CHAPTER 3

Metal-catalyzed Addition Polymers of Fluorinated Tricyclononenes for Advanced Lithographic Applications

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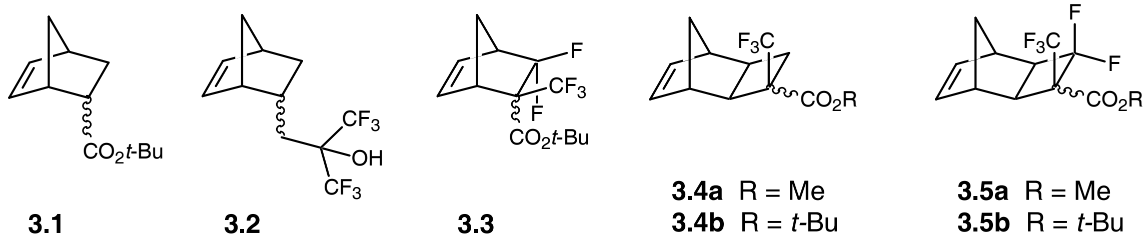
Metal-catalyzed Addition Polymers of Fluorinated Tricyclononenes for Advanced Lithographic Applications

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 offer enhanced transparencies at 157 nm relative to conventional ester-functionalized polynorbornenes as determined by variable angle spectroscopic ellipsometry (VASE). To demonstrate their utility in the development of photoresists for 157 nm lithography, a fluorinated ester-functionalized tricyclononene is copolymerized with a hexafluorocarbinol-functionalized norbornene to produce an imageable photoresist copolymer. This copolymer exhibits significantly improved transparency relative to its non-fluorinated norbornene analogue. The preliminary lithographic imaging performance of the tricyclononene-based resists is compared to that of other addition copolymer resists. All resists based on carboxylic acid ester solubility switches require the use of a dissolution inhibitor to control their characteristic swelling behavior during development. The higher transparency and absence of swelling behavior of *t*-butoxycarbonyl-protected hexafluorocarbinol-based resists result in high resolution patterns. These results indicate that protected hexafluorocarbinols are the preferred solubility switching motif for 157 nm photoresists based on norbornene addition 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] In order 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. Metal-catalyzed addition polymers of norbornene, based on such monomers as the norbornene *t*-butyl ester (NBTBE, **3.1**, Figure 3.1), were developed for use at 193 nm, with the carbon-rich and heteroatom-deficient norbornane backbone structures proving to be suitable replacements for the heavily absorbing, etch-resistant aromatics used in previous generations of photoresists. Unfortunately, like the majority of the polar functionalities (esters, carbonates, alcohols, and anhydrides) used in resist chemistry,[4] the high absorbance of ester-functionalized monomers such as **3.1** prevents their use at 157 nm.



3.1 **3.2** **3.3**

3.4a R = Me
3.4b R = *t*-Bu

3.5a R = Me
3.5b R = *t*-Bu

Figure 3.1. Norbornene-type monomers for 157 nm photoresists

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 hexafluoroisopropanol-functionalized norbornene (NBHFA, **3.2**) was found to be highly transparent.[6] In addition, due to the inductive effects of the two trifluoromethyl groups, the acidity of the this type of fluorinated alcohol is similar to phenol,[7] allowing this polar monomer to replace the highly absorbing phenolic structures used in previous generations of resists. The incorporation of an α-trifluoromethyl group was found to significantly reduce the absorption of carboxylic acid esters.[6] Systematic experimental[8] and computational[9] studies on the effect of fluorination on the transparency of norbornene indicate that substitution at the 2 position is more beneficial than at the 7 position and disubstitution is more effective than monosubstitution. With these design principles in hand, the fluorinated monomer **3.3** was subsequently designed as an ideal replacement for the highly absorbing norbornene **3.1**. 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.[10] The addition of an α-trifluoromethyl group in **3.3**, while addressing the transparency problem, hinders the polymerization. Thus, alternative approaches towards a polymerizeable monomer incorporating these transparent esters were investigated.

Recently, we synthesized a series of fluorinated ester-functionalized tricyclo[4.2.1.0^{2,5}]non-7-ene (TCN) monomers (**3.4** and **3.5**).[11] By moving the sterically bulky, geminal electron-withdrawing functionalities an additional carbon away from the double bond onto the cyclobutane ring (which is exclusively in the exo configuration), we hoped to improve the reactivity of the tricyclononene monomers towards metal-catalyzed addition polymerization. Initial gas phase transparency measurements of saturated TCN compounds revealed their enhanced transparencies at 157 nm relative to non-fluorinated norbornane analogues. While the use of TCN chemistry in photoresists is a potential solution to the polymerization difficulties of the partially fluorinated norbornenes mentioned previously, confirmation of the enhanced transparency and polymerization activity is required. Herein, we report the synthesis of ester-functionalized TCN homopolymers and copolymers for thin film transparency measurements. The initial imaging performance of a TCN-based photoresist is compared to other norbornene addition polymer resists under development.

