Design, Synthesis, and Characterization of Carbon-Rich Cyclopolymers for 193 nm Microlithography

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A series of cyclopolymers designed for use in 193 nm photoresist materials has been synthesized and characterized. These novel materials that provide both optical transparency at 193 nm and also reactive ion etch resistance are obtained via cyclopolymerization of suitably designed bifunctional monomers incorporating acrylic and olefinic double bonds. The approach is highly versatile and allows the preparation of a broad array of structurally related materials with different substituents providing the imaging function and the desired level of etch resistance. The cyclopolymerization process is experimentally forgiving, enabling control of the molecular weight as well as the incorporation of comonomers such as acrylic acid or maleic anhydride to fine-tune the lithographic properties.

Introduction

The microelectronics industry's drive toward devices with ever smaller component dimensions requires improvement upon the current 248 nm photolithographic manufacturing processes.[1] Promising experimental technologies for accessing feature sizes below 130 nm include photolithography at 193 and 157 nm.[2] To successfully provide these minute dimensions, the new polymers used as photoresists must adequately address the multiple constraints of the lithographic process. These factors, including transparency at the imaging wavelength, sensitivity, adhesion, aqueous base development compatibility, and etch resistance preclude a simple encompassing solution by their individual contradictory demands.[2] For example, etch resistance is empirically improved through the incorporation of high C/H ratio moieties,[3] but these same groups tend to degrade image transfer due to their hydrophobicity, leading to poor compatibility with the aqueous development process. The current commercial 248 nm resists based on the now widely used concept of chemical amplification[4] generally make use of poly(4-hydroxystyrene) with etch resistance provided by the aromatic rings. Unfortunately, these aromatic functionalities absorb essentially all light at 193 nm and therefore cannot be employed for imaging at this shorter wavelength.

In recent years, many polymer architectures have been proposed and tested toward possible application as resists for 193 nm lithography. Initially, several acrylate-based systems were examined.[5] These included ter- and tetrapolymers of monomers such as acrylic acid and methacrylic acid along with various acrylic esters (polymer **1** in Figure 1). Although this class of polymers was transparent at 193 nm and could be readily optimized for image quality through tuning parameters such as adhesion and aqueous base compatibility, etch resistance remained poor. This latter disappointing property, attributed to the linear, low C/H ratio polymer architecture, was only slightly improved through incorporation of pendant carbon-rich moieties,[5] though significant advances have been reported recently.[5f]

Cyclic aliphatic structures have been introduced in the polymer backbone in order to increase etch resistance. These polymers are accessed through processes such as ring-opening metathesis polymerization[6] (ROMP) or metal catalyzed vinyl addition[7] polymerization of cyclic olefins (polymers **2** and **3**, respectively). Unfortunately, both of these processes involve metal catalysts that remain in the polymers precluding their direct use

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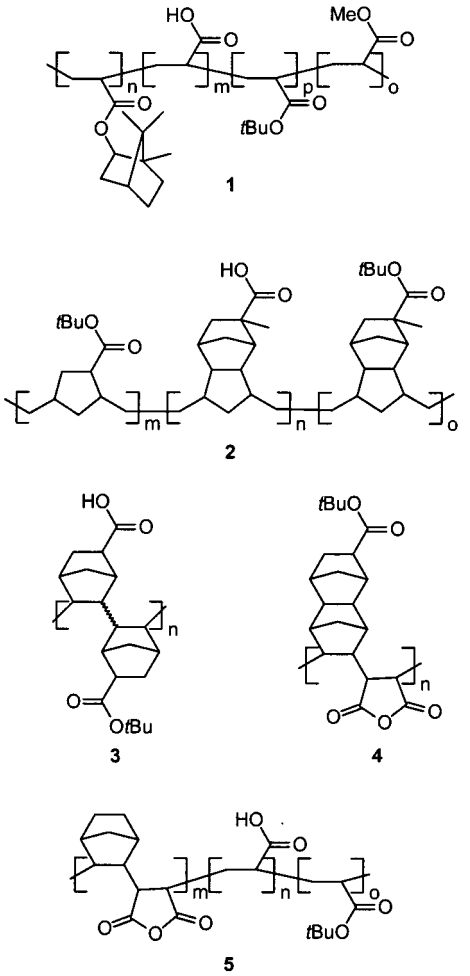

Figure 1. Some of the existing polymeric platforms for 193 nm resist formulations.[5−8]

in the semiconductor industry due to unsubstantiated fears of substrate contamination. As a result, extensive purification is required to remove the catalytic amounts of metal. Cycloolefin−maleic anhydride copolymers that retain the cyclic aliphatic rings in the backbone yet avoid the use of metal catalyzed chemistry have been prepared using standard free-radical polymerization (polymers **4** and **5** in Figure 1).[8] The use of maleic anhydride in these copolymers is an important innovation for the following reasons: (i) as a result of the alternating polymerization process that is commonly observed with maleic anhydride, it enables the incorporation of unactivated olefins containing endocyclic double bonds; and (ii) it increases the polarity of the copolymers with a beneficial effect on their lithographic properties, including adhesion and compatibility with aqueous development. Although this polymerization process only provides limited molecular weight control, excellent images with well-resolved features can be obtained and the material shows great promise for practical applications.

Previous work from our laboratory has focused on an alternative approach relying upon the free-radical cyclopolymerization[9] and cyclo-copolymerization of suitable bifunctional monomers. Initially, we considered the free-radical cyclopolymerization of monomers based on ester derivatives of norbornadiene moieties to afford polymers containing nortricyclene repeating units in the polymer backbone.[10] While these systems showed good etch resistance, the absorbance of the nortricyclene units was somewhat higher than initially expected. Other potential cyclopolymeric single layer resists materials were also prepared on the basis of a novel design containing spironorbornane structural units.[11] In this, and the accompanying, paper, we significantly extend the utility of cyclopolymers for resist applications, describing the synthesis, characterization, and lithographic properties of a family of cyclopolymers with imageable pendant groups, and their application as single-layer resists for 193 nm microlithography.

Results and Discussion

(a) Design Considerations. As its name implies, the process of free-radical cyclopolymerization[9] of a bifunctional monomer is particularly interesting since it affords not just a standard linear polymer but one that contains cyclic repeat units. Since a key property of resist materials is their ability to resist reactive ion etching, it is important to ensure that the polymer used in the formulation of a resist has this intrinsic property. As mentioned earlier, the etch resistant aromatic rings present in most conventional resists today cannot be used for imaging at 193 nm since their transparency at that wavelength is negligible. A key design feature of our approach is therefore to form etch resistant aliphatic rings during polymerization while also attaching moieties with a high C/H ratio to the polymer repeat unit for added etch resistance and, in some cases, to provide for imaging in a chemically amplified process. Following the seminal work of Butler[9a−c] on cyclopolymerization, Marvel[9d] and subsequently Mathias et al.[9e] have described the free radical polymerization of diacrylates to afford soluble, linear cyclopolymers with virtually complete cyclization. Our approach made use of their findings through a novel design of the bifunctional

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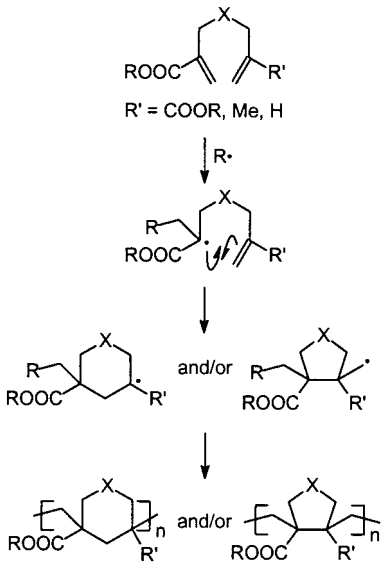


Figure 2. Cyclopolymerization mechanism for difunctional monomers.

