Metal-Catalyzed Addition Polymers for 157 nm Resist Applications. Synthesis and Polymerization of Partially Fluorinated, Ester-Functionalized Tricyclo[4.2.1.$0^{2,5}$]non-7-enes

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ABSTRACT: Fluorinated tricyclo[4.2.1.$0^{2,5}$]non-7-ene-3-carboxylic acid esters are shown to undergo metal-catalyzed addition polymerization. The resulting homopolymers are transparent at 157 nm and demonstrate the utility of these monomers in development of photoresists for 157 nm lithography. Fluorinated tricyclononene (TCN) structures with ester substituents exhibit up to 3 orders of magnitude more transparency at 157 nm than conventional ester-functionalized norbornene structures as determined by gas-phase vacuum-ultraviolet spectroscopy and variable angle spectroscopic ellipsometry. Unlike their fluorinated norbornene counterparts, the fluorinated, ester-functionalized TCN monomers successfully undergo transition-metal-catalyzed addition polymerization to produce polymers with high glass transition temperatures and the etch resistance required for photolithographic resist materials applications. The potential use of fluorinated TCN structures for 157 nm photoresists is demonstrated through the synthesis and characterization of TCN monomers and polymers.

Introduction

Specialized, alicyclic fluoropolymers are the focus of intense research as the semiconductor industry attempts to develop the functional photoresists required to enable the timely introduction of 157 nm optical lithography, as outlined in the International Technical Roadmap for Semiconductors (ITRS) timeline.[1,2] A prominent concern for 157 nm lithography is the feasibility of employing a practical resist thickness (>200 nm), which requires a photoresist with a low absorption coefficient.[3] To fulfill this requirement while retaining optimal imaging properties, a critical balance of several, often competing, material properties, such as transparency, etch resistance, glass transition temperature, thermal stability, and dissolution behavior, must be achieved. Carbon-rich and heteroatom-deficient norbornene structures, such as the norbornene *tert*-butyl ester (NTBE, **1**, Figure 1), were developed for use at 193 nm, proving to be suitable replacements for the heavily absorbing, etch-resistant aromatics used in previous generations of photoresists. Unfortunately, while the majority of the polar functionalities (esters, carbonates, alcohols, and anhydrides) used in resist chemistry are transparent at 193 nm, the absorption coefficients of carbon−carbon double bonds, carbon−oxygen single bonds, carbon−oxygen double bonds, and even some carbon−hydrogen bonds are all too high at 157 nm for these functionalities to be useful.[4]

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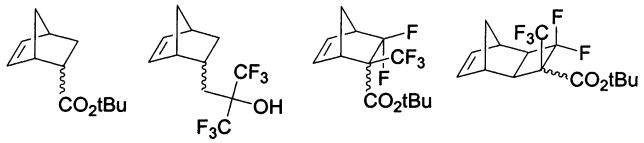

Figure 1. Norbornene-type monomers for lithography applications.

Fortunately, through computational[5] and experimental[6] efforts, it was discovered that the incorporation of fluorinated substituents dramatically reduces the absorption of various structures at 157 nm. For example, the hexafluoroisopropyl alcohol functionalized norbornene (NBHFA, **2**) was found to be highly transparent.[6] In addition, because of the inductive effects of the two trifluoromethyl groups, the acidity of the this type of fluorinated alcohol is similar to that of phenol,[7] allowing this polar monomer to replace the highly absorbing phenolic structures used in previous generations of resists. This discovery has renewed interest in resists based on metal-catalyzed addition polymers of functionalized norbornenes, originally developed for 193 nm,[8] as promising candidates for 157 nm photoresists. Protection of the hexafluoroisopropyl alcohol functionality of **2** with *t*-BOC groups has produced monomers suitable for resist development.[6] Efforts to expand the scope of 157 nm resists to include those based on the more thermally stable *tert*-butyl and tetrahydropyranyl esters have achieved only partial success due to the high absorbance of ester-functionalized monomers such as **1** at 157 nm. Fortunately, the incorporation of an

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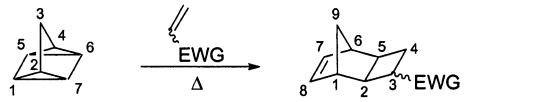


Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (Quadricyclane) 3-EWG-tricyclo[4.2.1.0^{2,5}]non-7-ene

Figure 2. Cyclizations of quadricyclane with electron-deficient olefins (EWG = electron-withdrawing group).

α-trifluoromethyl group was found to significantly reduce the absorption of these esters.[6] Similarly, the absorbance of norbornane structures could be reduced by the incorporation of judiciously positioned fluorine substituents.[6] The fluorinated monomer **3** was subsequently designed as an ideal replacement for the highly absorbing norbornene **1**. Unfortunately, norbornene monomers of this type with geminal electron-withdrawing ester and trifluoromethyl substituents were found to be unsuitable for polymerization with common nickel and palladium catalysts.[9] The addition of an α-trifluoromethyl group in **3**, while addressing the transparency problem, hinders the polymerization. Thus, alternative approaches toward a polymerizeable monomer incorporating these transparent esters were investigated.

Recently, Grubbs et al. reported that, in the copolymerization of ethylene and functionalized norbornene-type monomers to produce functionalized polyethylene, high incorporation (up to 31 mol %) of polar functionalities could be achieved through the use of functionalized tricyclo[4.2.1.0^{2,5}]non-7-ene (TCN) monomers.[10] The combination of reduced steric interference due to the 100% exo configuration of the cyclobutane ring (moving the geminal electron-withdrawing functionalities an additional carbon away from the double bond) and increased ring strain improved the reactivity of the tricyclononene monomers toward metal-catalyzed addition polymerization. The use of TCN chemistry in photoresists is a potential solution to the polymerization difficulties of the partially fluorinated norbornenes mentioned previously.

