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Polymers for 193-nm Microlithography: Regioregular 2-Alkoxycarbonylnortricyclene Polymers by Controlled Cyclopolymerization of Bulky Ester Derivatives of Norbornadiene[**]

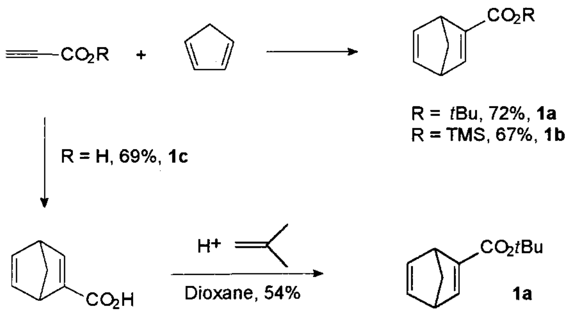
Q. Jason Niu and Jean M. J. Fréchet[*]

The rapid advances in miniaturization of microelectronic devices require that new imageable and etch-resistant polymeric materials be developed for use in 193-nm microlithography. Current research has focused on alicyclic polymers featuring adamantane or norbornane repeating units since such rigid units have been shown to be effective in terms of dry etch resistance.[1, 2] The absence of conjugated double bonds in these alicyclic building blocks is also a favorable feature since the polymers must be transparent at 193 nm. We now report the first synthesis of regioregular, uncross-linked poly(2-alkoxycarbonylnortricyclenes) that may be used for 193-nm microlithography.

In the early 1980s we described a novel family of chemically amplified resists for deep-UV (248 and 254 nm) microlithography.[3] These resists, which have been used commercially for more than a decade, operate on the basis of acid-catalyzed deprotection of a polymer in a process that renders the final product soluble in aqueous base. The chemistry of these resists is now well understood and has been reviewed recently.[4]

Early work by Graham et al. described the free radical polymerization of 2-ethoxycarbonylbicyclo[2.2.1]-2,5-heptadiene to afford an irregular product possessing a structure with more than one repeating nortricyclene-type unit as well as some unsaturated norbornene-type units.[5] As a result of a competing 5,6-directed polymerization, high conversion could not be achieved without gelation of the polymer. Our approach to overcome this problem, while both preserving the high reactivity of the C2–C3 double bond towards free-radical polymerization and introducing an imageable functional group in the side chain of the resulting polymer, is to increase the size of the ester group at the 2-position. This increased steric bulk of the monomer inhibits intermolecular addition at the crowded 2-position while favoring internal cyclopropanation through reaction with the neighboring C5–C6 double bond. As a result, monomers such as 2-*tert*-butoxycarbonylbicyclo[2.2.1]-2,5-heptadiene (**1a**) and 2-trimethylsiloxycarbonyl bicyclo[2.2.1]-2,5-heptadiene (**1b**), which have bulky ester groups, undergo ring-closing cyclopolymerization[6] instead of normal vinyl addition.

The bulky monomers **1a** and **1b** used in the preparation of the regioregular polynortricyclenes were obtained in good yield by Diels–Alder addition of propiolic acid esters to cyclopentadiene (Scheme 1).



Scheme 1. Synthesis of **1a** and **1b**.

Conversion of the adduct of propiolic acid and cyclopentadiene to the desired *tert*-butyl diene ester is also possible through acid-catalyzed esterification with 2-methylpropene. Monomer **1a** was easily purified by flash chromatography, while monomer **1b** was purified by vacuum distillation. These 2-substituted bicyclo[2.2.1]-2,5-heptadiene derivatives are colorless oils, which slowly polymerize upon extended storage at room temperature but can be stored for months as 10–25% solutions in dichloromethane at $-20^{\circ}C$ under nitrogen. In the presence of oxygen the monomers have a strong tendency to polymerize even at low temperature.

As shown in Scheme 2, the cyclopolymerizations of **1a** and **1b** were carried out using 0.5–2% of azoisobutyronitrile (AIBN) as the free-radical initiator in benzene at 65°C for 20 hours. A relatively large amount of AIBN (e.g. 2 mol%) is preferred for this polymerization since imaging applications generally require materials having a modest number average molecular weight.[4]

The resulting polymer **2a** was precipitated from methanol, while acetonitrile was used for the precipitation of **2b** to avoid complete loss of the trimethylsilyl protecting groups. All the

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[*] Prof. J. M. J. Fréchet, Dr. Q. J. Niu
Department of Chemistry, University of California at Berkeley
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-643-3079
E-mail: frechet@cchem.berkeley.edu