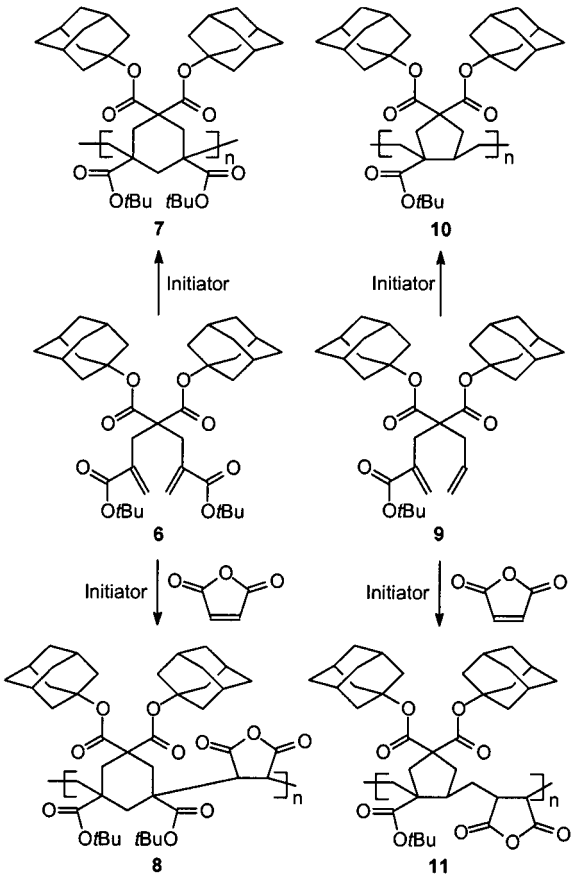
monomers incorporating both tertiary esters as imageable functionalities for chemical amplification and carbon-rich cage moieties for etch resistance. This approach and the general mechanism of the polymerization process are outlined in Figure 2. The two polymerizable double bonds are tethered at their allylic positions through a functional group "X". The reaction is expected to proceed via attack of the free radical initiator at an acrylic double bond to afford a resonance-stabilized radical. Entropically favored intramolecular propagation then gives rise to a cyclic structure, either a six- or a five-membered ring, and the following intermolecular propagation affords the polymer chains.

When R′ = COOR, it has been shown that the polymer, whose linear backbone is essentially acrylic, contains exclusively six-membered ring repeating units.[9e] When R′ = H or CH_3, cyclopolymerization also occurs, but it affords polymers in which the linear backbone can be considered as resulting from the incorporation of alternating olefin and acrylate groups. In this latter case, the nature of the cyclic repeating units—five- or six-membered rings—has not been fully ascertained, though a five-membered ring is thought to dominate.

Several functional groups X have been introduced as tethers between the two reactive double bonds in previous cyclopolymerization experiments. The use of malonate moieties in the preparation of the monomers is particularly advantageous because it enables the easy introduction of a variety of substituents in good yields via a stepwise alkylation process, while the ester groups of the malonate moiety itself may be used for the incorporation of imageable groups or carbon-rich cage compounds.[12]

(b) Monomer Synthesis. Preliminary studies[12] have suggested that cyclopolymers **7** and **8** obtained from monomer **6** afforded both a lower lithographic performance and lesser etch resistance than the related cyclopolymers **10** and **11** derived from monomer **9** (Scheme 1). We therefore proceeded with the systematic study of a series of structurally related cyclopolymers

Scheme 1



in which the position and nature of the substituents was systematically varied. A typical monomer synthesis involved the condensation of a functional malonate with building blocks such as **14** (Scheme 2). This was accomplished in two steps via first a Baylis−Hillmann reaction between acrylic ester **12**[13] and paraformaldehyde to afford **13** in 50−60% isolated yield. Crude product mixtures from this reaction contained an equilibrium amount of recoverable starting material, the acrylate, which could be recycled. Also, in some cases, amounts of an undesired ether-linked dimer, previously reported for similar substrates, were produced.[14] Subsequent conversion of the desired allylic alcohol into the tosylate afforded **14** in high yield after purification by column chromatography.

The bis-1-adamantyl malonate or the corresponding bis-*tert*-butyl malonate could be monoalkylated via the enolate with either allyl or methallyl bromide. To avoid significant formation of a bis-alkylated product, the reaction was conducted under dilute conditions (20 mM) in dry tetrahydrofuran (THF). A second alkylation was then carried out with compound **14** or its *tert*-butyl 2-(bromomethyl)acrylate analogue **20**[15] to insert the acrylic double bond into the final monomer structure (Scheme 2). Both the first and the second alkylation reactions proceed in good yields with complete disappearance of the corresponding starting materials.

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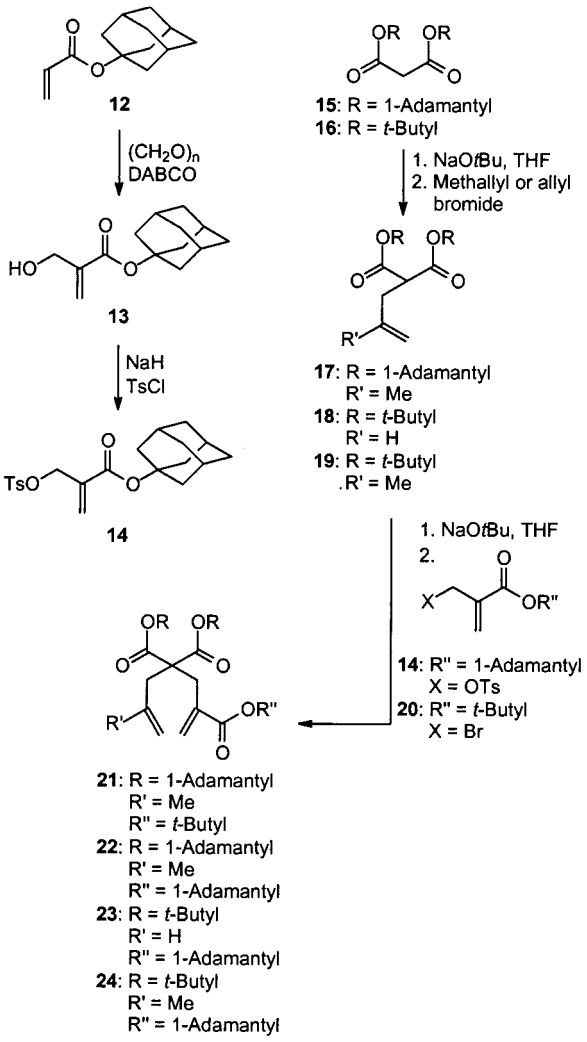
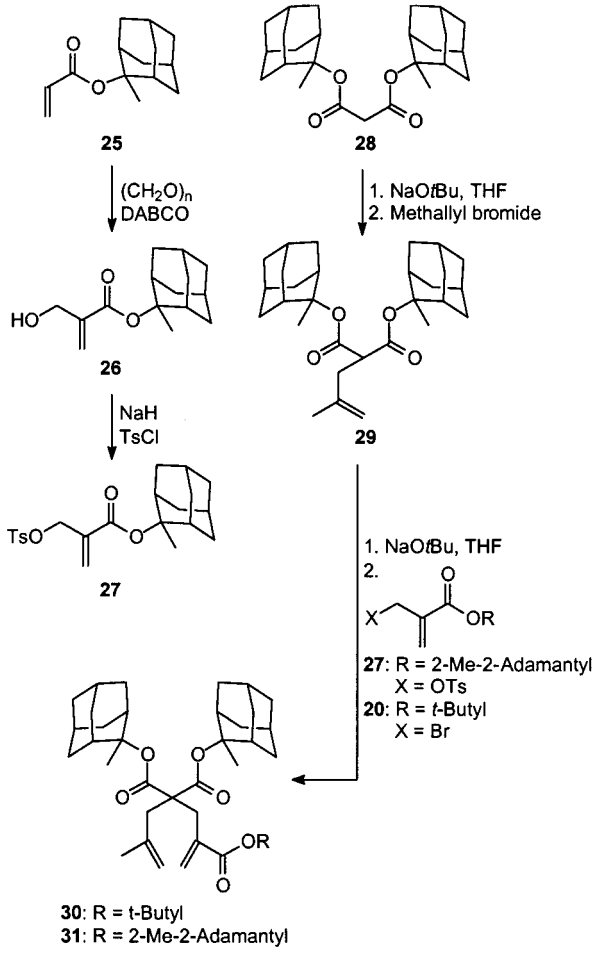
Scheme 2



Scheme 3



The choice of 1-adamantyl substituents as etch resistant groups merits some further consideration. Monomers **21**−**24** contain two different types of tertiary esters, both of which can be cleaved in solution with strong acids such as CF_3COOH. Importantly, 1-adamantyl ester cleavage also requires addition of a cation scavenger.[16] Only the *tert*-butyl ester is capable of favorable β-proton elimination to isobutene resulting in regeneration of the catalytic proton necessary for cleavage propagation via the mechanism generally accepted for chemically amplified resist systems.[3] In contrast, a 1-adamantyl ester, through a similar mechanism, would provide a highly strained bridge-head double bond. Consequently, only formation of the 1-adamantyl cation followed by quenching with an extraneous anion can occur through a nonchemically amplified process. In practice, we believe that little or no deprotection of the 1-adamantyl esters of our cyclopolymers occurs under the action of photogenerated strong acids during resist imaging, leaving the very hydrophobic 1-adamantyl moieties essentially untouched in the resist. We therefore examined the possibility of replacing the 1-adamantyl esters with analogous cage-like 2-methyl-2-adamantyl esters. Since these tertiary esters can form an exocyclic double bond under the acidolytic conditions of chemically amplified imaging,[17] they can simultaneously provide the etch resistance *and* the imaging function required of the resist material.