Results and Discussion

Synthesis of TCN Homopolymers The most common late transition metal catalyst systems used to polymerize norbornene systems by an addition mechanism are based on nickel[12] and palladium.[13-15] To produce model polymers, monomers **3.1**, **3.2**, **3.4**, and **3.5** were polymerized using cationic palladium allyl hexafluoroantimonate catalyst reported by Risse,[14] 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 hours 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.[14,15] Indeed, due to 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,[16] analogous to the functionalized norbornene-maleic anhydride copolymers[17] developed for 193 nm lithography.

During polymerization of monomers containing *t*-butyl esters (such as **3.1** and **3.4b**), catalytic deprotection of the *t*-butyl esters was observed (with the generation of isobutylene and carboxylic acid observed by ^{1}H NMR), resulting in precipitation of the deprotected polymers. Unlike our experiences with a (η_6-tolyl)nickel(perfluorophenyl)$_2$ catalyst, some acid is apparently formed during polymerization using the cationic palladium catalyst, presumably as a result of chain transfer reactions. This formation of $HSbF_6$, a very strong acid, is disastrous. This premature deprotection presented a large problem because selective reprotection of some acidic functionalities with acid-labile protecting groups (for solubility switching) in the presence of other polar functionalities (for adhesion, dissolution properties, etc.) is not a trivial process on multi-component polymers. This problem was solved through the introduction of sterically hindered, polymer-bound 2,6-di-*t*-butyl pyridine as “proton sponge” to neutralize any acid that is produced. This hindered amine does not effectively bind to the active catalyst, so the rate of polymerization is not significantly affected. In addition, the proton sponge beads can be easily filtered away from the reaction media, providing a convenient way to eliminate any residual highly absorbing, basic pyridine species which could interfere with resist performance.

In order to mimic the low molecular weights (3-8 kDa) of the successful poly(norbornene-*co*-maleic anhydride) alternating copolymers developed for 193 nm, a method to control the polymer molecular weight must be employed, particularly in the case of the highly active, yet slow initiating (η_6-tolyl)nickel(perfluorophenyl)$_2$ catalyst. All efforts to reduce the molecular weight of the nickel-catalyzed norbornene addition polymers through the use of chain transfer agents such as 1-hexene (to promote β-hydride elimination[18]) or increased catalyst loadings (up to 10 mol%) met with little success.[19] While the addition of 1-hexene was unable to reduce the molecular weight to the level desired, use of catalyst loadings in excess of 5 mol% was successful in producing addition polymers with molecular weights below 10,000.[20] While this is an expensive solution to the problem, it is sufficient to produce quantities of material for resist evaluation. If metal-catalyzed addition polymers are to be commercialized, levels of residual metal contamination must be brought down to less than 20 parts per billion. That, however, is an issue which will have to be addressed by resist suppliers. All of the polymers discussed in this work were prepared with a cationic allyl palladium catalyst using the procedure shown in Figure 3.2.

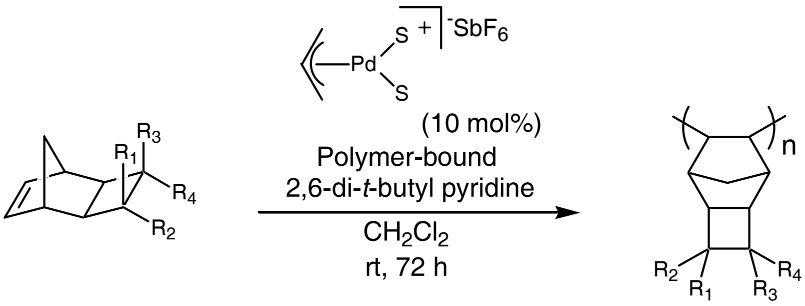


Figure 3.2. Palladium-catalyzed addition polymerization

Polymerization of fluorinated TCN monomers **3.4a** and **3.5a** afforded good yields of TCN homopolymers **3.8** and **3.9**, in stark contrast to the trace yields[10] achieved with norbornene monomers like **3.3** under identical conditions. The facts that polymerization proceeds in the presence of basic pyridine moieties and the observed unreactivity of TCN monomers towards radical initiators at moderate temperatures[17] 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 < PDI < 2.7) of the polymers are typical of polymerizations with palladium catalysts.[13-15] It should be noted that the fluorinated TCN compound **3.4a** 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 polymers sufficiently clean for analysis by variable angle spectroscopic ellipsometry. The VASE spectra agree with the trends observed in the VUV spectra (Figure 3.3), although the reduction in absorbance afforded by additional fluorine substituents seems to be larger when measured by VASE. The homopolymer of NBTBE (**3.6**) has an absorbance at 157 nm of 6.02 μm^{-1}, compared to the homopolymer of NBHFA (**3.7**) which is around 1.14 μm^{-1}. In any copolymer of these two

