	900	50

[a] Polymerization was carried out neat in a serum bottle. [b] Polymerization was carried out in propylene glycol monomethyl ether acetate in a round-bottom flask under a nitrogen atmosphere. [c] Polymerization was carried out in a glass tube sealed under vacuum.

Table 3. Free Radical Polymerization[a] Using AIBN Initiator

monomer, M	initiator, I	M/I[c]	temp. (°C)	time (h)	M_w	M_n	yield (%)
CBN/NBCA = 70/30	AIBN	100	65	24	1200	800	10
CBN/NBCA[b] = 80/20	AIBN	10	70	24	900	500	10
CBN/MAH = 60/40	AIBN	50	65	24	7000	5000	20
CBN/MAH = 60/40	AIBN	10	65	48	3600	1800	35
CBN/MAH = 50/50	AIBN	50	65	18	6500	5000	40
CBN/MAH = 50/50	AIBN	10	65	48	2500	1200	80
CBN/MAH/NBE	AIBN	50	65	48	6000	4000	50
CBN/MAH/MTDCA = 41/50/9	AIBN	50	65	40	4000	1700	30
CBN/MTDCA = 80/20	AIBN	65	50	24			0
NBCA	AIBN	65	25	43	1500	1100	8

[a] All polymerizations were carried out in THF. [b] Polymerization was carried out in benzene. [c] Monomer catalyst molar ratio.

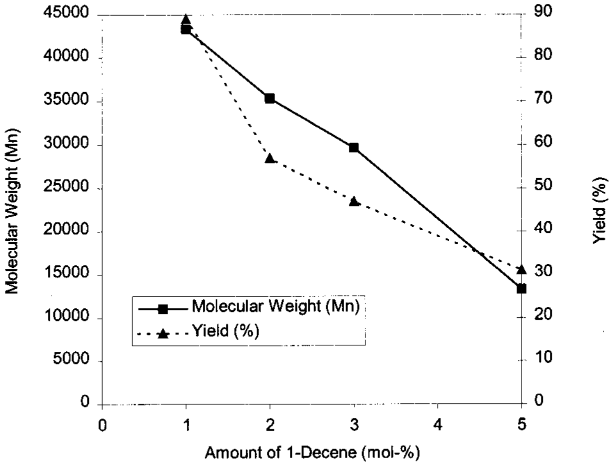


Figure 1. Control of ROMP polymer molecular weight with 1-decene.

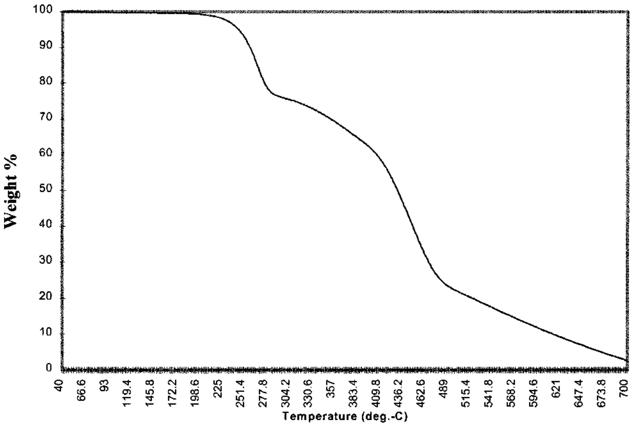


Figure 2. TGA curve of a typical resist copolymer poly(CBN-*co*-NBCA). The other resist polymers, poly(CBN-*alt*-MAH), poly(CBN-*co*-MTDCA), and poly(CBN-*alt*-MAH-*alt*-NBE), show similar TGA profiles. The decomposition temperatures are all above 240 °C.

Under these conditions, there is a tradeoff between yield and molecular weight as shown in Figure 2. Photoresist formulations are best prepared from polymers with somewhat lower molecular weights so that solutions with higher solid content and lower viscosity can be prepared. Therefore, the ability to control molecular weight by this means and other means is desirable.

The results of our attempts to polymerize CBN with various ROMP catalysts are summarized in Table 4. 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 yields [28.3% (in the absence of α-olefins such as 1-decene) and ca. 86% (in the presence of 1 mol % 1-decene)]. (See Figure 1.) It was also possible to copolymerize CBN with CMN and MTDCA under these conditions. However, this catalyst system was unable to homopolymerize norbornene carboxylic acid. This may be due to the formation of a complex between Ir^{4+} and the carboxylic acid group.

There exist numerous sophisticated catalysts that can be used in ROMP. Noteworthy among these are the catalysts developed by Grubbs and co-workers[47] and Schrock and co-workers.[48] We chose not to employ these catalysts in our screening work because most of them require anhydrous conditions which were not readily available in our laboratory.