Compound **25** was obtained by esterification of acrylic acid with 2-methyl-2-adamantanol. Since procedures involving acid catalysis could not be used, and basic-catalyzed couplings (Et_3N, catalytic 4-(dimethylamino)-pyridine (DMAP), CH_2Cl_2) gave poor yields, we applied a phosphorodiamidic chloride mediated coupling methodology[18] that afforded **25** in nearly quantitative yields. A subsequent Baylis−Hillmann reaction with paraformaldehyde in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) followed by conversion of the allylic alcohol into the tosylate under standard conditions afforded compound **27**.

Monomers **30** and **31**, incorporating either two or three 2-methyl-2-adamantyl esters per monomer unit, were prepared via stepwise alkylation on the malonate ester as described in Scheme 3. All the monomers were characterized by standard spectroscopic techniques and gave correct elemental analyses.

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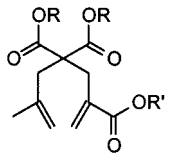
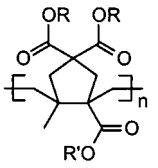
Scheme 4



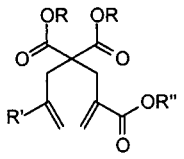
21: R = 1-Adamantyl
R' = *t*-Butyl
22: R = 1-Adamantyl
R' = 1-Adamantyl
24: R = *t*-Butyl
R' = 1-Adamantyl

Initiator



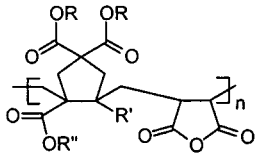
32: R = 1-Adamantyl
R' = *t*-Butyl
33: R = 1-Adamantyl
R' = 1-Adamantyl
34: R = *t*-Butyl
R' = 1-Adamantyl

Scheme 5



21: R = 1-Adamantyl
R' = Me
R" = *t*-Butyl
23: R = *t*-Butyl
R' = H
R" = 1-Adamantyl
24: R = *t*-Butyl
R' = Me
R" = 1-Adamantyl

Initiator



35: R = 1-Adamantyl
R' = Me
R" = *t*-Butyl
36: R = *t*-Butyl
R' = H
R" = 1-Adamantyl
37: R = *t*-Butyl
R' = Me
R" = 1-Adamantyl

(c) Polymer Synthesis and Characterization. Monomers **21**, **22,** and **24** undergo smooth cyclopolymerization under free-radical conditions in deoxygenated solvents to give the cyclopolymerized products **32**−**34** (Scheme 4). Analysis of the polymers by IR and NMR spectroscopy confirmed the absence of residual olefins in the polymers after purification by precipitation. In selected runs, the crude polymerization mixture was also examined by ^{1}H NMR spectroscopy in an attempt to detect unpolymerized olefinic moieties. In all cases, no olefinic signals could be detected, and the resulting polymers showed good solubility in a variety of organic solvents, suggesting cyclized, un-cross-linked structures.

To avoid incorporation of nitrile functionalities in the polymer backbone, the methyl ester analogue, namely, methyl azoisobutyrate,[19] of AIBN was used as the radical initiator. Nitrile moieties are deemed undesirable because they contribute to the overall absorbance at 193 nm, and, most importantly, they may reduce the photospeed of chemically amplified resists because of their inherent basicity.[20]

Monomers **21**, **23,** and **24** (Scheme 5) can also be cyclocopolymerized with maleic anhydride (1:1 feed ratio) to afford copolymers in moderate to high yields (up to 92%). Even though the crude polymerization mixtures were purified by precipitation in MeOH, IR spectroscopy indicated virtually no opening of the maleic anhydride repeat units. Maleic anhydride incorporation results in

Table 1. Cyclopolymerization and Cyclo-copolymerization with Maleic Anhydride of Monomers 9−31 under Free Radical Conditions (2 mol % Initiator)[a]

entry	monomer	polymer	solvent/[M]	M_n[b]	M_w[b]	PD[b]	yield (%)
1	**9**	**11**	THF/1.5	4 100	6 700	1.6	70
2	**9**	**11**	THF/1.0	2 300	2 900	1.3	48
3	**9**	**11**	benzene/1.0	4 600	8 500	1.8	92
4	**21**	**35**	THF/1.0	2 900	4 300	1.5	50
5	**21**	**35**	benzene/1.0	6 900	19 500	2.8	80
6	**23**	**36**	THF/1.0	1 500	2 000	1.3	69
7	**23**	**36**	toluene/1.0	6 900	12 200	1.8	59
8	**23**	**36**	benzene/1.0	10 000	16 700	1.7	68
9	**24**	**37**	THF/1.0	4 700	6 100	1.3	27[c]
10	**24**	**37**	benzene/1.0	21 300	52 700	2.5	81
11	**31**	**39**	THF/1.5	2 700	4 200	1.5	53
12	**31**	**39**	benzene/1.0	7 300	15 200	2.1	66
13[d]	**31**	**40**	benzene/1.0	8 400	20 000	2.4	82
14[d]	**31**	**41**	benzene/1.0	6 700	22 700	3.4	82
15	**21**	**32**	THF/0.1	2 600	3 900	1.5	53
16	**22**	**33**	THF/0.1	2 300	3 700	1.6	73
17	**24**	**34**	THF/0.1	4 500	6 500	1.4	40

[a] Polymerizations were run for 30 h with a total monomer concentration indicated as [M]. Maleic anhydride and the various monomers were in equal feed ratios. Polymer purified by precipitation in MeOH. [b] As determined by GPC relative to polystyrene standards. PD = polydispersity. [c] Polymer purified by precipitation in Me_2CO/MeOH. [d] Terpolymer; molar ratio monomer: maleic anhydride: methacrylic acid = 0.4:0.5:0.1.

Table 2. Cyclo-copolymerization of Monomer 30 and Maleic Anhydride under Free Radical Conditions in the Presence of Dodecanethiol as a Chain-Transfer Agent[a]

entry	thiol (mol %)	M_n[b]	M_w[b]	PD[b]
1	0	6 500	14 500	2.2
2	3	3 900	8 600	2.2
3	6	2 900	8 800	3.0
4	10	1 800	3 700	2.0

[a] Polymerizations were run in benzene for 30 h with a total monomer concentration of 1 M. Maleic anhydride and the monomer were in equal feed ratios. [b] As determined by GPC relative to polystyrene standards.

the appearance of two new carbonyl bands at 1860 and 1780 cm^{-1} similar to those characteristic of succinic anhydride, both absent in the IR spectra of the corresponding homopolymers. A more quantitative assessment of purity of the copolymers is provided by the elemental analyses that correctly reflect the feed ratios.

The molecular weights of selected polymers measured by gel permeation chromatography (GPC) with polystyrene calibration are presented in Table 1. Several trends clearly emerge: (i) other conditions being equal, the molecular weight of the polymer can be controlled by varying monomer concentration in the polymerization mixture (entry 1 vs 2); (ii) as expected polymerizations run in benzene or toluene afford higher molecular weights than polymerization run in tetrahydrofuran (THF), as a result of the differences in chain-transfer constants to solvent (see, for example, entries 7 and 8 vs entry 6); (iii) methallyl-containing monomers afford higher molecular weights than allyl-containing monomers (entries 6 and 8 vs entries 9 and 10).[21] As expected, the addition of increasing amounts of dodecanethiol as a chain-transfer agent[22] reduces the molecular weight of the polymer (see Table 2, polymer **39**).