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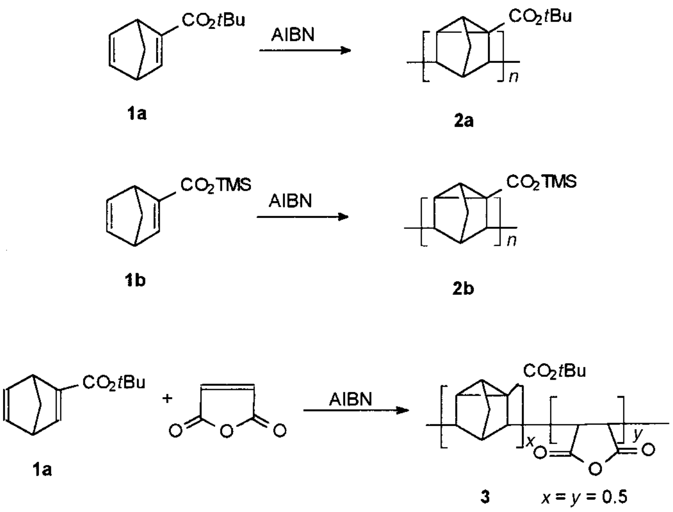


Scheme 2. Copolymerization of **1a** and **1b**.

polynortricyclenes that were obtained in 56–75 % yield after precipitation and drying (Table 1) could readily be redissolved in most organic solvents including THF, benzene, acetone, chloroform, dichloromethane, and cyclohexane, which confirmed the absence of cross-linking. Table 1 also reports the results of a spontaneous polymerization that occurred in the bulk with a sample of monomer kept in a refrigerator for an extended time in the presence of oxygen. Obviously this spontaneous polymerization affords only a low yield of polymer (37 %), but the product obtained is also free of cross-linking. The results of GPC analyses in THF are given in Table 1. All of the materials have a polydispersity in the range expected for a free-radical polymerization.

Table 1. Cyclopolymerization of **1a** and **1b** with AIBN as free-radical initiator (I).

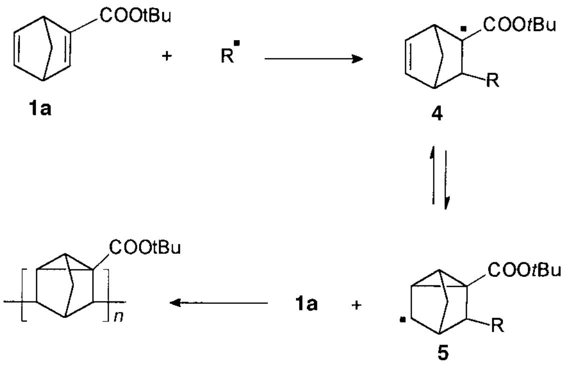
T [°C]	[M] [wt %]	[I] [mol %]	M_n	M_w	Yield [%]
65	33 (**1a**)	2	15400	29100	56
65	50 (**1a**)	2	26900	59100	71
65	50 (**1a**)	0.5	44100	153500	66
75	50 (**1a**)	2	35000	107800	75
5	100 (**1a**)[a]	0	37200	83800	37
65	50 (**1a**)[b]	2	43500	172200	74
65	50 (**1b**)	2	20700	40800	67
65	50 (**1b**)	2	19500	33700	65

[a] Spontaneous bulk polymerization. [b] Polymerization performed in 2-methylpropanol.

The FTIR spectrum of polymer **2a** displays a peak characteristic of carboxylic esters at 1750 cm^{-1} and no peaks arising from the C=C bond of the monomer (1605 and 1560 cm^{-1}). The ^1H NMR and ^{13}C NMR spectra after polymerization show both the complete disappearance of the vinyl resonances and the appearance of new ^1H NMR resonances centered at $\delta = 1-2$, corresponding to the saturated polymer backbone. The ^{13}C NMR spectrum of polymer **2a** also shows a chemical shift typical for a cyclopropyl carbon at $\delta = 21.4$ (in $CDCl_3$), providing further evidence for the nortricyclene structure. In the case of **2b**, the cyclopropyl carbon signal is seen at $\delta = 22.9$ (in $[D_5]$pyridine).