Olefinic unsaturation (as occurs in the backbone of ROMP-derived polymers) in general has appreciable absorption at 193 nm. In the presence of oxygen the

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Table 4. Evaluation of the Catalytic Capacity of Some ROMP[a] Catalysts to Initiate the Polymerization of CBN

trial	catalyst[e]	solvent	temp. (°C)	time (h)	yield (%)
1	$WCl_6/AlEt_3$	CB	25	24	0
2	$WCl_6/AlEt_3$	toluene	80	24	0
2	TBAHT	hexanes	25	72	0
3	TBAHM	hexanes	25	72	0
4	TBAOM	hexanes	25	72	0
5	TBATHDV	hexanes	25	72	0
7	$RuCl_3{\cdot}3H_2O$	W/E.	50	24	6
8	$RuCl_3$	W/E/D[d]	50	24	0
9	$IrCl_3$	W/E/D[d]	50	48	0
10	K_3IrCl_6 (Ir^{3+})	W/E/D[d]	50	24	0
11	K_2IrCl_6 (Ir^{4+})[b]	W	50	24	20
12	K_2IrCl_6 (Ir^{4+})[c]	W/E/D[d]	50	24	28.3
13	BTPR	THF	50	72	0
14	BTPR	toluene	50	72	4.4

[a] Polymerization was carried out using 50 mmol of CBN and 0.5 mmol (1 mol %) of catalyst in 15 mL of solvent. [b] 5 mmol of Zn/50 mmol of acetic acid was used as reducing agent; 5 mmol of sodium dodecyl sulfate was used as the emulsifying agent. [c] 5 mmol of Zn/50 mmol of acetic acid was used as reducing agent. [d] W(water)/E(ethanol)/D(*p*-dioxane) = 3/5/7 by volume. [e] CB: chlorobenzene. THF: tetrahydrofuran. BTPR: bis(tricyclohexylphosphine)benzylidineruthenium dichloride. TBAHT: tetrabutylammonium hexatungstate(VI), prepared using literature procedure.[33] TBAHM: tetrabutylammonium hexamolybdate(VI), prepared using literature procedure.[33] TBAOM: tetrabutylammonium octamolybdate(VI), prepared using literature procedure.[33] TBATHDV: tetrabutylammonium trihydrogen decavanadate(V), prepared using literature procedure.[33]

tertiary allylic hydrogens in these structure can undergo autoxidation and radical-mediated cross-linking, essentially making them unusable in 193 nm resist applications. To this end, we exposed some representative ROMP polymers to atmospheric oxygen over the span of 1 year and, at a regular intervals, evaluated the physical and chemical properties of small portions of the samples. To our surprise, we observed no significant change in the color or solubility of these polymers in common solvents, or in the molecular weight, over a 1 year span.

We hydrogenated the ROMP-derived polymers, using literature procedures.[49,50] The results of our attempts to hydrogenate poly(CBN), a typical ROMP polymer, are summarized in Table 5. The procedure developed by Hahn[51] provided 100% hydrogenation yield for the ROMP polymers. Also, this procedure removes residual metal catalyst bound to the polymer, and it is possible to remove the reduced catalyst by Celite filtration. Removing the catalyst provided polymers with excellent transparency at 193 nm (see Table 6 for the UV absorption data of typical resist polymers at 193 nm).

Thermal Analysis. A thermogravimetric analysis of a typical resist copolymer, poly(CBN-*co*-NBCA) is shown in Figure 2. All of the resist polymers and co- and terpolymers show similar TGA profiles. The deprotection temperature and decomposition temperature for the polymers are roughly 250 and 400 °C, respectively. The glass transition temperature (T_g) of the ROMP-derived poly(CBN) is 90 °C; the vinyl addition and free radical derived poly(CBN) show no thermal transition below the decomposition temperature at 250 °C.

Table 5. The Results of the Hydrogenation Reaction of Poly(CBN)[a]

oxidant (mol %)	solvent	M_n[b] ($\times 10^4$)	temp. (°C)	time (h)	conversion[c] (mol %)
air	PGME/THF	4.33	25	24	76
air	PGME/THF	3.54	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_2O_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

[a] Hydrogenation 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. [b] Determined by GPC. [c] Determined by ^{1}H NMR. [d] TBPO: *tert*-butyl peroxide. [e] Hydrogenation was carried out using 10 mmol of PCBN, *p*-toluenesulfone hydrazine (25 mL), and tripropylamine in 50 mL of 1,4-dioxane.

Table 6. UV Absorption at 193 nm of the Photoresist Polymers

polymer	UV absorption/ μm at 193 nm	mode of polymerization
P(CBN-*co*-NBCA)	0.31	Pd(II)-catalyzed addition
P(CBN-*alt*-MAH)	0.32	free radical
P(CBN-*co*-MTDCA)	0.43	ring-opening metathesis
P(CBN-*co*-NME)	0.46	Pd(II)-catalyzed addition
P(CBN-*alt*-MAH-*alt*-MTDCA)	0.50	free radical
P(CBN-*alt*-MAH-*alt*-NBE)	0.72	free radical

Summary. We have synthesized and characterized a series of co- and terpolymers of alicyclic olefins and maleic anhydride by free radical, Pd(II)-catalyzed vinyl addition and ring-opening metathesis polymerization techniques. The polymers made by free radical and Pd(II)-catalyzed vinyl addition polymerization have high glass transition temperatures and are extremely thermally stable (T_g > 250 °C), but those made by ROMP have much lower glass transition temperatures. Hydrogenation of the ROMP polymers afforded yet another class of these materials. All of the polymers are soluble in common organic solvents. Their saturated cycloaliphatic backbone provides dry etch resistance, thermal stability, and low absorption at 193 nm; these attributes in turn make them attractive candidates for 193 nm photoresist applications. The lithographic evaluation of these materials is detailed in a companion paper.[8]

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