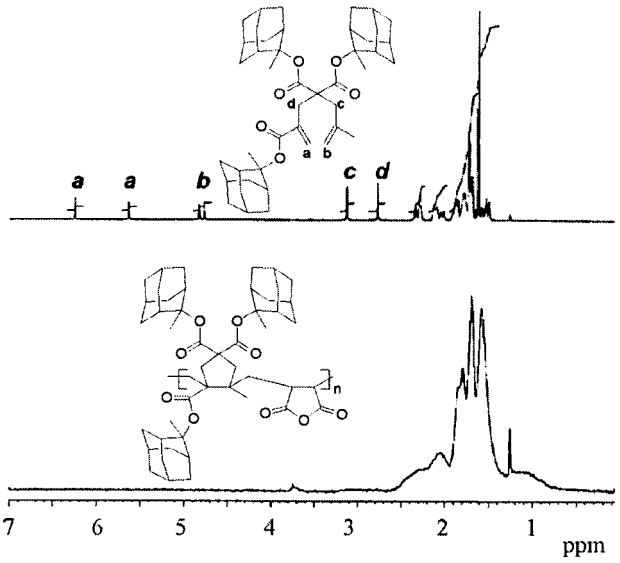


Figure 3. ^1H NMR Spectra (400 MHz, $CDCl_3$) of monomer **31** (top) and the corresponding cyclo-copolymer **39** (bottom).

Monomers **30** and **31** can also be cyclo-copolymerized in a similar fashion to afford copolymers **38**, **39** and, by introducing 10 mol % of methacrylic acid, terpolymers **40** and **41** (Scheme 6). Figure 3 shows a comparison between the ^1H NMR spectra of monomer **31** and of the corresponding cyclo-copolymer **39**. Once again, no olefinic signals are detectable, and the two resonances for the formerly allylic methylene protons shift upfield to disappear under the other aliphatic signals.

Scheme 6

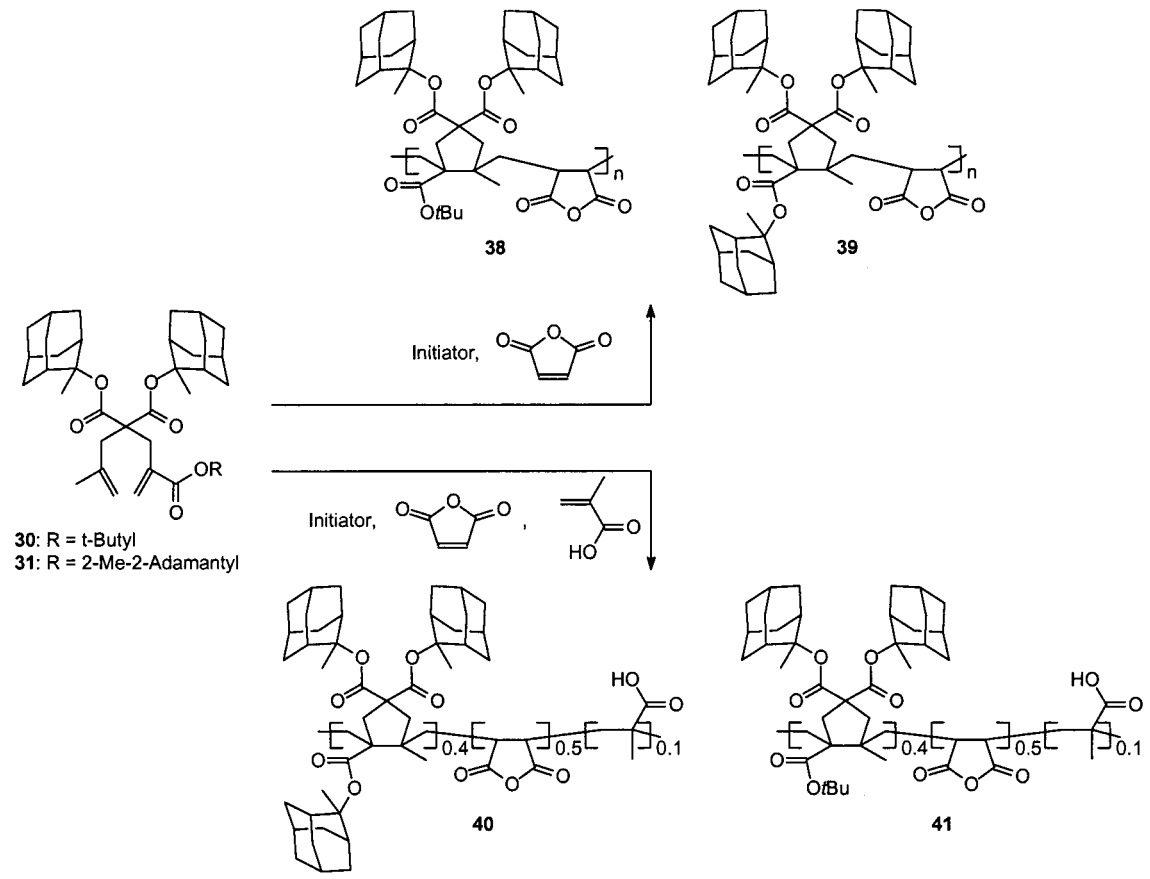


Table 3. Thermogravimetric Analyses for Cyclopolymers 7−41

		% weight loss		
entry	polym	calcd	obsd	T_{dec}[a] (°C)
1	**7**	17	17	248
2	**8**	15	15	230
3	**10**	10	10	270
4	**11**	9	10	253
5	**34**	23	30	258
6	**38**	51	50	193
7	**39**	57	57	195
8	**40**	54	50	191
9	**41**	48	47	195

[a] Temperature corresponding to the midpoint of weight loss curve.

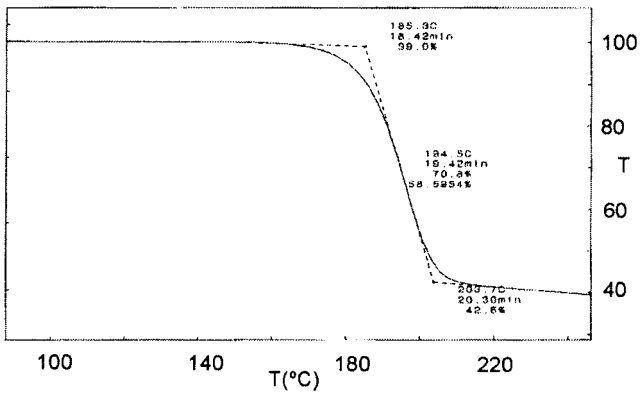


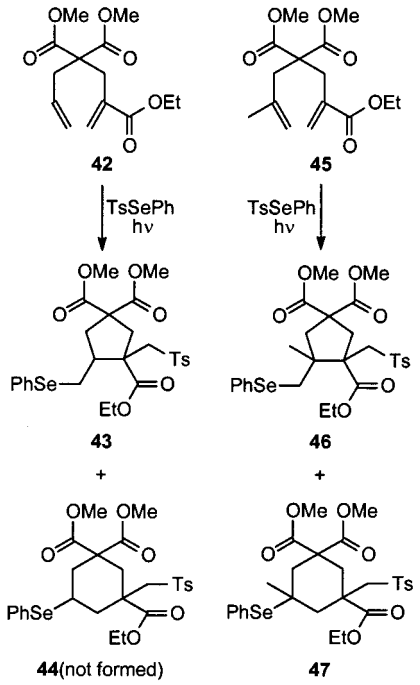
Figure 4. Thermogravimetric analysis of cyclo-copolymer **39**.

Thermogravimetric analysis data (Table 3) for all of the polymers was in close agreement with the observed and calculated weight losses for the relatively facile thermolysis of the *tert*-butyl or 2-methyl-2-adamantyl ester functionalities that occur below 260 °C as expected for tertiary esters.