Differential scanning calorimetry (DSC) analysis of nortricyclene polymer **2a** shows no glass transition below the temperature of polymer decomposition. Thermogravimetric analysis (TGA) of this polymer shows a large loss in weight below 240°C, corresponding to the loss of the thermally labile *tert*-butyl ester groups. This thermal elimination is key to the ultimate application of polymer **2a** in a chemically amplified resist system.[3, 4, 7] It occurs at a temperature similar to those observed for several tertiary, allylic, and benzylic esters of poly(4-vinyl benzoic acid) used previously as positive/negative tone high-temperature resists for 248- or 254-nm microlithography.[8] In addition, a sudden weight loss of ~7 % is observed at about 380°C in the TGA trace of polymer **2a**, which corresponds to the retro-Diels–Alder reaction of the polymer to form carbene and to break the bridge in the polymer backbone. Risse had also observed this phenomenon in the study of the TGA of poly(norbornene).[9] The TGA trace of polymer **2b** shows that this polymer is stable up to 300°C, then slowly decomposes above that temperature.

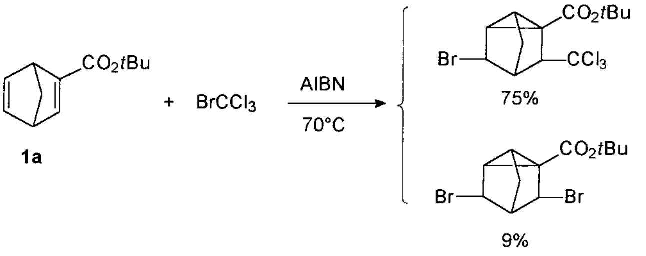
Bicyclo[2.2.1]-2,5-heptadiene, a model compound of monomers **1a** and **1b**, reacts with a variety of compounds to give the nortricyclene-type products, and formation of the cyclopropyl ring is believed to be the driving force for these reactions.[10] Although Graham et al.[5] had proposed two reaction pathways for the polymerization of 2-ethoxycarbonylbicyclo-[2.2.1]-2,5-heptadiene, our data shows that only one mechanism can account for the polymerization of bulky 2-alkoxycarbonylbicyclo[2.2.1]-2,5-heptadiene monomers (Scheme 3).



Scheme 3. Mechanism of the free-radical cyclopolymerization of **1a**.

It is apparent that the polymerization of such bicyclo[2.2.1]-2,5-heptadiene monomers requires a suitable substituent (e.g. ester group) to both activate one of the double bonds and provide resonance stabilization for the initially formed radical **4**. Instead of acting as a propagation point for the addition of more monomer, this stabilized free radical can also readily react with the unactivated double bond, which is held in close proximity, in a ring-closing process that affords radical intermediate **5**, which, in turn, serves as the point of propagation. Therefore, in order to facilitate cyclization and simultaneously block 2,3-vinyl addition, which would leave residual double bonds in the growing polymer chain, sufficient steric bulk is required at the 2-position of these bicycloheptadiene systems. Theoretical calculations on intramolecular ring-closing processes by Gravel et al.[11] have shown that cyclopropanation is a favorable process in activated norbornene structures. In addition, Mathias and co-workers[6] have reported a similar effect in the cyclopolymerization of linear bifunctional acrylate monomers: the bis-*tert*-butyl ester yielded a soluble product, while the corresponding unhindered bis-ethyl esters cross-linked upon polymerization.

Further support for the free-radical addition mechanism involving both double bonds is provided by model studies, in which bromotrichloromethane is added to **1a** under conditions analogous to those employed in the polymerizations. After workup, two nortricyclene derivatives were isolated in 84 % total yield (Scheme 4). In contrast, a similar reaction with 2-ethoxycarbonylbicyclo[2.2.1]-2,5-heptadiene affords a complex mixture of products too numerous to warrant further characterization. These results also indicate that the steric interactions between the *tert*-butoxycarbonyl substituents in this model system favor intramolecular cyclopropanation and thus control the regioselectivity of the final products.



Scheme 4. Model reaction: addition of $BrCCl_3$ to **1a**.

For a preliminary assessment of the value of the nortricyclene moieties for 193-nm imaging, a 1:1 copolymer of **1a** and maleic anhydride was prepared. A solution of copolymer **3** containing a photoacid generator was then imaged with a 193-nm excimer laser to afford the high-resolution images with feature sizes well below 0.20 nm (Figure 1).