Tricyclo[4.2.1.0^{2,5}]non-7-enes (TCNs) are formed from the [2σ + 2 σ + 2π] cycloaddition of quadricyclane (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane) with electron-deficient dieneophiles, such as alkenes, alkynes, and azo compounds (Figure 2).[11,12] The cycloadditions proceed readily at moderate temperature with electron-deficient olefins to produce norbornene-like structures with a fused cyclobutane ring in the exo configuration. While the allowed thermal homo-Diels−Alder [2π + 2π + 2π] reaction between norbornadiene and electron-deficient olefins[13] can be catalyzed by nickel and cobalt species[14] to produce deltacyclanes, in certain cases metal-catalyzed [2π + 2π] cycloadditions can also occur to produce a mixture of tricyclononenes in which the cyclobutane ring appears be in either the exo or the endo configuration.[14b,15] Unfortunately, the tri- and tetrasubstituted double bonds of the resulting tricyclononenes,[16] coupled with the complex mixture of exo and endo isomers, renders this route unattractive for the production of valuable monomers. At present, the quadricyclane pathway is the only viable synthetic route toward TCN monomers suitable for metal-catalyzed addition polymerization.

The wide variety of electron-withdrawing groups (nitriles, anhydrides, esters, etc.) able to undergo cyclizations with quadricyclane allows TCNs to retain the versatility of established norbornene chemistry. While most reports of TCN chemistry to date have investigated the regio- and stereospecificity[11] and concertedness of the cyclization reaction,[17] the value of photoresist materials prompted us to consider these compounds for materials development. In this paper, we report the development of partially fluorinated tricyclo[4.2.1.0^{2,5}]-non-7-ene-3-carboxylic acid esters, such as monomer **4**, as transparent, ester-functionalized norbornene-like monomers useful for incorporation into addition-type photoresist polymers.

Experimental Section

Materials. All manipulations and polymerizations were carried out in a N_2-filled drybox or using standard Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å[18] molecular sieves. Dichloromethane was rigorously degassed in 18 L reservoirs and passed through two sequential purification columns consisting of activated alumina. All starting materials were procured from Aldrich except methyl 2-(trifluoromethyl)-3,3,3-trifluoropropenoate (Synquest) and (2-trifluoromethyl)acrylic acid (Honeywell) and were used as received unless noted otherwise. 2,2-Difluoronorbornane was synthesized according to the literature procedures.[6a] 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.

Methods. Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300, Varian Unity Plus 300, or a Varian Gemini 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{19}F, 282 MHz). Select NMR spectra for compound **10** were obtained using a Varian 500 MHz spectrometer (^{13}C, 125 MHz; ^{19}F, 470 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, $CFCl_3$) or to the chemical shift of the residual proteo solvent. Infrared spectra were recorded on either a Nicolet Avatar 360 or a Perkin-Elmer Paragon 1000 IR spectrometer. Mass spectra were measured on a Finnigan MAT TSQ-700 spectrometer. Molecular weights (M_n) and polydispersity indices (PDI) were measured from THF solutions by size exclusion chromatography (SEC) using a Viscotek gel permeation chromatograph (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. Select samples were analyzed by SEC using a GPC apparatus equipped with two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP digital refractometer (both from Wyatt Technology). No calibration standards were used and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns. 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.[19] 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.

General Synthesis Procedure for Tricyclononene Compounds. One equivalent of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane

(quadricyclane) and 1−3 equiv of acrylate were placed in a thick-walled Schlenk tube. The components were degassed, and the flask was sealed under an atmosphere of argon. For reactions in which radical polymerization of the olefin occurs readily, small amounts (0.001 equiv) of suitable radical inhibitors, such as hydroquinone, were added. The reaction mixture was heated to 96 °C for 24−72 h. The tricyclononene product was separated from the residual quadricyclane starting material and norbornadiene and polymeric byproducts by Kugelrohr vacuum distillation to yield colorless liquids (or solids).

Tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylic Acid (5). 3-Cyano-tricyclo[4.2.1.0^{2,5}]non-7-ene (prepared by the cycloaddition of quadricyclane with acrylonitrile[20]) (23.6 g, 0.162 mol) was dissolved into 40 mL of ethylene glycol and added to a 250 mL round-bottom flask charged with 1.5 equiv of potassium hydroxide (13.7 g, 0.244 mol) in 25 mL of H_2O. The resulting biphasic system was stirred vigorously while refluxing at 140 °C for 24 h. The resulting mixture was acidified with 20 mL of HCl (37% solution in H_2O). The product was extracted into ethyl ether and dried over $MgSO_4$. Removal of the solvent in vacuo produced a viscous, colorless oil, which crystallized overnight into a white crystalline material. Removal of residual ethylene glycol was achieved via Kugelrohr distillation (80 °C, 60 mTorr) to produce 16.4 g (0.098 mol) of a viscous, colorless oil, which crystallized overnight into a white crystalline material. Yield: 61%. Isomer composition: >98% anti. Anti isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 11.27 (br s, COOH), 6.01 (dd, J = 2.7, 6.0 Hz, 1H, H-7), 5.96 (dd, J = 2.7, 6.0 Hz, 1H, H-8), 2.78 (s, 1H, H-1), 2.70 (s, 1H, H-6), 2.50 (m, 1H, H-3), 2.40 (m, 1H, H-4), 2.23 (m, 1H, H-2), 2.05 (m, 1H, H-5), 1.67 (d, J = 8.7 Hz, 1H, H-9 anti), 1.62 (m, 1H, H-4), 1.37 (dt, J = 1.7, 9.6 Hz, 1H, H-9 syn). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.91 (COOH), 136.07 (CH, C-7), 134.68 (CH, C-8), 44.31 (CH, C-6), 44.13 (CH, C-1), 40.72 (CH, C-2), 40.48 (CH_2, C-9), 37.55 (CH, C-3), 34.47 (CH, C-5), 24.02 (CH_2, C-4). IR (KBr, Nujol, cm^{-1}): 3050, 1700, 1464, 1417, 1267, 1240, 1211, 927, 692. HRMS-EI (m/z): [M + H]$^+$ calcd for $C_{10}H_{13}O_2$: 165.0916; found: 165.0903.