For the polymers containing *tert*-butyl ester functionalities, the decomposition takes place at a temperature of ca. 250 °C, whereas, for the 2-methyl-2-adamantyl esters, loss of the alkene moiety occurred at a lower temperature (ca. 200 °C, Figure 4). It is interesting to note that, even in polymers containing both functionalities, such as **38**, the transition remained at ca. 200 °C even though the total weight change accounted for loss of all of the tertiary esters. This is likely due to the catalyzed thermolysis of the *tert*-butyl esters that can take place once the thermally labile adamantyl esters are removed: the carboxylic acid produced by loss of the adamantyl moiety is able to catalyze the thermolysis of the *tert*-butyl esters at this lower temperature. Differential scanning calorimetry (DSC) analysis of all of the polymers showed no transitions below the decomposition temperature of the tertiary esters, suggesting these rodlike polymers are quite rigid.

(d) Model Cyclization Studies. Throughout this paper, the cyclopolymers obtained from monomers containing both an acrylic moiety and an allylic or methallylic substituent are drawn as containing five-membered ring structural units. Related previous work had shown that a similar cyclopolymer (poly[ethyl α-(allyloxy)methyl] acrylate) consisted exclusively of five-membered ring repeat units, as demonstrated by extensive NMR studies.[23] Similarly, malonate esters containing both an allylic and an acrylic substituent undergo free radical cyclization reactions to afford exclusively cyclopentyl systems.[24] In contrast, a more recent report concerning the cyclopolymerization of dimethyl malonate monomers containing acrylic and methallyl substituents hinted at the presence of both five- and six-membered ring structural units within the backbone of the resulting polymer.[21] To elucidate this point, we prepared model compounds **42** and **45** and allowed them to react under free radical cyclization conditions with TsSePh.[24] Since initiation occurs with tosylate radical followed by trapping with SePh, only two distinct monomeric cyclic regioisomers are possible. ^{77}Se NMR spectroscopy is quite sensitive to the substitution of a carbon atom adjacent to a phenylselenium unit and can be used to distinguish α-secondary, tertiary, and quaternary centers.[25]

Scheme 7



As shown in Scheme 7, the free radical cyclization of compound **42** containing an allylic substituent produced only regioisomeric compound **43** (apparently along with some oligomers) containing five-membered rings and none of the six-membered-ring product **44** (Figure 5). As a result, the ^{77}Se NMR spectrum of the purified reaction mixture showed only signals at $\delta \cong 300$ ppm, consistent with a secondary alkyl carbon adjacent to the phenyl−selenium substituent. Chemical shifts for an

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(25) From analysis of tables of chemical shifts provided in: Klapotke, T. M.; Broschag, M. *Compilation of Reported ^{77}Se NMR Chemical Shifts: Up to year 1994*; Wiley: New York, 1996.

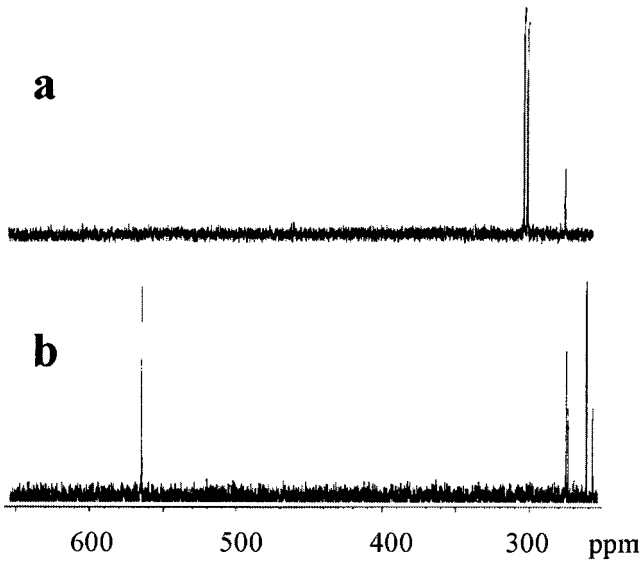

Figure 5. ^{77}Se NMR spectra of reaction mixtures obtained by radical cyclization of compounds **42** (a) and **45** (b) with TsSePh.

adjacent tertiary carbon, which would be present in the six-membered ring at $\delta \cong 400$ ppm, are clearly absent. In contrast, the ^{77}Se NMR spectrum of the purified reaction mixture for the cyclization reaction of compound **45** with its methallyl substituent showed signals at both $\delta \cong 500$ ppm and $\delta \cong 300$ ppm, consistent with the presence of both secondary and quaternary alkyl carbons adjacent to the phenylselenium substituents, suggesting the formation of regioisomeric compounds **46** and **47** (and perhaps some oligomers in the five-membered-ring case) with five- and six-membered rings. It should be noted that these results are consistent with reported substituent effects for kinetic control of the similar 5-hexenyl radical ring closure.[26]

Conclusions

This study demonstrates the feasibility and flexibility of a cyclopolymerization protocol that allows the rapid adjustment of carbon density, or, in other words, etch resistance, within a family of polymer structures targeted for application to 193 nm photolithography. The versatility in the design, ready availability of simple starting materials, ease of cyclopolymerization, and ability to introduce comonomers are attractive features that make this system easily scalable. The rapid access to structural diversity allows specific issues related to the physical properties of the polymers—such as etch resistance, wettability, adhesion, etc.—to be simply addressed. In addition, employment of free radical initiation eliminates the issue of potential metal contamination of the underlying semiconductor substrate by the resist. It is clear that these concepts can be used in the design of other families of resists for application at other wavelengths including for example 157 nm resists.

Experimental Section

General Experimental Methods. All commercially available compounds were purchased from Aldrich and used as received. Tetrahydrofuran (THF) (sodium, benzophenone) and CH_2Cl_2 (CaH_2) were dried before use. Compounds **6**−**11**,[12] **15**,[13] **20**,[15] di-*tert*-butyl 2-prop-2-enylpropane-1,3-dioate,[27] 2-(hydroxymethyl) ethyl acrylate,[28] dimethyl 2-prop-2-enylpropane-1,3-dioate,[29] and dimethyl 2-(2-methylprop-2-enyl)propane-1,3-dioate[30] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on Bruker AMX300, AMX400, AM400, and DRX500 spectrometers with the solvent residual proton signal as a standard. ^{77}Se NMR spectra (95 MHz) were recorded from solutions in $CDCl_3$ on a Bruker DRX500. Thermogravimetric analyses (TGA) were performed on a Seiko II (SSC/5200) device at 10 °C min^{-1} heating rate. Differential scanning calorimetry measurements were performed on a Seiko II (DSC 6200) differential scanning calorimeter at 10 °C min^{-1} heating rate. Infrared spectra were recorded on a Mattson Genesis II FT-IR using potassium bromide with a diffuse reflectance accessory (Pike). Size-exclusion chromatography was carried out on a Waters chromatograph (Waters 150-CV plus) equipped with a 486 tunable absorbance detector ($\lambda = 254$ nm) and a DRI detector. Polystyrene standards were used for the calibration, and the mobile phase was tetrahydrofuran (1 mL/min, 45 °C). A bank of four 5 μm PL Gel columns (Polymer Laboratories) with porosities of 100, 500, and 1000 Å and Mixed C (packed with beads of all three mixed porosities) was used. Elemental analyses were performed at M−H−W Laboratories.

Compound 13. To a solution of 5.17 g (25.1 mmol) of adamantyl acrylate and 1.13 g (37.7 mmol) of paraformaldehyde in 12 mL of 1:1 water/ethylene glycol dimethyl ether was added 564 mg (5.02 mmol) of 1,4-diazabicyclo[2.2.2]octane. After the mixture had been heated overnight at reflux, it was cooled to room temperature. To the crude mixture was added 50 mL of saturated, aqueous NH_4Cl and 150 mL of Et_2O. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 150 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting oil using a solvent gradient of 1:6 ethyl acetate/petroleum ether to 1:1.5 ethyl acetate/petroleum ether yielded 2.54 g (43%) of ester **13**. IR (KBr): 3410, 2910, 1710, 1295, 1170, 1055 cm^{-1}. ^{1}H NMR (300 MHz): δ 6.16 (s, 1H), 5.73 (s, 1H), 4.28 (s, 2H), 2.33 (bs, 1H), 2.16−2.19 (m, 9H), 1.68 (bs, 6H). ^{13}C NMR (100 MHz): δ 165.3, 140.8, 124.7, 81.4, 62.8, 41.3, 36.1, 30.8. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.95; H, 8.31.