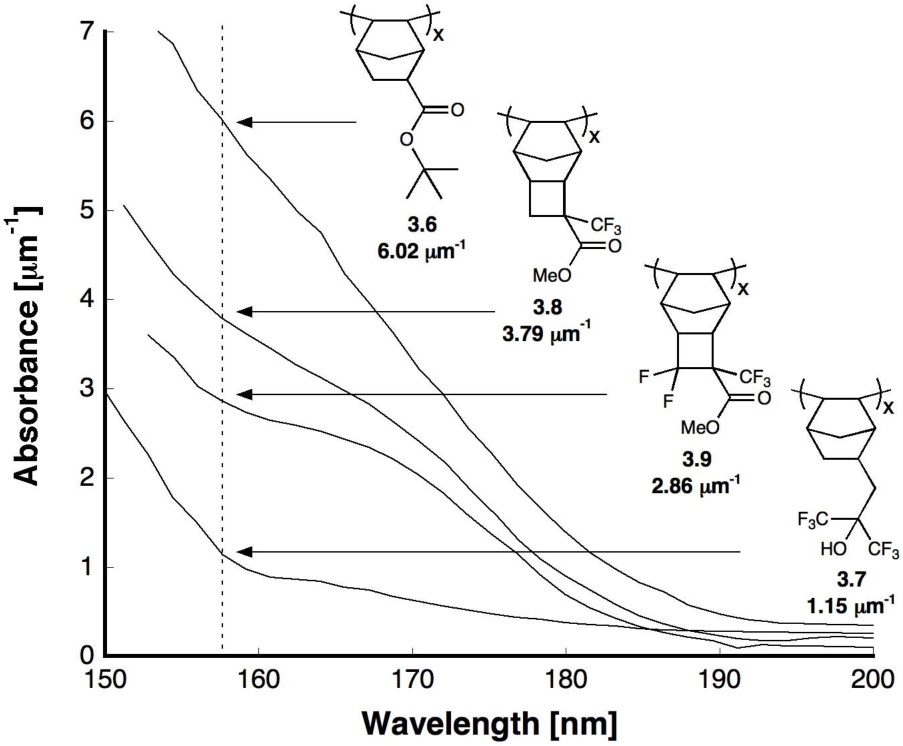
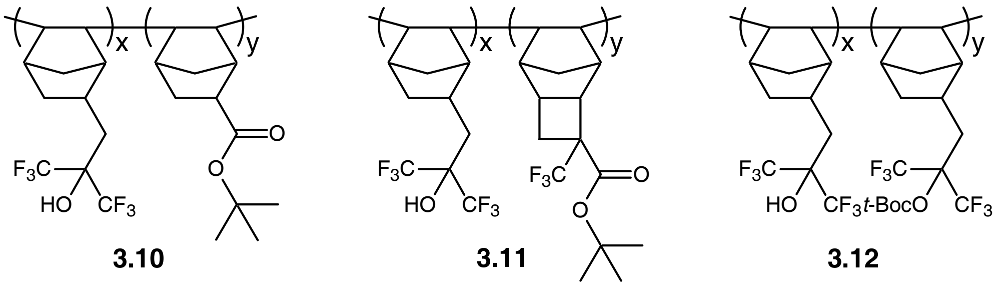


Figure 3.3. VASE spectra of TCN homopolymers

monomers, even small amounts of the highly absorbing ester-containing monomer **3.1** will raise the overall absorbance of the polymer considerably. In comparison, the TCN homopolymer **3.8** possesses an absorbance coefficient of 3.79 μm^{-1}at 157 nm. The addition of the trifluoromethyl group alpha to the ester increases the transparency of the material by approximately 2 orders of magnitude. The further incorporation of fluorine in TCN **3.5a** serves to increase the transparency of the homopolymer (**3.9**) by another order of magnitude ($\alpha_{10} = 2.86\ \mu m^{-1}$ at 157 nm).

These thin film measurements of transparency support the gas-phase measurements previously reported. In fact, the thin film measurements indicate the benefits of increased fluorination are greater than the gas-phase VUV measurements indicate. Using these fluorinated TCN monomers, polymers with identical ester content and higher transparency or identical transparency and higher ester content, relative to copolymers of NTBE (**3.1**), can be synthesized. The higher transparency of these materials offers the possibility of ester-containing norbornene-type addition polymers as single layer resists. Towards this end, the synthesis and copolymerization of a number of fluorinated TCN monomers with *t*-butyl ester functionalities to produce imageable resist materials is reported here.[20] However, given the potential benefits of the TCN framework in 157 nm photolithography, exploration of other potential pathways to produce photoresist polymers from a wide range of TCN monomers via free radical, ring-opening metathesis (ROMP), and addition polymerization have been undertaken.[22]

Synthesis of TCN Resist Copolymers The extremely high transparency (1.15 μm^{-1}) and excellent dissolution behavior of polyNBHFA (**3.7**) provide a suitable base material which can be tailored by the incorporation of various functionalized monomers. The ester-functionalized resist **3.10** (Figure 3.4) was the first norbornene addition polymer resist synthesized for 157 nm lithography. While the high absorbance of the ester results in only moderate transparency for the copolymer, it offers sufficient performance for it to have been commercialized for preliminary tool testing while more transparent resists are developed. Therefore, it serves as a good benchmark for evaluating other norbornene addition polymer-based photoresists. Replacement of the heavily absorbing NBTBE (**3.1**) with the more transparent tricyclononene **3.4b** affords the TCN-based resist **3.11.** Comparison of the lithographic performance of **3.10** and **3.11** will allow the effect of additional transparency on the resist performance to be evaluated. Finally, these resists will be compared to the partially protected hexafluorocarbinol-based resist **3.12**. Copolymer **3.12** is a 157 nm analogue of the partially protected poly(hydroxystyrene) resists[22] such as APEX-E used at 248 nm. A complete list of polymers studied along with their absorption coefficients and molecular weights are given in Table 3.1.[11,20]