***tert*-Butyl Tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (6).** Quadricyclane (15 mL, 14.7 g, 0.16 mol) and 4 equiv of *tert*-butyl acrylate (92 mL, 80.7 g, 0.63 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 28.0 g (0.13 mol) of colorless liquid. Yield: 80%. Isomer composition: 57% syn, 43% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.94 (m, 4H, H-7 + H-8, syn + anti), 3.12 (ddd, J = 7.8, 9.6, 11.1 Hz, 1H, H-3, syn), 2.90 (s, 1H, H-1, syn), 2.70 (s, 1H, H-1, anti), 2.63 (s, 2H, H-6, syn + anti), 2.34−2.05 (5H, syn + anti), 2.02−1.87 (2H, H-5 syn + anti), 1.68 (dd, J = 4.8, 7.8 Hz, 1H, H-4, syn), 1.65−1.58 (2H, H-9 anti, syn + anti), 1.57−1.48 (1H, H-4, anti), 1.44 (s, 9H, C(CH_3)$_3$, syn), 1.43 (s, 9H, C(CH_3)$_3$, anti), δ 1.29 (dt, J = 1.5, 8.1 Hz, 1H, H-9 syn, anti), 1.17 (dt, J = 1.5, 9.6 Hz, 1H, H-9 syn, syn). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.22 (*C*OOtBu, anti), δ 173.40 (*C*OOtBu, syn), 136.07 (olefin C, syn), 135.81 (olefin C, anti), 135.13 (olefin C, syn), 134.61 (olefin C, anti), 80.03 (*C*(CH$_3$)$_3$, syn), 79.77 (*C*(CH$_3$)$_3$, anti), 44.92 (CH, C-6, syn), 44.17 (CH, C-6, anti), 43.96 (CH, C-1, anti), 42.46 (CH, C-1, syn), 40.57 (CH, C-2, anti), 40.41 (CH_2, C-9, anti), 40.36 (CH_2, C-9, syn), 40.14 (CH, C-2, syn), 38.48 (CH, C-3, anti), 35.56 (CH, C-3, syn), 34.26 (CH, C-5, anti), 33.50 (CH, C-5, syn), 28.30 (COOC(*C*H$_3$)$_3$, syn), 28.18 (COOC(*C*H$_3$)$_3$, anti), 23.79 (CH_2, C-4, anti), 23.07 (CH_2, C-4, syn). IR (KBr, cm^{-1}): 3057 (alkene), 2972, 1723 (C=O), 1456, 1391, 1367, 1349, 1322, 1256, 1228, 1215, 1154, 848, 754, 698. HRMS-EI (m/z): [M + H]$^+$ calcd for $C_{14}H_{21}O_2$: 221.1542; found: 221.1546.

***tert*-Butyl 3-(Methyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (7).** Quadricyclane (15 mL, 14.7 g, 0.16 mol) and 3 equiv of *tert*-butyl methacrylate (78 mL, 68.2 g, 0.48 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 3.0 g (0.013 mol) of colorless liquid. Yield: 8%. Isomer composition: 55% syn, 45% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.98 (m, 4H, H-7 + 8, syn + anti), 2.95 (s, 1H, H-1, syn), 2.74 (s, 1H, H-1, anti), 2.65 (s, 2H, H-6, syn + anti), 2.44 (m, 1H), 2.1−1.6 (6H, syn + anti), 1.56−1.48 (m, 1H), 1.46 (s, 9H, C(CH_3)$_3$, syn), 1.45 (s, 9H, C(CH_3)$_3$, anti), 1.40 (d, 3H, −CH_3, syn), 1.36−1.18 (4H, syn + anti), 1.16 (d, 3H, −CH_3, anti). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 178.25 (*C*OOtBu, anti), 176.43 (*C*OOtBu, syn), 136.37 (olefin C, anti), 136.23 (olefin C, syn), 135.71 (olefin C, anti), 135.48 (olefin C, syn), 79.94 (*C*(CH$_3$)$_3$, syn), 79.79 (*C*(CH$_3$)$_3$, anti), 48.91 (CH, C-2, syn), 44.63 (CH, C-6, syn), 44.30 (CH, C-2, anti), 43.53 (CH, C-6, anti), 42.99 (CH, C-1, syn), 41.88 (CH_2, C-9, anti), 41.52 (CH, C-1, anti), 41.35 (quat. C, C-3, syn), 41.07 (quat. C, C-3, anti), 40.65 (CH_2, C-9, syn), 33.09 (CH, C-5, anti), 31.36 (CH_2, C-4, anti), 31.08 (CH_2, C-4, syn), 30.48 (CH, C-5, syn), 28.37 (CH_3, syn), 28.32 (C(*C*H$_3$)$_3$, syn), 28.17 (C(*C*H$_3$)$_3$, anti), 16.91 (CH_3, anti). IR (KBr, cm^{-1}): 3057 (alkene), 2972, 1720 (C=O), 1470, 1456, 1391, 1367, 1313, 1281, 1256, 1227, 1131, 849, 757, 703. HRMS-EI (m/z): [M + H]$^+$ calcd for $C_{15}H_{23}O_2$: 235.1698; found: 235.1698.

Methyl 3-(Trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (8). Quadricyclane (1.5 equiv, 4.25 g, 0.046 mol) and methyl (2-trifluoromethyl)acrylate[6a] (1 equiv, 4.55 g, 0.30 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 6.78 g (0.028 mol) of colorless liquid. Yield: 94%. Isomer composition: 32% syn, 68% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 6.1−5.9 (m, 4H, H-7 + H-8, syn + anti), 3.80 (s, 3H, COOC*H*$_3$, syn), 3.78 (s, 3H, COOC*H*$_3$, anti), 3.06 (s, 1H, H-1, syn), 2.99 (s, 1H, H-1, anti), 2.82 (s, 1H, H-6, syn), 2.74 (s, 1H, H-6, anti), 2.68 (ddd, J = 3.0, 7.5, 13.2 Hz, 1H, anti), 2.5−1.9 (7 H), 1.48−1.24 (4 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 171.16 (d, J = 2.9 Hz, *C*OOMe, syn), 168.85 (d, J = 2.4 Hz, *C*OOMe, anti), 136.74 (olefin C, anti), 136.62 (olefin C, syn), 135.24 (olefin C, syn), 135.06 (olefin C, anti), 126.32 (q, J = 280 Hz, CF_3, anti), 125.16 (q, J = 281 Hz, CF_3, syn), 53.30 (COO*C*H3, syn), 52.81 (COO*C*H$_3$, anti), 49.56 (q, J = 28.6 Hz, quat. C, C-3, syn), 49.40 (q, J = 26.5 Hz, quat. C, C-3, anti), 44.50 (CH, C-6, anti) 44.18 (CH, C-6, syn), 44.15(CH, C-2, syn), 42.86 (CH, C-1, syn), 42.50 (CH, C-1, anti), 41.95 (m, J = 2.0 Hz, CH, C-2 anti), 41.14 (m, CH_2, C-9, anti), 40.71 (CH_2, C-9, syn), 32.98 (CH, C-5, syn), 32.83 (CH, C-5, anti), 26.07 (d, J = 2.4 Hz, CH_2, C-4, anti), 25.93 (d, J = 1.9 Hz, CH_2, C-4, syn). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm) (referenced to external C_6F_6 standard at −166.717 ppm): δ −66.25 (s, 3F, $-CF_3$, syn), δ −75.13 (s, 3F, $-CF_3$, anti). IR (KBr, cm^{-1}): 3060 (alkene), 2970, 2892, 1742 (C=O), 1473, 1436, 1333, 1322, 1275, 1225, 1163, 1132, 1087, 712, 671. HRMS-EI (m/z): [M]$^+$ calcd for $C_{12}H_{14}F_3O_2$: 246.0868; found: 246.0868.