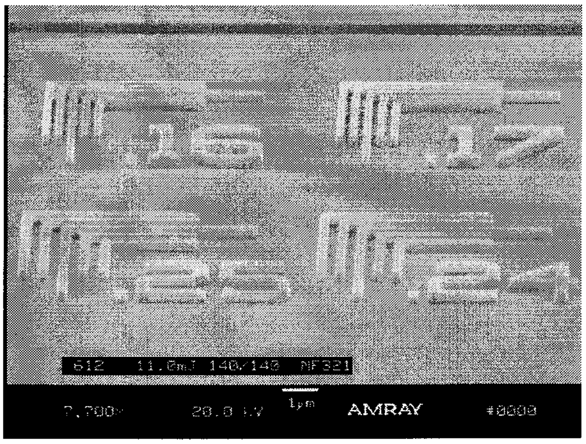


Figure 1. Image obtained with copolymer **3** by exposure to a 193-nm excimer laser and development with aqueous base.

The polymerization of bulky monomers such as 2-alkoxycarbonylbicyclo[2.2.1]-2,5-heptadiene can be accomplished without gelation to afford stable polymers with regioregular nortricyclene repeating backbone units. Polymers containing nortricyclene units derived from **1a** and **1b** or derivatives thereof are being applied successfully in combination with suitable photoacid generators as chemically amplified photoresist materials[7] in state-of-the art 193-nm microlithography.

Experimental Section

1a: Freshly distilled cyclopentadiene (4.0 g, 0.061 mol) was added to *tert*-butyl propiolate[12] (5.0 g , 0.04 mol) in benzene (5.0 g). The reaction mixture was heated to 60°C for 24 h in a sealed tube and cooled to room temperature. After removal of the solvent, the resulting mixture was separated by column chromatography to afford **1a** as a colorless oil (5.56 g , 72 %). FTIR (neat): $\tilde{\nu} = 3000, 1715, 1605, 1560, 1490, 1465, 1300, 1155\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.50$ (d, 1 H), 6.90 (m, 1 H), 6.70 (m, 1 H), 3.83 (s, 1 H), 3.66 (s, 1 H), 2.10 (m, 2 H), 1.47 (s, 9 H); ^{13}C NMR ($CDCl_3$): $\delta = 164.3$, 154.1, 151.1, 143.7, 141.7, 79.9, 74.2, 51.3, 49.9, 28.1; C,H analysis calcd for $C_{12}H_{16}O_2$: C 74.97, H 8.39; found: C 74.79, H 8.16.

1b: To a solution of trimethylsilyl propiolate[13] (7.5 g, 0.052 mol) in 7.5 g of benzene was added freshly distilled cyclopentadiene (4.2 g, 0.064 mol). The solution was heated at 60°C for 24 h in a sealed tube. After cooling, the reaction mixture was distilled under vacuum to afford 7.2 g (67 %) of product, which is moisture sensitive. FTIR (neat): $\tilde{\nu} = 2970, 1680, 1595, 1555, 1330, 1295, 1250, 1155, 1055, 855\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.59$ (d, 1 H), 6.91 (m, 1 H), 6.71 (m,1 H), 3.84 (s, 1 H), 3.68 (s, 1 H), 2.13 (m, 2 H), 0.28 (s, 9 H); ^{13}C NMR: $\delta = 164.9$, 156.6, 151.0, 143.8, 141.5, 74.4, 51.5, 49.9, -0.2. C,H analysis calcd for $C_{11}H_{16}SiO_2$, or $(C_{11}H_{16}SiO_2)_n$: C 63.42, H 7.74; found: C 63.49, H 7.90; FAB-MS: *m/z*: 208.093 [M^+] (calcd: 208.092).

Polymerization of **1a**: Freshly purified **1a** (2.0 g, 0.010 mol) was mixed with 2.0 g benzene. After the solution had been purged with nitrogen for 10 min, AIBN (33 mg, 0.00020 mol) was added, and the resulting mixture was heated at 65°C under nitrogen for 20 h. After cooling, the solution was diluted with 5 mL THF and added to methanol (ca. 500 mL). The precipitated polymer was collected by filtration, washed thoroughly with methanol, and then dried under vacuum for 24 h to afford a finely divided, white polymer (1.42 g, 71 %). FTIR (KBr): $\tilde{\nu} = 3000, 1715, 1485, 1450, 1360, 1165, 1120\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.0-2.4$ (m, 16 H); ^{13}C NMR ($CDCl_3$): $\delta = 172.5$, 79.7, 44.4, 38.9, 32.5, 28.1, 21.4; C,H analysis calcd for $(C_{12}H_{16}O_2)_n$: C 74.97, H 8.39; found: C 75.16, H 8.35.