3.10 **3.11** **3.12**

Figure 3.4. Metal-catalyzed addition copolymers for 157 nm resist applications

Table 3.1. Absorption coefficients and molecular weights of polymers studied[11,20]

Polymer	x	y	M_n [g/mol]	PDI	α_{10}^{157nm} [μm^{-1}]	α_{10}^{193nm} [μm^{-1}]	α_{10}^{248nm} [μm^{-1}]
3.6			5380	1.79	6.02	0.39	0.10
3.7			8150	2.11	1.15	0.27	0.20
3.8			66300	2.11	3.79	0.18	0.03
3.9			7200	2.58	2.86	0.12	0.02
3.10a	65	35	3150	3.38	2.74	0.02	0.03
3.10b	80	20	-	-	2.28	0.26	0.04
3.11a	74	26	13800	2.19	1.97	< 0.01	0.05
3.11b	83	17	5200	2.78	1.67	< 0.01	0.02
3.12	67	33	-	-	2.17	0.49	0.11
3.13			1590	1.45	3.62	0.22	0.06

Synthesis and Characterization of TCN-based Resists Copolymers (**3.11a** and **3.11b**) from the more readily accessible *t*-butyl ester-functionalized TCN monomer **3.4b** were synthesized for initial imaging studies.[20] The more transparent and lithographically useful TCN monomer **3.5b** has been scaled up, but was unable to be evaluated prior to the dismantling of the 157 nm exposure tool at SEMATECH. Copolymerization of **3.4b** and **3.2** afforded copolymers **3.11a/b** with compositions that closely mirrored the respective feed ratios. That these compositions are obtained at modest yields suggest they are the result of nearly identical inherent reactivities and not simply a result of full conversion. This allows for control of the copolymer composition by controlling the feed ratio. The nearly identical reactivities of NBHFA (**3.2**) and TCN **3.4b** illustrate the effectiveness of the additional cyclobutane ring in relieving the steric and electronic impacts of increased fluorination on the polymerization activity of the TCN monomer.

As expected, the more fluorinated TCN copolymer **3.11b** exhibits greatly enhanced transparency relative to the NBTBE-based copolymer **3.10b** with nearly identical ester content (Figure 3.5). While the difference of the vacuum ultraviolet spectra measured by variable angle spectroscopic ellipsometry does not seem extraordinary at first glance, replacing only ~ 20% of the polymer with a more transparent monomer results in a polymer that is ~53% more transparent (for a 300 nm thick film). Back of the envelope calculations suggest a copolymer with the more transparent **3.5b** (with the same 83/17 composition) should have an absorbance of ~1.45 μm^{-1} and exhibit ~78 % more transparency for a 300 nm thick film relative to **3.10b**.

Lithographic Performance of TCN-based Resists Initial lithographic evaluation of the TCN-based resist **3.11b** revealed the presence of significant swelling in the developer (A, Figure 3.6).[20] This is similar to the behavior encountered with **3.10** (C, Figure 3.6) and seems to be characteristic of ester-functionalized norbornene addition polymers.[23] Likely, it is the presence of some readily ionizable carboxylic acid groups attached to the rigid polymer backbone which induces the swelling. It is clear that simple reduction of the resist molecular weight is insufficient to alleviate this swelling behavior. Alternatively, the addition of a dissolution inhibitor (DI) can