(Triethylamino)boron Trifluoride.[21] To a cooled (dry ice/acetone) 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 an 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. A slight modification of the literature procedure was used.[22] 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-trifluoropropionate (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 −58.5 (m, 1F, RC=CF_2), −59.1 (m, 3F, CF_3), −59.5 (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 (9). To a 300 mL Parr pressure reactor equipped with a magnetic stir bar were added quad-

ricyclane (1.5 g, 16.3 mmol) and methyl 3,3-difluoro-2-(trifluoromethyl)acrylate (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%). In a subsequent synthesis, it was found that if the reaction was allowed to sit at room temperature for 14 days after the initial heating, the isolated yield increased to 73%. Isomer composition: 49% syn, 51% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.27 (dd, J = 2.7, 5.7 Hz, olefin H, 1H, anti), 6.05−6.15 (m, olefin H, 3H, 2 syn + 1 anti), 3.87 (s, COOCH_3, 3H, anti), 3.86 (s, COOCH_3, 3H, syn), 3.53 (s, 1H, H-1, syn), 3.22 (2H, H-1, H-6, anti), 3.13 (s, 1H, H-6, syn), 2.84−2.75 (m, 1H, H-5, anti), 2.75−2.6 (m, 1H, H-5, syn), 2.39−2.31 (m, 1H, H-2, syn), 2.10 (d, J = 10.2 Hz, 1H, H-2, anti), 1.50−1.30 (m, 4H, H-9 syn, H-9 anti, syn+anti). ^{13}C NMR (C_6D_6, 75 MHz, ppm): 165.11 (COOMe, syn), 162.91 (COOMe, anti), 139.62 (olefin C, anti), 137.82 (olefin C, syn), 136.93 (olefin C, syn), 136.77 (olefin C, anti), 123.97, (q, J = 283 Hz, CF_3, syn), 123.68 (q, J = 280 Hz, CF_3, anti), 116.72 (t, J = 292 Hz, C-5), 114.09, (t, J = 296 Hz, C-5), 53.32 (COOCH_3, anti), 52.64 (COOCH_3, syn), 50.70 (dd, J = 19.2, 26 Hz, CH, C-5, anti), 50.36 (t, J = 23 Hz, CH, C-5, syn), 43.71 (CH, C-1, anti), 43.26 (CH, C-1, syn), 43.11 (dd, J = 4.4, 8.2 Hz, CH_2, C-9, anti), 42.82 (d, J = 6.6 Hz, CH_2, C-9, syn), 42.08 (CH, C-6, anti), 41.29 (t, J = 2.3 Hz, CH, C-6, syn), 37.21 (dd, J = 4.9, 12 Hz, CH, C-2, anti), 36.90 (m, CH, C-2, syn). ^{19}F NMR (acetone, 282 MHz, ppm): δ −61.67 (d, J = 6.7 Hz, 3F, CF_3, anti), −68.36 (d, J = 2.0 Hz, 3F, CF_3, syn), −85.70 (dm, J = 211 Hz, 1F, F-4 syn, anti), −97.15 (dm, J = 217 Hz, 1F, F-4 anti, syn), −106.87 (d, J = 217 Hz, 1F, F-4 syn, syn), −113.94 (d, J = 211 Hz, 1F, F-4 anti, anti). IR (NaCl, cm^{-1}): 3058 (alkene), 2991, 2909, 1752 (C=O), 1429, 1317, 1219, 1045, 897, 794, 697. HRMS−CI (m/z): [M + H]$^+$ calcd for $C_{12}H_{12}F_5O_2$: 283.0757; found: 283.0755.

4,4-Difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylic Acid (10). Hydrolysis of **9** with KOH and water under standard conditions produced the carboxylic acid. One of the isomers selectively crystallized from solution and was determined to be the syn isomer by X-ray crystallography. Syn isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.6−8.4 (br s, 1H, COOH), 6.16 (m, 2H, H-7 + H-8), 3.50 (s, 1H, H-1), 3.16 (s, 1H, H-6), 2.69 (m, J = 4.2 Hz, 1H, H-5), 2.35 (m, 1H, H-2), 1.45 (s, 2H, H-9 syn, H-9 anti). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.63 (COOH), 137.94 (C-8), 137.082 (C-7), 122.93 (q, J = 282 Hz, CF_3), 116.08 (t, J = 290 Hz, C-4), 59.5 (quat C, C-3), 50.25 (t, J = 23 Hz, CH, C-5), 43.04 (CH, C-1), 42.80 (d, J = 6.4 Hz, CH_2, C-9), 41.25 (t, J = 1.8 Hz, CH, C-6), 36.77 (m, CH, C-2). ^{19}F NMR ($CDCl_3$, 470 MHz, ppm): δ −68.94 (dd, J = 2.4, 17.0 Hz, 3F, CF_3), −97.81 (dm, J = 217 Hz, 1F, F-4 anti), −107.95 (d, J = 217 Hz, 1F, F-4 syn). HRMS−CI (m/z): [M + H]$^+$ calcd for $C_{11}H_{10}F_5O_2$: 269.0601; found: 269.0589.