Compound 14. To a stirred solution of 2.54 g (10.8 mmol) of ester **13** and 2.46 g (12.9 mmol) of *p*-toluenesulfonyl chloride in 100 mL of CH_2Cl_2 under N_2 at 0 °C was added 520 mg (12.9 mmol) of NaH (60% dispersion in mineral oil). After the mixture had been allowed to warm to room temperature overnight, 75 mL of water was added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were washed with water (1 × 75 mL) and brine (1 × 75 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting solid in 4:1 methylene chloride/hexanes yielded 3.24 g (77%) of tosylate **14** as a white solid. IR (KBr): 2900, 1950, 1710, 1360, 1190, 950, 810, 665, 560 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.81 (d, 2H), 7.35 (d, 2H), 6.27 (s, 1H), 5.82 (s, 1H), 4.70 (s, 2H), 2.45 (s, 3H), 2.17 (s, 3H), 2.08, (s, 6H), 1.65 (s, 6H). ^{13}C NMR (100 MHz): δ 163.2, 144.8, 134.9, 129.8, 127.9, 127.5, 81.8, 67.9, 41.1, 36.0, 30.7, 21.6. Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71; S, 8.21. Found: C, 64.67; H, 6.67; S, 8.37.

Compound 17. To 520 mg (5.38 mmol) of sodium *tert*-butoxide in 45 mL of THF was added a solution of 2.0 g (5.38

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mmol) of ester **15** in 5 mL of THF. The mixture was stirred under N_2 at room temperature. After 30 min, 540 μL (5.38 mmol) of 3-bromo-2-methylpropene was added dropwise and reaction was continued for 6 h. At this time, 10 mL of a saturated, aqueous NH_4Cl solution, 10 mL of water, and 100 mL of Et_2O were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting solid in 1:49 ethyl acetate/hexanes yielded 1.85 g (81%) of ester **17** as a white solid. IR (KBr): 2910, 1720, 1460, 1280, 1230, 1200, 1060, 910 cm^{-1}. ^1H NMR (400 MHz): δ 4.75 (d, 2H), 3.36 (t, 1H), 2.51 (d, 2H), 2.16 (s, 6H), 2.10 (s, 12H), 1.74 (s, 3H), 1.66 (bs, 12H). ^{13}C NMR (100 MHz): δ 168.2, 142.1, 111.9, 81.3, 52.4, 41.1, 36.5, 36.1, 30.7, 22.2. Anal. Calcd for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98. Found: C, 75.91; H, 8.88.

Compound 19. The procedure described for the synthesis of compound **17** was followed substituting di-*tert*-butyl malonate for ester **15**. Chromatography of the resulting oil in 1:49 ethyl acetate/hexanes yielded 940 mg (78%) of ester **19** as a colorless liquid. IR (KBr): 2980, 1730, 1460, 1370, 1250, 1140, 890, 850 cm^{-1}. ^1H NMR (400 MHz): δ 4.75 (d, 2H), 3.37 (t, 1H), 2.52 (d, 2H), 1.74 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz): δ 168.4, 141.9, 111.9, 81.2, 52.1, 36.4, 27.8, 22.1. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.69; H, 9.48.

Compound 21. To 213 mg (2.22 mmol) of sodium *tert*-butoxide in 22 mL of THF was added a solution of 900 mg (2.11 mmol) of ester **17** in 4 mL of THF. The mixture was stirred under N_2 at room temperature. After 45 min, 490 mg (2.22 mmol) of 2-(bromomethyl) *tert*-butyl acrylate was added dropwise and reaction was continued overnight. At this time, 5 mL of a saturated, aqueous NH_4Cl solution, 5 mL of water, and 75 mL of Et_2O were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting oil in 1:49 ethyl acetate/hexanes yielded 660 mg (55%) of ester **21,** as a colorless liquid. IR (KBr): 2910, 1720, 1460, 1220, 1050, 890 cm^{-1}. ^1H NMR (300 MHz): δ 6.15 (s, 1H), 5.56 (s, 1H), 4.76 (d, 2H), 2.93 (s, 2H), 2.59 (s, 2H), 2.16 (bs, 6H), 2.11 (s, 12H), 1.71 (s, 3H), 1.66 (s, 12H), 1.47 (s, 9H). ^{13}C NMR (100 MHz): δ 169.9, 166.4, 141.3, 138.0, 126.2, 114.2, 81.3, 80.3, 57.8, 41.0, 40.0, 36.1, 32.9, 30.7, 27.9, 23.9. Anal. Calcd for $C_{35}H_{50}O_6$: C, 74.17; H, 8.89. Found: C, 73.98; H, 8.98.

Compound 22. To 190 mg (1.97 mmol) of sodium *tert*-butoxide in 19 mL of THF was added a solution of 800 mg (1.88 mmol) of ester **17** in 4 mL of THF. The mixture was stirred under N_2 at room temperature. After 45 min, a solution of 770 mg (1.97 mmol) of tosylate **14** in 4 mL of THF was added dropwise and the reaction was continued for 6 h. At this time, 5 mL of a saturated, aqueous NH_4Cl solution, 5 mL of water, and 75 mL of Et_2O were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting solid in 1:49 ethyl acetate/hexanes yielded 800 mg (66%) of ester **22** as a sticky solid. IR (KBr): 2910, 1720, 1460, 1190, 1060, 890, 740 cm^{-1}. ^1H NMR (400 MHz): δ 6.15 (s, 1H), 5.55 (s, 1H), 4.75 (d, 2H), 2.90 (s, 2H), 2.60 (s, 2H), 2.05−2.20 (m, 27H), 1.70 (s, 3H), 1.65 (s, 18H). ^{13}C NMR (100 MHz): δ 170.1, 166.3, 141.5, 138.1, 126.3, 114.6, 80.6, 80.5, 58.0, 41.2, 41.1, 40.2, 36.2(2), 33.0, 30.8(2), 24.0. Anal. Calcd for $C_{41}H_{56}O_6$: C, 76.36; H, 8.75. Found: C, 76.03; H, 8.50.

Compound 23. To 1.25 g (4.88 mmol) of di-*tert*-butyl 2-prop-2-enylpropane-1,3-dioate **18**[27] in 18 mL of THF was added 516 mg (5.37 mmol) of sodium *tert*-butoxide rinsing with 3 mL of THF. The mixture was stirred under N_2 at room temperature. After 10 min, a solution of 2.19 g (5.61 mmol) of tosylate **14** in 4 mL of THF was added dropwise and the reaction was continued overnight. At this time, 10 mL of water and 100 mL of Et_2O were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 75 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting oil in 1:49 ethyl acetate/hexanes yielded 2.00 g (87%) of ester **23** as a colorless liquid. IR (KBr): 2910, 1730, 1460, 1370, 1290, 1150, 1050, 840 cm^{-1}. ^1H NMR (500 MHz): δ 6.10 (s, 1H), 5.79 (m, 1H), 5.53 (s, 1H), 5.05 (m, 2H), 2.87 (s, 2H), 2.48 (d, 2H), 2.13 (m, 9H), 1.64 (s, 6H), 1.42 (s, 18H). ^{13}C NMR (125 MHz): δ 169.8, 166.1, 138.0, 133.2, 127.1, 118.3, 81.4, 80.7, 58.6, 41.1, 36.7, 36.1, 32.5, 30.8, 27.9. Anal. Calcd for $C_{28}H_{42}O_6$: C, 70.86; H, 8.92. Found: C, 70.66; H, 8.71.