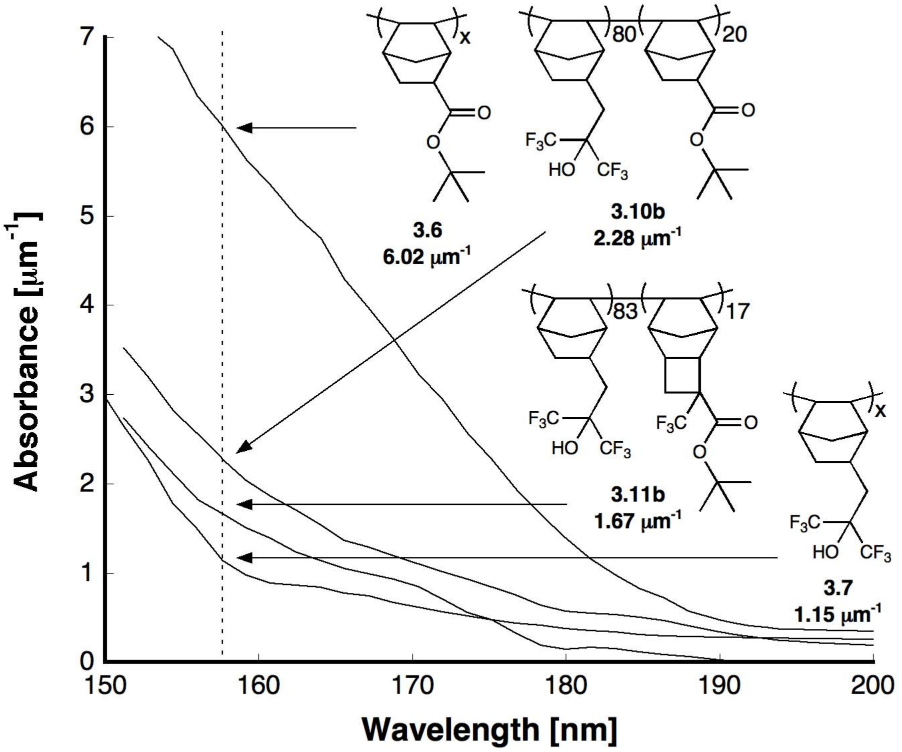


Figure 3.5. VASE spectrum of TCN-based photoresist copolymer **3.11b**

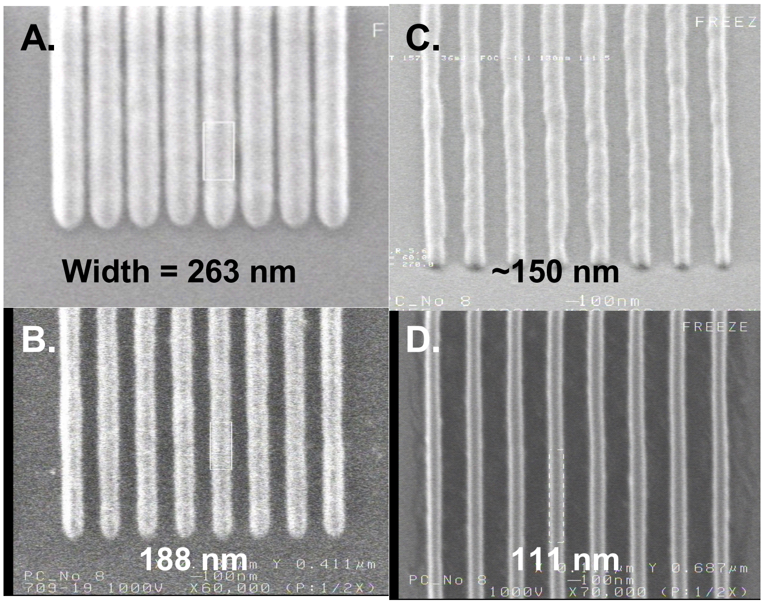
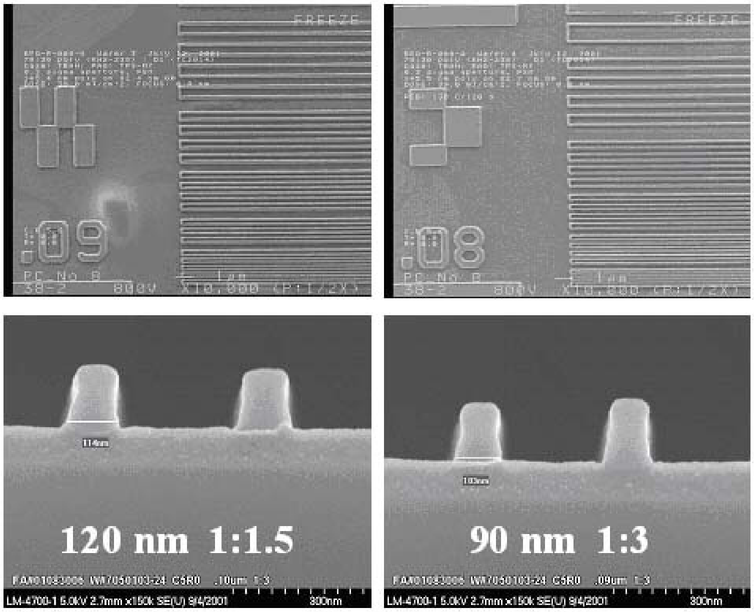


Figure 3.6. Scanning electron micrograph images ester-functionalized copolymers A. **3.11b** B. 50/50 blend of **3.11a** with **3.13** C. **3.10b** D. 70/30 blend of **3.10a** with **3.13** Note evidence of swelling and increase line edge roughness without **3.13**.

be used to control the dissolution rate eliminate swelling behavior of resist polymers during development.[24] Presumably, these DIs sequester the carboxylic acid groups in the unexposed regions with intermolecular hydrogen bonds and reduce their availability to react with the developer. Fortunately, addition of moderate amounts of the fluorinated dissolution inhibitor **3.13** (Figure 3.8) was successful in alleviating this swelling behavior (B, Figure 3.6). Initial lithographic results with **3.11b**/**3.13** system revealed its capability for high resolution imaging (Figure 3.7).[20]



Formulation: 70/30 blend of **3.11b** with **3.11**, 6 wt% TPS-Nf, 0.3 wt% TBAH in PGMEA

Conditions: 157 nm exposure (0.6 NA-0.3σ, 39.0 mJ/cm^2), phase shift mask, 146 nm thick resist on 82nm antireflective layer (AR19), 140 °C-60s PAB, 130 °C-90s PEB, 20s 0.26N TMAH development