General Hydrogenation Procedure. Norbornene or tricyclononene monomer (5.86 mmol) was dissolved in 16 mL of ethyl acetate in a 250 mL Parr bomb (Parr Instrument Co., MAWP 3000 psi at 350 °C). Palladium (10% on carbon, 0.015 g) was added to the bomb, which was pressurized to 50 psi with H_2. The reaction mixture was stirred overnight at room temperature, the catalyst was removed with a 0.45 μm PTFE syringe filter, and the solvent was removed by rotary evaporation to yield a clear oil.

General Polymerization Procedure. To a 20 mL vial equipped with a stir bar were added allyl palladium chloride dimer (13.0 mg, 0.032 mmol) and silver hexafluoroantimonate (28 mg, 0.064 mmol) in a drybox. Dichloromethane (5 mL) was added, and the mixture was stirred at room temperature for 20 min. The mixture was filtered through a 0.45 μm PTFE syringe filter into a 25 mL round-bottom flask containing a solution of tricyclononene monomer (3.25 mmol, [M]/[C] = 50:1) in dichloromethane (10 mL). For resist evaluation, higher catalyst loadings ([M]/[C] = 10) were used to ensure only low molecular weight polymer (<10 000 g/mol) was formed. For monomers with *tert*-butyl ester functionalities, the resulting solution was stirred for 10 min at room temperature and then transferred to a 25 mL round-bottom flask containing polymer-bound 2,6-di-*tert*-butylpyridine (1 mg/mg catalyst). The reaction mixture was stirred at room temperature for 96 h, then filtered through a 0.45 μm PTFE syringe filter to remove the polymer-bound base, concentrated in vacuo, and precipitated into hexanes (100 mL). The crude polymer was dissolved in ethyl acetate (50 mL) and stirred vigorously under a hydrogen atmosphere overnight. The solution was allowed to sit, unstirred, for another hour, at which time a black solid (Pd) aggregated and precipitated. 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.

Poly(*tert*-butylbicyclo[2.2.1]hept-5-ene-2-carboxylate) (Poly-1). *tert*-Butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (NBTBE, **1**) was polymerized by the general procedure mentioned previously ([M]/[C] = 10:1) to produce a 60% yield of white polymeric powder. ^{1}H NMR (acetone-d_6, 300 MHz, ppm): δ 3.0−1.0 (m, aliphatic), 1.40 (br s, COOC(CH_3)$_3$). IR (KBr, cm^{-1}): 2971, 2879, 2571, 1724 (C=O), 1455, 1392, 1367, 1290, 1151, 1049, 886, 846, 660. GPC: M_n = 5380; PDI = 1.79. A_{157} = 6.02 μm^{-1}.

Poly(3-(bicyclo[2.2.1]hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol) (Poly-2). 3-(Bicyclo[2.2.1]-hept-5-en-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol (NB-HFA, **2**)[6a] was polymerized by the general procedure mentioned previously ([M]/[C] = 10:1) to produce a 55% yield of white powdery polymer. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): δ 7.6 (br s, OH), 2.80−0.50 (br m, aliphatic). ^{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_n = 3860; PDI = 2.11. A_{157} = 1.15 μm^{-1}.

Poly(*tert*-butyltricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate) (Poly-6). *tert*-Butyl tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate was polymerized by the general procedure mentioned previously ([M]/[C] = 50:1) to produce a white polymeric powder. ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 3.3−2,9 (br m, aliphatic), 2.8−1.9 (br m, aliphatic), 1.9−1.0 (br m, aliphatic), 1.4−1.2 (br s, COOC(CH)$_3$). SEC (GPC-MALLS): M_n = 18 800, PDI = 2.01.

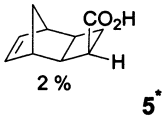
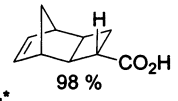
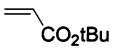
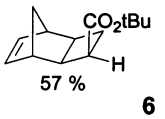
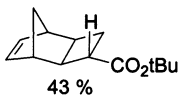
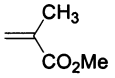
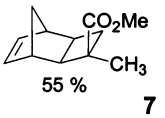
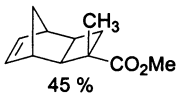
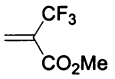
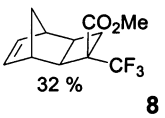
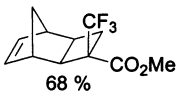
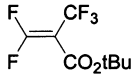
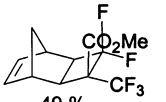
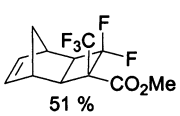
Poly(methyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate) (Poly-8). Methyl 3-(trifluoromethyl)-tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate was polymerized by the general procedure mentioned previously ([M]/[C] = 50:1) to produce a 79% yield of white polymeric powder. ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 4.20−3.30 (br s, COOCH_3), 0.50−3.20 (br m, aliphatic). A_{157} = 3.79 μm^{-1}. SEC (GPC): M_n = 66 300, PDI = 2.11

Poly(methyl 4,4-difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (Poly-9). Methyl 4,4-difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylate was polymerized by the general procedure mentioned previously ([M]/[C] = 10:1) to produce a 50% yield of white polymeric powder. A_{157} = 2.86 μm^{-1}. SEC (GPC): M_n = 7200, PDI = 2.58.