Compound 24. The procedure described for the synthesis of compound **23** was followed substituting ester **19** for **18**. This yielded 1.64 g (91%) of ester **24** as a colorless liquid. IR (KBr): 2910, 1720, 1460, 1370, 1270, 1160, 850 cm^{-1}. ^1H NMR (400 MHz): δ 6.15 (s, 1H), 5.50 (s, 1H), 4.75 (d, 2H), 2.90 (s, 2H), 2.60 (s, 2H), 2.10 (bs, 9H), 1.70 (s, 3H), 1.65 (s, 6H), 1.40 (s, 18H). ^{13}C NMR (100 MHz): δ 170.2, 166.1, 141.3, 138.1, 126.1, 114.3, 81.4, 80.4, 57.6, 41.1, 39.9, 36.1, 32.9, 30.7, 27.8, 23.9. Anal. Calcd for $C_{29}H_{44}O_6$: C, 71.28; H, 9.08. Found: C, 71.40; H, 9.01.

Compound 25. To a stirred solution of 526 mg (7.29 mmol) of acrylic acid and 1.55 g (15.29 mmol) of triethylamine in 9 mL of CH_2Cl_2 under N_2 at room temperature was added a solution of 1.15 g (6.95 mmol) of 2-methyl-2-adamantanol in 17 mL of CH_2Cl_2 followed by 1.95 g (7.65 mmol) of bis(2-oxo-3-oxazolindinyl)phosphinic chloride. After 30 min, 10 mL of CH_2Cl_2 was added, and after another 30 min, 726 mg (7.17 mmol) of triethylamine followed by 1.05 g (4.12 mmol) of bis-(2-oxo-3-oxazolindinyl)phosphinic chloride was added. After the mixture had been stirred at room temperature overnight, 20 mL of a saturated, aqueous $NaHCO_3$ solution and 20 mL of water were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 75 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed in vacuo, and chromatography of the resulting oil in 1:19 ethyl acetate/hexanes yielded 1.40 g (92%) of acrylate **25** as a colorless liquid. IR (KBr): 2910, 1720, 1640, 1450, 1400, 1270, 1200, 1100, 1050, 960, 810 cm^{-1}. ^1H NMR (500 MHz): δ 6.31 (d, 1H), 6.08 (dd, 1H), 5.73 (d, 1H), 2.32 (s, 2H), 2.02 (d, 2H), 1.88 (d, 2H), 1.68−1.80 (m, 6H), 1.64 (s, 3H), 1.56 (d, 2H). ^{13}C NMR (125 MHz): δ 165.1, 130.4, 129.2, 87.0, 38.1, 36.1, 34.4, 33.0, 27.3, 26.7, 22.2. Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.17; H, 8.98.

Compound 26. The procedure described for the synthesis of compound **13** was followed substituting acrylate **25** for adamantyl acrylate. Chromatography of the resulting oil using a solvent gradient of 1:9 ethyl acetate/hexanes to 1:4 ethyl acetate/hexanes yielded 6.18 g (37%) of acrylate **26** as a colorless liquid. IR (KBr): 3470, 2910, 1700, 1640, 1450, 1320, 1170, 1100, 1050, 980, 890, 820 cm^{-1}. ^1H NMR (500 MHz): δ 6.19 (s, 1H), 5.75 (s, 1H), 4.30 (s, 2H), 2.53 (bs, 1H), 2.33 (s, 2H), 2.00 (d, 2H), 1.88 (d, 2H), 1.70−1.81 (m, 6H), 1.65 (s, 3H), 1.58 (d,2H). ^{13}C NMR (125 MHz): δ 165.2, 141.0, 124.5, 88.0, 65.8, 62.7, 38.0, 36.2, 34.4, 33.1, 27.3, 26.6, 22.3, 15.2. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.13; H, 8.82.

Compound 27. The procedure described for the synthesis of compound **14** was followed substituting ester **26** for ester **13**. Chromatography of the resulting solid in 1:9 ethyl acetate/hexanes yielded 1.86 g (93%) of tosylate **27** as a white solid. IR (KBr): 2910, 1700, 1650, 1600, 1450, 1370, 1330, 1180, 1100, 1000, 960, 840, 810, 680, 550 cm^{-1}. ^1H NMR (500 MHz): δ 7.79 (d, 2H), 7.33 (d, 2H), 6.30 (s, 1H), 5.84 (s, 1H), 4.73 (s, 2H), 2.44 (s, 3H), 2.27 (s, 2H), 1.69−1.92 (m, 10H), 1.60 (s, 3H), 1.54 (d, 2H). ^{13}C NMR (125 MHz): δ 163.1, 144.9, 135.1, 133.0, 129.8, 127.9, 127.5, 88.5, 67.9, 38.0, 36.1, 34.4, 33.0, 27.2, 26.5, 22.2, 21.6. Anal. Calcd for $C_{22}H_{28}O_5S$: C, 65.32; H, 6.98; S, 7.93. Found: C, 65.21; H, 6.90; S, 8.13.

Compound 28. To a stirred solution of 1 g (6.0 mmol) of 2-methyl-2-adamantanol, 612 mg (6.0 mmol) of triethylamine, and 293 mg (2.4 mmol) of DMAP in 50 mL of CH_2Cl_2, 424 mg (3 mmol) of malonyl dichloride was slowly added with a syringe. The solution was stirred at room temperature for 8 h and then partitioned between with Et_2O (3 × 100 mL) and H_2O. The organic layer was dried ($MgSO_4$) and stripped of the solvent in vacuo. Purification of the crude mixture by flash column chromatography (SiO_2/CH_2Cl_2) afforded **28** as a white solid (700 mg, 59%) ^{1}H NMR (300 MHz): δ 3.46 (s, 2H), 2.29 (bs, 4H), 2.04 (d, 4H),1.4−1.9 (m, 28H). ^{13}C NMR (75 MHz): δ 165.5, 88.3, 44.3, 37.9, 35.9, 34.3, 32.8, 27.2, 26.5, 22.0. Anal. Calcd for $C_{25}H_{36}O_4$: C, 75.00; H, 9.00. Found: C, 74.86; H, 8.82.

Compound 29. The procedure described for the synthesis of compound **17** was followed substituting ester **28** for ester **15**. The product was purified by flash column chromatography (SiO_2/CH_2Cl_2) to give **29** as a glassy solid (3.8 g, 58%). ^{1}H NMR (300 MHz): δ 4.85 (s, 1H), 4.78 (s, 1H), 3.52 (t, 1H), 2.59 (d, 2H), 2.28 (d, 4H), 2.07 (dd, 4H), 1.4−1.9 (m, 29H). ^{13}C NMR (75 MHz): δ 168.1, 142.0, 112.0, 88.5, 53.1, 52.5, 38.1, 36.5, 36.1, 34.5, 32.8, 27.3, 26.6, 22.0. Anal. Calcd for $C_{29}H_{42}O_4$: C, 76.65; H, 9.25. Found: C, 76.59; H, 9.16.

Compound 30. To a stirred solution of 2.3 g (5.1 mmol) of **29** in 100 mL of dry THF at 0 °C was added 0.5 g (5.1 mmol) of sodium *tert*-butoxide and allowed to stir for 10 min. A solution of 1.12 g (5.1 mmol) of 2-(bromomethyl) *tert*-butyl acrylate **20** was added and the reaction mixture was allowed to stir up to room temperature and subsequently for 48 h as a white precipitate formed. The reaction mixture was quenched with MeOH and H_2O, extracted with Et_2O (3 × 300 mL), and dried ($MgSO_4$). The product was purified by flash column chromatography (SiO_2/CH_2Cl_2) to give **30** as a viscous oil (2.42 g, 80%). ^{1}H NMR (300 MHz): δ 6.18 (s, 1H), 5.62 (s, 2H), 4.83 (s, 1H), 4.77 (s, 1H), 3.11 (s, 2H), 2.74 (s, 2H), 1.4−2.4 (m, 46H). ^{13}C NMR (75 MHz): δ 169.9, 166.7, 141.0, 138.0, 127.3, 114.5, 89.0, 80.4, 59.1, 39.6, 38.1, 36.5, 36.3, 34.6, 32.9, 28.0, 27.3, 26.5, 24.4, 21.9. Anal. Calcd for $C_{37}H_{54}O_6$: C, 74.75; H, 9.09. Found: C, 74.60; H, 8.73.