Figure 3.7. Scanning electron micrographs of images from TCN copolymer **3.11b**

Additional efforts toward optimization of the lithographic imaging performance of this TCN/dissolution inhibitor system would result in significantly better results. Copolymers incorporating the more transparent TCN monomer **3.5b** would be expected to offer improved imaging performance. However, one of the biggest factors in the imaging performance of these ester-functionalized resists is the transparency of the dissolution inhibitor which can account for as much as 50% of the material in some formulations. The VUV spectrum of the fluorinated dissolution inhibitor **3.13** used in these lithographic evaluations is shown in Figure 3.8.[20]

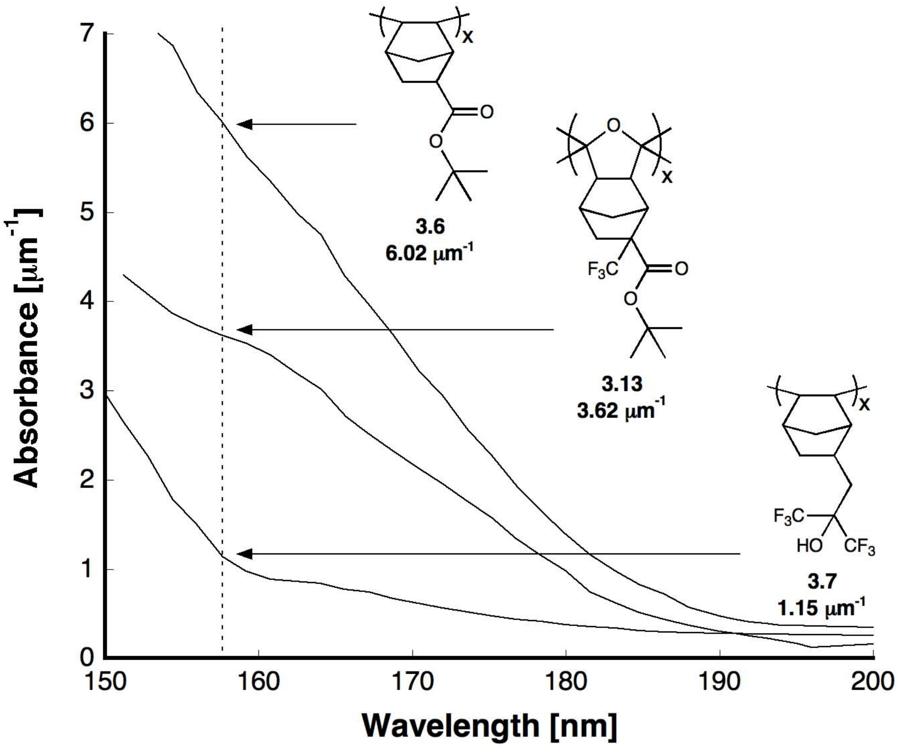


Figure 3.8. VASE spectrum of dissolution inhibitor **3.13**[20]

While the low molecular weight (x < 6) ketal carbon monoxide oligomers **3.13** serve as an effective dissolution inhibitor, its absorption coefficient is 3.6 μm^{-1} at 157 nm (Figure 3.8) – significantly higher than any of the ester-functionalized resists.[25] The presence of such a highly absorbing dissolution inhibitor decreases the transparency and lithographic performance of the photoresist polymer substantially. It also masks the true effect of the increased transparency of the TCN component on the imaging properties. Since this work was completed, a number of groups have reported a number of more transparent dissolution inhibitors for use at 157 nm that would significantly improve the initial imaging results shown here.[26]

Partially Protected Hexafluorocarbinol-based Resists As mentioned previously, partial protection of poly(NBHFA) homopolymer **3.7** affords copolymer **3.12**, a 157 nm analogue of the partially protected poly(hydroxystyrene) copolymers (APEX-E)[22] used at 248 nm. The t-butoxycarbonyl protecting group increases the absorbance of the resultant polymer, albeit not as dramatically as the comparable use of NBTBE. Resists formulated from **3.12** afforded high resolution images without the use of any dissolution inhibitor despite its higher absorbance than the TCN copolymer **3.11b**.[20] While the transparencies of **3.10a** and **3.12** are very similar, the developed images obtained using these materials are very different due to the swelling behavior exhibited by carboxylic acid ester-based resists. These results indicate that solubility switches based on protected hexafluorocarbinols are superior for 157 nm photoresists based on norbornene addition polymers.