Results and Discussion

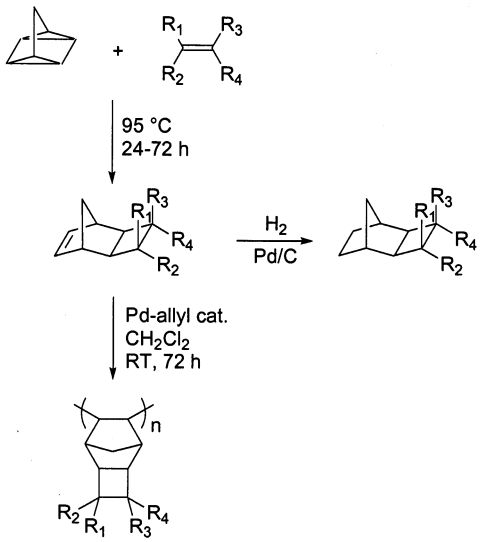
Synthesis of TCN Monomers A series of tricyclononene compounds (**5**−**9**, Table 1) were synthesized from quadricyclane and the appropriate olefin as shown in Scheme 1. The numbering system and nomenclature used are shown in Figure 2 and Table 1, respectively. The methylene bridge (C9) hydrogens will be referred to as either syn or anti to the C(7)−C(8) olefin. The most important substituent (nitrile or ester) at C(3) on the cyclobutane ring will be referred to as being syn or anti to the C(1)−C(2) bond, to avoid confusion with the exo notation used to describe the cyclobutane ring fusion. Since the majority of TCN compounds reported in the literature[11] were made from symmetrical 1,1- or 1,2-

Table 1. Selectivity in TCN Monomer Synthesis

Olefin	TCN Products	
	Syn	*Anti*
	 2 % **5***	 98 %
	 57 % **6**	 43 %
	 55 % **7**	 45 %
	 32 % **8**	 68 %
	 49 % **9**	 51 %

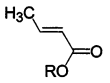
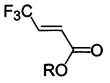
* After hydrolysis

Scheme 1. Synthesis of TCN Monomers, Model Compounds, and Polymers



disubstituted olefins, less is known about the resultant TCN isomer distribution produced using nonsymmetrical 1,1-disubstituted olefins. Particular attention will be paid to the syn/anti isomer distribution as it may significantly affect the rate of polymerization and/or incorporation ratio in copolymerizations. The syn/anti isomer distributions produced by the quadricyclane cyclizations will be compared with the more familiar exo/endo isomer distributions achieved by Diels−Alder reactions with cyclopentadiene. Finally, while esters with readily removable *tert*-butyl or cyclic acetal protecting groups are required for use in imageable photoresists, the more synthetically and commercially accessible methyl esters of the fluorinated acrylates were employed in this initial study.

Table 2. Comparison of Cyclopentadiene and Quadricyclane Cycloadditions

Olefin	Cyclopentadiene (% *endo*, 25 °C)	Cyclopentadiene (% *endo*, 100 °C)	Quadricyclane (% *syn*, 97 °C)
	74.3 (R=Me) [25c]	70.5 (R=Me) [25c]	57 (R=*t*-Bu)
	30.1 (R=Me) [25c]	31.8 (R=Me) [25c]	55 (R=*t*-Bu)
	67 (R=H) [29]		32 (R=Me)
	50.9 (R=Me) [25c]	50.8 (R=Me) [25c]	
	26.3 (R=H) [28d]		

The nitrile-functionalized TCN monomer was synthesized by the cycloaddition of quadricyclane and acrylonitrile, using the procedure of Noyori,[20] to produce 3-cyano-tricyclo[4.2.1.$0^{2,5}$]non-7-ene with a 2:1 syn:anti ratio and 100% exo cyclobutane ring fusion. Subsequent base-catalyzed hydrolysis of the nitrile afforded the carboxylic acid (**5**) with a syn:anti ratio of approximately 2:98. During the hydrolysis, epimerization around the C(3) position converts the syn isomer into the more stable anti isomer, consistent with the results of Tabushi et al.[11e] regarding the base-catalyzed isomerization of cis and trans diester and dinitrile-substituted tricyclononenes.

Cyclization of quadricyclane with acrylonitrile or *tert*-butyl acrylate produced high yields (80%+ with respect to quadricyclane) of TCN products with a preference for the syn product. While this syn structure is formed via a transition state with the maximal orbital overlap on C(2) and C(4) of quadricyclane as is the case in Diels−Alder reactions, the role of electrostatic effects or intermolecular attractive forces remains unknown. The predominant byproducts of the reaction are norbornadiene formed by slow isomerization of quadricyclane under the reaction conditions and acrylate or acrylonitrile homopolymer.[23]

tert-Butyl methacrylate and methacrylonitrile also undergo cyclizations with quadricyclane, albeit in dramatically reduced yields (∼8% for *tert*-butyl methacrylate).[24] Interestingly, no appreciable difference in the syn/anti ratio is observed despite the introduction of the α-methyl group. This is in direct contrast to the cycloaddition behavior of cyclopentadiene, as shown in Table 2. In cycloadditions with cyclopentadiene, the presence of an α-methyl group on an acrylate induces a preference for the exo isomer (∼70% exo vs ∼30% exo for acrylate), while a trans *β*-methyl group has only a small effect.[25] This deviation from endo selectivity has been attributed to either steric interference between the α-methyl group and the methylene hydrogens of cyclopentadiene or secondary attractive forces between the methyl and the unsaturated carbons.[25] Since the transition state in the quadricyclane cycloaddition is centered

on C(6) and C(7) (Figure 2), steric interference by the C-3 methylene hydrogens appears to be minimal as exhibited in the small effect on the syn/anti ratio upon incorporation of the α-methyl group (**6** and **7**, Table 1).

Cyclization of quadricyclane with methyl 2-(trifluoromethyl)acrylate proceeded nearly quantitatively by ^{1}H NMR to produce **8** in 94% isolated yield after 72 h. The inability of the fluorinated methacrylate to undergo radical homopolymerization prevents it from being consumed in the production of polymeric byproducts, leading to a high yield. The facile cycloaddition is consistent with the observed behavior of olefins with trifluoromethyl substituents in 1,3-dipolar[26] and Diels−Alder cycloaddition reactions.[27] Unlike the previous acrylate and methacrylate cyclizations, this reaction produced predominantly the anti product (syn/anti = 32:68), similar to the cycloaddition of cyclopentadiene and either *trans*-crotonic acid or *trans*-4,4,4-trifluorocrotonic acid (Table 2).[28] In contrast, the cycloaddition of 2-(trifluoromethyl)acrylic acid with cyclopentadiene exhibits little change in exo/endo preference relative to acrylic acid.[29] Since the trifluoromethyl group is more sterically bulky than a methyl group (being more similar to an isopropyl group),[30] the high yield in the cyclization with the methyl 2-(trifluoromethyl)acrylate (unlike the cyclizations with *tert*-butyl methacrylate or methacrylonitrile) demonstrates the importance of the electronics of the dienophile in cyclizations with quadricyclane.