Polymerization of **1b**: Freshly purified **1b** (2.08 g, 0.010 mol) was mixed with 2.08 g benzene. After the solution had been purged with nitrogen for 10 min, AIBN (33 mg, 0.00020 mol) was added, and the resulting mixture was heated at 65°C under nitrogen for 20 h. After cooling, the solution was diluted with 5 mL THF and added to acetonitrile (ca. 500 mL). The precipitate was filtered and washed through with acetonitrile. It was then dried under vacuum for 24 h to afford a white powder polymer (1.39 g, 67 %). FTIR (KBr): $\tilde{\nu} = 2960, 1700, 1420, 1255, 1125, 1045, 845\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.0-2.4$ (m, 7 H), 0.3 (s, 9 H); ^{13}C NMR ([D_5]pyridine): $\delta = 176.2$, 45.4, 39.1, 33.0, 30.2, 28.5, 22.9, 2.2; C,H analysis calcd for $(C_{11}H_{16}SiO_2)_n$: C 63.42, H 7.74; found: C 63.49, H 7.90. The TMS protecting groups in **2b** can be removed to give the nortricyclene carboxylic acid polymer by simply using methanol as the precipitation solvent.

Copolymer **3**: A mixture of freshly purified monomer **1a** (3.84 g, 0.020 mol) and maleic anhydride (1.96 g, 0.020 mol) in benzene (5.80 g) was purged with nitrogen for 10 min, AIBN (0.131 g, 0.00080 mol) was added, and the mixture was heated at 65°C under nitrogen for 20 h. After cooling, the solution was diluted with 10 mL THF and poured into methanol (ca. 500 mL). The precipitated polymer was collected by filtration, washed with methanol, and dried under vacuum for 24 h to afford 4.88 g (84 %) copolymer **3**. GPC (THF, calibrated with polystyrene standards): $M_n = 11400$; $M_w = 21600$; IR (KBr): $\tilde{\nu} = 2950, 1860, 1785, 1610\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.8-3.4$ (m, 14 H); ^{13}C NMR ($CDCl_3$): $\delta = 171.4$, 81.7, 46.0, 38.9, 31.1, 28.0, 25.9; C,H analysis calcd for 1:1 copolymer: C 66.19, H 6.25; found: C 64.75, H 6.26.

Imaging of copolymer **3**: A solution of 99 wt % **3** and 1 wt % triphenylsulfonium hexafluoroantimonate in propylene glycol methyl ether acetate (12 % of solid content) was filtered through a 0.45 μm filter, then spin-coated at 2500 rpm on an antireflection-treated silicon wafer. After heating at 140°C for 1 min, the 0.35-μm thick film was exposed (11 mJ cm^{-2})

through a mask to a 193-nm excimer laser. The wafer was then heated to 140°C for 1 min and developed with 0.52 N aqueous tetramethylammonium hydroxide (0.5 min) to afford the image shown in Figure 1.

Model reaction: A mixture of **1a** (1.30 g, 0.0068 mole), $BrCCl_3$ (5.38 g, 0.0272 mol), and AIBN (0.022 g, 0.000132 mol) was heated at 70°C for 5 h. After the unreacted $BrCCl_3$ had been removed under vacuum, the residue was separated by flash chromatography to afford two solid products. Major product (1.99 g, 75 %): m.p. 105–106°C; FTIR (neat): $\tilde{\nu} = 2975, 1705, 1475, 1365, 1315, 1165\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.03$ (s, 1 H), 3.32 (d, 1 H), 2.73 (s, 1 H), 2.40 (d, 1 H), 2.20 (dd, 2 H), 2.26 (d,1 H), 1.45 (s, 9 H); ^{13}C NMR ($CDCl_3$): $\delta = 166.2$, 98.8, 81.7, 63.3, 51.6, 46.3, 36.5, 33.9, 28.2, 28.0, 22.7; C,H analysis calcd for $C_{13}H_{16}BrCl_3O_2$: C 39.98, H 4.13; found: C 40.04, H 4.29. Minor product (0.22 g, 9 %): m.p. 77–79°C; IR (neat): $\tilde{\nu} = 3005, 1715, 1485, 1375, 1295, 1165\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.01$ (s, 1 H), 3.96 (s, 1 H), 2.67 (s, 1 H), 2.26 (m. 4 H), 1.46 (s, 9 H); ^{13}C NMR ($CDCl_3$): $\delta = 168.9$, 81.7, 63.9, 53.0, 46.3, 34.6, 34.3, 29.5, 28.0, 25.0; C,H analysis calcd for $C_{12}H_{16}Br_2O_2$: C 40.94, H 4.58; found: C 40.75, H 4.66.

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