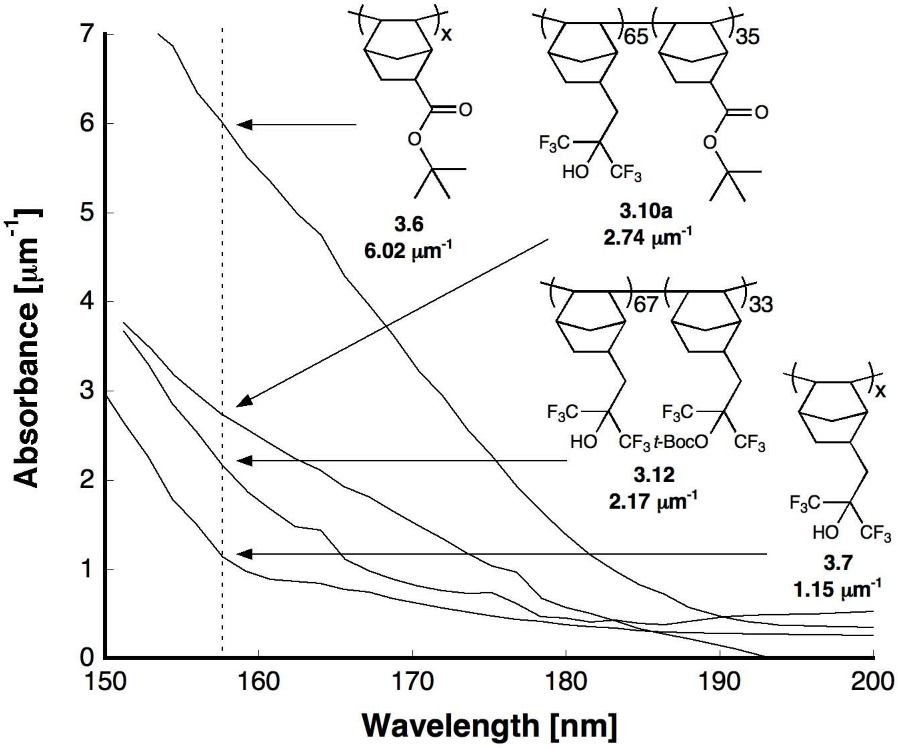


Figure 3.9. Absorbances of hexafluorocarbinol and carboxylic acid ester-based resists[20]

Conclusions

While fluorinated geminally disubstituted norbornenyl esters were unable to be polymerized via metal-catalyzed addition polymerization, fluorinated tricyclononenes were readily polymerized to afford ester-functionalized polymers with enhanced transparency at 157 nm relative to their non-fluorinated norbornene analogues. The exo configuration of cyclobutane ring of the tricyclononene framework allows it to serve as a scaffold capable of bearing fluorinated substituents while protecting the olefin from the steric and electronic affects of these groups. Copolymerization of a fluorinated tricyclononene with a hexafluorocarbinol-functionalized norbornene afforded photoresist copolymers with compositions nearly identical to the feed ratio. While this tricyclononene-based photoresist offered improved transparency relative to its less fluorinated norbornene analogue, both systems exhibited swelling behavior during development due to their carboxylic acid ester solubility switching functionalities. When a fluorinated dissolution inhibitor was incorporated into the formulation to control this swelling, promising lithographic images were obtained. A partially protected hexafluorocarbinol-based resist, while less transparent than the tricyclononene resist, offers good imaging performance due to its lack of swelling. These results illustrate the remarkable influence of the solubility switch chemistry on the dissolution behavior and imaging performance of the resist polymers. Specifically, they indicate that a hexafluorocarbinol-based solubility switch is the preferred design motif for high performance addition polymer resists for 157 nm. Further developments in transparent ester-functionalized norbornene-like monomers (such as the tricyclononene monomers described here) must be accompanied by the development of extremely transparent dissolution inhibitors. Additionally, these studies suggest the most promising pathway toward a successful 157 nm photoresist based on norbornene-addition polymers is the development of hexafluorocarbinol-functionalized norbornene or norbornene-like monomers with increased fluorine contents to afford an absorbance below 0.70 μm^{-1}.

Experimental

Materials: All manipulations and polymerizations with air-sensitive materials were carried out in an 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[36] 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 1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol (AZ Clariant), triphenylsulfonium nonaflate (AZ Clariant), 1,4-bis(2-hydroxy-hexafluoroisopropyl)benzene (Oakwood), and 2-(trifluoromethyl)acrylic acid (Honeywell and Central Glass Co.) and used as received, unless noted otherwise. Poly(NBHFA-*co*-NBTBE) (Composition: 80/20) (**3.10b**) was generously provided by Ralph Dammel and AZ-Clariant. The syntheses of monomers **3.1**, **3.2**, and **3.4b** and polymers **3.6**, **3.7**, **3.10a**, **3.11a/b**, **3.12**, and **3.13** have been performed by colleagues at the University of Texas, Austin. [20] Select data are reproduced here only for comparison.

Instruments and Equipment: Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300, Varian *Unity Plus 300*, or Varian *Mercury 300* spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, $CFCl_3$ unless otherwise noted) or to the chemical shift of the solvent. Infrared spectra were recorded on a Nicolet *Avatar 360* 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 using a Viscotek GPC equipped with a set of two 5 mm crosslinked polystyrene columns (linear mix and 100 Å) from American Polymer Standards and are reported relative to polystyrene standards. 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 multi-angle laser light scattering (MALLS) detector and an Optilab DSP digital refractometer (both from Wyatt Technology). No calibration standards were used and *dn/dc* values were obtained for each injection by assuming 100% mass elution from the columns. Polymers containing acidic functional groups were pre-treated with either diazomethane or iodomethane/DBU before GPC measurement, unless noted otherwise. Differential scanning calorimetry (DSC) measurements and thermal gravimetric analysis (TGA) were performed on a Perkin Elmer *Series-7* thermal analysis system. Gas chromatographs were recorded on a Hewlett Packard *5890 Series II* with an *HP-5* (crosslinked 5% PH ME siloxane) capillary column and flame ionization detector (FID).