Unfortunately, the cyclization with the methyl 3,3-difluoro-2-(trifluoromethyl)acrylate produced only a moderate yield (∼25%) of TCN **9** after 72 h. This was in distinct contrast to the excellent yields obtained in the Diels−Alder reaction of this perfluorinated olefin with cyclopentadiene. The yield was increased to 73% upon allowing the reaction mixture to continue at room temperature for several days. This is similar to some cycloadditions with furan in which high yields are observed after long reaction times at room temperature.[31] Further work is required to explain the reluctance of this fluorinated methacrylate to undergo cyclization with quadricyclane.

Assignment of TCN Isomers As mentioned previously, little has been published on TCN compounds obtained from nonsymmetric 1,1-disubstituted olefins. Therefore, we endeavored to find a simple diagnostic to determine the isomeric product distribution in these compounds. Fortunately, because of epimerization during the hydrolysis reaction, the TCN carboxylic acid (**5**) is almost exclusively the anti isomer. ^{1}H, ^{13}C, ^{13}C DEPT, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMQC, and HETCOR NMR experiments were used to assign the carbon and proton resonances in this compound. The spectra were compared with the available published spectral data[10e,16,31] for other tricyclo[4.2.1.0^{2,5}]non-7-ene compounds. The exo configuration of the cyclobutane ring fusion was established by the W-coupling between H(9_{syn}) and H(2) and H(5) (^4J = 1.7 Hz), that is similar to the reported values for *exo*-3-thiatricyclo[4.2.1.0^{2,5}]non-7-ene-3,3-dioxide.[32]

The bridgehead protons H(1) and H(6) each appear as distinct unresolved multiplets with the H(1) proton appearing about 0.08 ppm downfield from H(6). The $\Delta\delta$ for H(1)−H(6) is diagnostic of syn and anti due to deshielding by the nearby substituents on C(3). For example, in the *tert*-butyl ester TCN compound (**6**), H(6) of both the syn and anti isomer are identical; however, while H(1) of the anti isomer appears 0.07 ppm downfield of H(6), H(1) of the syn isomer is shifted 0.27 ppm downfield due to closer proximity of the ester group, in agreement with the reported NMR assignments for the isolated anti isomer of **6**.[10] Since the bridgehead hydrogens in TCNs **5**−**9** appear between 2.5 and 3.6 ppm (well resolved from each other and the other protons in these compounds) and agree with the integration of the protons belonging to any ester substituents for the corresponding isomer, the isomer ratio for each compound was determined by integration of the H(1) and H(6) bridgehead protons.

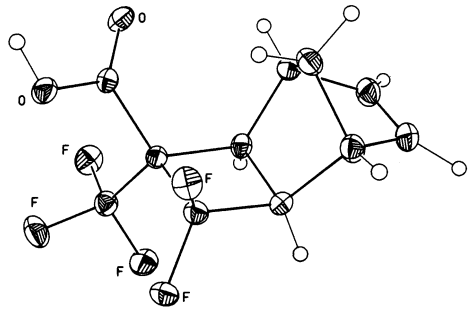


Figure 3. X-ray crystal structure of the carboxylic acid **10**. Displacement ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary size.

The hydrolysis of the fluorinated TCN methyl ester (**9**) produced a mixture of carboxylic acid isomers, one of which was isolated by crystallization. X-ray crystallographic analysis revealed that this isomer is the syn compound (**10**, Figure 3). The crystal structure of **10** is similar to that of an imide-functionalized TCN structure reported in the literature.[33] From the crystal structure, the proximity of the carboxylic acid in the syn position to the bridgehead H(1) proton, responsible for significant deshielding of the proton, is apparent. The crystal structure and NMR data from the syn isomer of the fluorinated TCN carboxylic acid (**10**) complement the NMR data from the anti isomer of the nonfluorinated TCN carboxylic acid (**5**), confirming the assignments of the isomers and the validity of using the $\Delta\delta$ for H(1)−H(6) as a diagnostic.

Synthesis of Saturated TCN Compounds The first concern with these TCN monomers was preservation of the transparency demonstrated in the analogous norbornane structures. It was unknown whether the addition of the fused cyclobutane ring would pose any absorbance problems at 157 nm, similar to those of cyclopropane rings in nortricyclane-based polymers at 193 nm.[34] To investigate this, several tricyclononane compounds were produced by hydrogenating the double bonds of various TCN monomers. Gas-phase vacuum-ultraviolet (VUV) spectra of the fluorinated tricyclononane compounds, shown in Figure 4, reveal promising transparency. In fact, the saturated version of **9** exhibits even higher transparency than norbornane. While still more heavily absorbing than 2,2-difluoronorbornane (one of the most transparent norbornanes at 157 nm discovered to date), these results were encouraging enough to pursue additional experimental verification of transparency. Variable angle spectroscopic ellipsometry (VASE), currently the most accurate and representative technique to measure lithographic material transparency at 157 nm,[35] necessitated the synthesis of TCN homopolymers for the analysis of thin films.

Synthesis of TCN Homopolymers The most common late-transition-metal catalyst systems used to

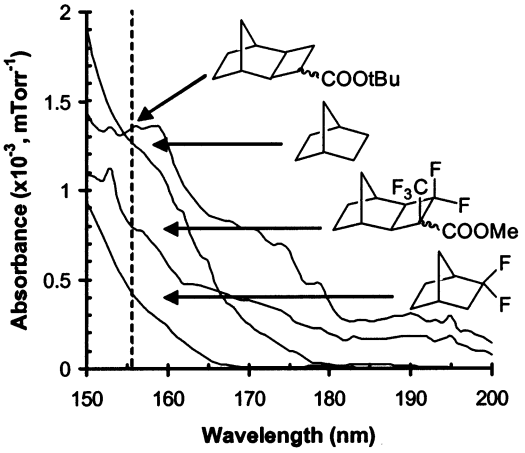


Figure 4. Vacuum-UV spectra of model tricyclononane structures.

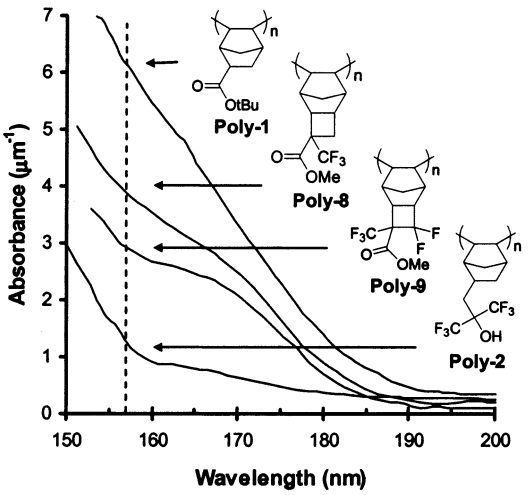


Figure 5. VASE spectra of TCN homopolymers.

polymerize norbornene systems by an addition mechanism are based on palladium[36] and nickel.[37] To produce model polymers, TCN compounds **6**−**9** were polymerized using cationic palladium allyl hexafluoroantimonate catalyst reported by Risse,[36e] selected for its ready availability, ease of preparation, and tolerance to polar functionalities. Polymerization proceeded at room temperature with quantitative disappearance of the monomer after 24−36 h by ^{1}H NMR. While the reaction is considerably slower than the polymerization of norbornene, it is comparable to the polymerization of norbornenes possessing polar substituents.[36e,38] Indeed, because of the nearly identical olefin structure, the behavior of TCN monomers is similar to that of norbornene monomers. For example, we have observed that TCN monomers undergo facile radical copolymerization with maleic anhydride to produce alternating copolymers,[39] analogous to the functionalized norbornene−maleic anhydride copolymers[40] developed for 193 nm lithography.

During polymerization of the TCN monomers containing *tert*-butyl esters (such as **6** and **7**), catalytic deprotection of the *tert*-butyl esters was observed (with the generation of isobutylene and carboxylic acid observed by ^{1}H NMR), resulting in aggregation and precipitation of the deprotected polymers. Use of sterically hindered bases to inhibit this catalytic deprotection was successfully employed and will be discussed in more detail in a separate publication.[41]

Polymerization of fluorinated TCN compounds **8** and **9** proceeded similarly to the nonfluorinated TCN compounds, in stark contrast to the very low yields[9] achieved with norbornene monomers like **3** under identical conditions. The facts that polymerization proceeds in the presence of basic pyridine moieties and the observed unreactivity of TCN monomers toward radical initiators at moderate temperatures[39] rule out any cationic or radical polymerization mechanism. The lack of double bonds (as observed by ^{1}H NMR) and the high glass transition temperatures of TCN polymers confirm the 2,3-addition polymer structure. Furthermore, the moderate molecular weights and polydispersity indices ($1.7 < \text{PDI} < 2.7$) of the polymers are typical of polymerizations with palladium catalysts.[36] It should be noted that the fluorinated TCN compound **8** was also readily polymerized by nickel systems such as Ni(tolyl)-(perfluorophenyl)$_2$.

VASE Analysis of TCN Homopolymers Removal of the palladium from the polymer chains by treatment with hydrogen followed by filtration and multiple precipitations produced polymer sufficiently clean for VASE analysis (Figure 5). The homopolymer of NTBE (Poly-**1**) has an absorbance coefficient at 157 nm of 6.02 μm^{-1} compared to the homopolymer of NBHFA (Poly-**2**), which is around 1.14 μm^{-1}. In any copolymer of these two monomers, even small amounts of the highly absorbing ester-containing monomer **1** will raise the overall absorbance of the polymer considerably. In comparison, the homopolymer of TCN **8** (Poly-**8**) possesses an absorbance coefficient of 3.79 μm^{-1}at 157 nm. The addition of the trifluoromethyl group α to the ester increases the transparency of the material by approximately 2 orders of magnitude. The further incorporation of fluorine in TCN **9** serves to increase the transparency of the homopolymer (Poly-**9**) by another order of magnitude ($A_{157} = 2.86$ μm^{-1} at 157 nm).

With these fluorinated TCN monomers, polymers with identical ester content and higher transparency or identical transparency and higher ester content, relative to copolymers of NTBE (**1**), can be synthesized. The extremely high transparency of these materials offers the possibility of ester-containing norbornene-type addition polymers as single layer resists. Toward this end, the synthesis and copolymerization of a number of fluorinated TCN monomers with *tert*-butyl ester functionalities to produce imageable resist materials have been investigated and are reported elsewhere.[41] Exploration of other potential pathways to producing photoresist polymers with a wide range of TCN monomers via free radical, ring-opening metathesis (ROMP), and addition polymerization is currently underway.

Conclusions

Partially fluorinated tricyclo[4.2.1.0^{2,5}]non-7-ene monomers containing ester functionalities undergo metal-catalyzed addition polymerization to produce polymers with transparency suitable for 157 nm resist applications. A number of nonfluorinated and partially fluorinated acrylic and methacrylic acid esters undergo cyclizations with quadricyclane to produce tricyclononene structures in moderate to high yield. The exo configuration of the cyclobutane ring relieves steric crowding of the olefin and reduces inductive effects by locating the highly electron-withdrawing fluorine, trifluoromethyl, and carboxylic acid ester functionalities further from the double bond. In this way, the electronic

and steric issues of the transparent ester motif are balanced with the polymerizability of the monomer. The tricyclononene monomers are readily polymerized in the presence of palladium and nickel catalysts, in marked contrast to the norbornene monomers with geminal trifluoromethyl and carboxylic acid ester groups. Vacuum-UV measurements on saturated model TCN systems and VASE measurements on TCN homopolymers show the high transparency imparted by the selective incorporation of trifluoromethyl and fluorine substituents. These TCN polymers demonstrate improvements in transparency of up to 3 orders of magnitude over conventional polymers of *tert*-butyl ester-functionalized norbornene and constitute a new viable route toward advanced photoresist materials. Copolymerization of these TCN monomers with transparent, polar norbornene monomers will lead to transparent, ester-functionalized 157 nm photoresists.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{19}F NMR spectra for compounds **5**−**10** and crystallographic data (experimental procedure, labeled drawings, table of atomic coordinates, complete bond distances and angles, and anisotropic displacement parameters) for compound **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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