Vacuum UV Spectroscopy: 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 minutes prior to analysis. All absorbance data reported are in base 10.

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

Methyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (TCNCF$_3$ME 3.4a). 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$_6$F$_6$ standard at -166.717 ppm): δ -66.25 (s, 3F, -CF$_3$, syn), -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$_3$O$_2$, 246.0868; found, 246.0868.

***tert*-Butyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (TCNCF$_3$TBE, 3.4b).**[20] To a 300 mL Parr pressure reactor equipped with a stir bar were added quadricyclane (20.0 g, 217 mmol) and *tert*-butyl 2-(trifluoromethyl)acrylate (**9**, 46.0 g, 238 mmol). The pressure reactor was sealed, and the reaction mixture was stirred overnight at 100°C. The crude product was allowed to cool to room temperature and fractionally distilled under vacuum. The product was collected at 90-94°C / 6 mm Hg as a clear oil (52.0 g, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.50 (s, 9H, t-Bu), 1.25-3.02 (m, 8H, aliphatic), 5.95-6.05 (m, 2H, CH=CH). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -65.0, -74.0. IR (NaCl, cm^{-1}): 3050, 2975, 1736 (C=O), 1475, 1372, 1316, 1280 (C-F), 1255, 1157, 1127, 840. HRMS-CI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{17}F_3O_2$, 289.141; found, 289.142.

Methyl 4,4-difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylate ($TCNF_2CF_3ME$, 3.5a). To a 300 mL Parr pressure reactor equipped with a magnetic stir bar were added quadricyclane (1.5 g, 16.3 mmol) and methyl 3,3-difluoro-2-(trifluoromethyl)acrylate (3.9 g, 20.4 mmol). The pressure vessel was sealed, and the reaction mixture was stirred at 100°C for 72 hours. After cooling to room temperature, the residue was purified by fractional vacuum distillation (39-40°C / 0.30 mm Hg) 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.

General Polymerization Procedure: To a 20ml 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 dry box. Dichloromethane (5 mL) was added and the mixture was stirred at room temperature for 20 minutes. 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 *t*-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-*t*-butyl-pyridine (1 mg/mg catalyst). The reaction mixture was stirred at room temperature for 96 hours, 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 hours. 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(NBTBE) (3.6).[20] GPC: M_n = 5380; PDI = 1.79. $\alpha_{10}^{157nm} = 6.02\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.39\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.10\ \mu m^{-1}$.

Poly(NBHFA) (3.7).[20] GPC: M_n = 3,860; PDI= 2.11. $\alpha_{10}^{157nm} = 1.15\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.27\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.20\ \mu m^{-1}$.

Poly(TCNCF$_3$ME) (3.8). Methyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (**3.4a**) 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). GPC (GPC): M_n = 66,300, PDI = 2.11. $\alpha_{10}^{157nm} = 3.79\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.18\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.03\ \mu m^{-1}$.

Poly(TCNF$_2$CF$_3$ME) (3.9). Methyl 4,4-difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (**3.5a**) was polymerized by the general procedure mentioned previously ([M]/[C] = 10:1) to produce a 50% yield of white polymeric powder. GPC: M_n = 7,200, PDI = 2.58. $\alpha_{10}^{157nm} = 2.86\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.12\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.02\ \mu m^{-1}$.

Poly(NBHFA-*co*-NBTBE) (3.10a).[20] Composition as determined by TGA: NBHFA/ NBTBE = 65/35. $\alpha_{10}^{157nm} = 2.74\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.02\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.03\ \mu m^{-1}$.

Poly(NBHFA-*co*-NBTBE) (3.10b).[20] Courtesy of Ralph Dammel and AZ-Clariant. NBHFA/ NBTBE = 80/20. $\alpha_{10}^{157nm} = 2.28\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.26\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.04\ \mu m^{-1}$.

Poly(NBHFA-*co*-TCNCF$_3$TBE) (3.11).[20] For **3.11a**, Composition as determined by TGA: NBHFA/TCNCF$_3$TBE = 74/26. $\alpha_{10}^{157nm} = 1.97\ \mu m^{-1}$. $\alpha_{10}^{193nm} < 0.01\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.05\ \mu m^{-1}$. For **3.11b**, Composition as determined by TGA: NBHFA/TCNCF$_3$TBE = 83/17. $\alpha_{10}^{157nm} = 1.67\ \mu m^{-1}$. $\alpha_{10}^{193nm} < 0.01\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.02\ \mu m^{-1}$.

Poly(NBHFA-*co*-NBHFABOC) (3.12).[20] Composition as determined by TGA: NBHFA/NBHFABOC = 67/33. $\alpha_{10}^{157nm} = 2.17\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.49\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.11\ \mu m^{-1}$.

Poly(NBCF$_3$TBE-*co*-carbon monoxide) (3.13).[20] GPC: M_n= 1590; PDI = 1.45. $\alpha_{10}^{157nm} = 3.62\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 0.22\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.06\ \mu m^{-1}$.

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