Compound 31. The procedure described for the synthesis of compound **23** was followed substituting ester **29** for **18** and tosylate **27** for tosylate **14**. Chromatography of the resulting oil in 1:49 ethyl acetate/hexanes yielded 1.93 g (92%) of ester **31** as a colorless liquid. IR (KBr): 2900, 1720, 1640, 1450, 1200, 1100, 950, 890, 840, 820 cm^{-1}. ^{1}H NMR (400 MHz): δ 6.25 (s, 1H), 5.63 (s,1H), 4.80 (d, 2H), 3.12 (s, 2H), 2.77 (s, 2H), 2.28−2.33 (m, 6H), 2.01−2.12 (m, 6H), 1.49−1.87 (m, 42H). ^{13}C NMR (100 MHz): δ 169.9, 166.0, 141.0, 138.0, 125.9, 114.6, 89.1, 87.0, 59.0, 39.5, 38.1, 36.4, 36.3, 36.2, 34.5, 34.4, 33.2, 33.0, 32.8, 27.3, 27.2, 26.7, 26.5, 24.3, Anal. Calcd for $C_{44}H_{62}O_6$: C, 76.93; H, 9.10. Found: C, 76.77; H, 8.92.

Compound 42. The procedure described for the synthesis of compound **14** was followed substituting 2-(hydroxymethyl) ethyl acrylate[28] for ester **13**. Chromatography of the resulting solid using a solvent gradient of 1:9 ethyl acetate/hexanes to 1:4 ethyl acetate/hexanes yielded 22.19 g (81%) of 2-((4-methylphenylsulfonyloxy)methyl) ethyl acrylate as a white solid. IR (KBr): 2980, 1720, 1600, 1370, 940, 800, 690, 550 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.81 (d, 2H), 7.35 (d, 2H), 6.37 (s, 1H), 5.92 (s, 1H), 4.73 (s, 2H), 4.17, (q, 2H), 2.45 (s, 3H), 1.26 (t, 3H). ^{13}C NMR (100 MHz): δ 164.3, 144.9, 133.7, 132.8, 129.8, 128.5, 127.9, 67.6, 61.1, 21.5, 14.0. Anal. Calcd for $C_{13}H_{16}O_5S$: C, 54.91; H, 5.67; S, 11.28. Found; C, 54.97; H, 5.70; S, 11.16. The procedure described for the synthesis of compound **23** was followed substituting dimethyl 2-prop-2-enylpropane-1,3-dioate[29] for **18** and 2-((4-methylphenylsulfonyloxy)methyl) ethyl acrylate for tosylate **14**. Chromatography of the resulting oil in 1:9 ethyl acetate/hexanes yielded 1.30 g (100%) of ester **42** as a colorless liquid. IR (KBr): 2950, 1740, 1630, 1440, 1220, 1020, 970, 850, 670 cm^{-1}. ^{1}H NMR (500 MHz): δ 6.26 (s, 1H), 5.67−5.75 (m, 1H), 5.63 (s, 1H), 5.09 (s, 1H), 5.07 (d, 1H), 4.17 (q, 2H), 3.68 (s, 6H), 2.96 (s, 2H), 2.58 (d, 2H), 1.28 (t, 3H). ^{13}C NMR (125 MHz): δ 170.9, 166.8, 136.1, 132.4, 128.9, 119.1, 60.9, 57.8, 52.3, 37.2, 33.8, 14.1.

Compound 43. To 240 mg (1.27 mmol) of benzeneselenic acid in 25 mL of chloroform was slowly added 237 mg (1.27 mmol) of *p*-toluenesulfonhydrazide. The mixture was stirred under N_2 at room temperature. After 1 h, this solution was added to 300 mg (1.06 mmol) of ester **42** and exposed to 300 nm light in a Rayonet reactor for 3 h. At this time, 10 mL of water and 75 mL of EtOAc were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with water (3 × 10 mL). The aqueous layers were combined and extracted with EtOAc (1 × 75 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting liquid in a gradient of 1:4 to 3:7 ethyl acetate/hexanes yielded 520 mg (82%) of cyclic **43** as a colorless liquid. ^{1}H NMR (500 MHz): δ 7.1−7.7 (m, 9H), 2.2−4.2 (m, 20H), 1.2−1.4 (t, 3H). ^{13}C NMR (125 MHz): δ 173.1, 172.3, 171.8, 171.4, 144.7, 138.0, 133.7, 133.1, 132.9, 129.8, 129.7, 129.3, 129.2, 129.0, 128.0, 127.7, 127.6, 127.4, 127.3, 63.1, 61.7, 61.6, 57.6, 57.5, 57.1, 54.0, 53.6, 53.1, 53.0, 52.9, 52.7, 50.1, 49.0, 40.4, 39.3, 38.4, 38.3, 38.2, 27.4, 26.9, 21.5.

Compound 45. The procedure described for the synthesis of compound **23** was followed by substituting dimethyl 2-(2-methylprop-2-enyl)propane-1,3-dioate[30] for **18** and 2-((4-methylphenylsulfonyloxy)methyl) ethyl acrylate for tosylate **14**. Chromatography of the resulting oil in 1:9 ethyl acetate/hexanes yielded 1.35 g (99%) of ester **45** as a colorless liquid. IR (KBr): 2950, 1740, 1640, 1440, 1210, 900, 820 cm^{-1}. ^{1}H NMR (500 MHz): δ 6.24 (s, 1H), 5.67 (s, 1H), 4.85 (s, 1H), 4.71 (s, 1H), 4.15 (q, 2H), 3.67 (s, 6H), 3.00 (s, 2H), 2.68 (s, 2H), 1.66 (s, 3H), 1.28 (t, 3H). ^{13}C NMR (125 MHz): δ 171.3, 166.9, 140.6, 136.2, 128.6, 115.0, 60.8, 56.9, 52.3, 41.1, 34.5, 23.4, 14.1.

Compounds 46 and 47. To 228 mg (1.21 mmol) of benzeneselenic acid in 25 mL of benzene was slowly added 225 mg (1.21 mmol) of *p*-toluenesulfonhydrazide. The mixture was stirred under N_2 at room temperature. After 1 h, this solution was added to 300 mg (1.06 mmol) of ester **45** and exposed to 300 nm light in a Rayonet reactor for 3 h. At this time, 10 mL of water and 75 mL of EtOAc were added. The resulting mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with water (3 × 10 mL). The aqueous layers were combined and extracted with EtOAc (1 × 75 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and chromatography of the resulting liquid in a gradient of 1:4 to 3:7 ethyl acetate/hexanes yielded cyclic **46** and **47** as a colorless liquid. ^{13}C NMR (125 MHz): δ 170−173 (multiple signals), 127−143 (multiple signals), 13−63 (multiple signals).

Typical Polymerization Procedure. Freshly purified monomers were dissolved in the appropriate solvent as indicated in Table 1 for selected runs. AIBN or methyl azoisobutyrate (2 mol %) was added and the mixture was purged with nitrogen and further deoxygenated with two freeze−thaw cycles. The reaction mixture was heated at 70 °C for 30 h.

*Polymer **32***. Reprecipitated into MeOH. Yield: 53%. IR (KBr): 2910, 1730, 1360, 1480, 1250, 1150, 1060, 850 cm^{-1}. ^{1}H NMR (400 MHz): δ 1.90−2.30 (bs), 0.80−1.80 (bm). Anal. Calcd for $(C_{35}H_{50}O_6)_n$: C, 74.17; H, 8.89. Found: C, 73.96; H, 8.91.

*Polymer **33***. Reprecipitated into MeOH. Yield: 73%. IR (KBr): 2910, 1730, 1460, 1250, 1060, 900 cm^{-1}. ^{1}H NMR (400 MHz): δ 2.00−2.40 (bs), 1.50−1.80 (bm), 0.80−1.20 (bm). Anal. Calcd for $(C_{41}H_{56}O_6)_n$: C, 76.36; H, 8.75. Found: C, 76.19; H, 8.78.

*Polymer **34***. Reprecipitated into MeOH. Yield: 40%. IR (KBr): 2910, 1730, 1460, 1370, 1250, 1170, 1060, 850 cm^{-1}. ^{1}H NMR (400 MHz): δ 2.00−2.30 (bm), 1.30−1.70 (bm), 0.80−1.20 (bm). Anal. Calcd for $(C_{29}H_{44}O_6)_n$: C, 71.28; H, 9.08. Found: C, 71.12; H, 9.08.

*Polymer **35***. Reprecipitated into MeOH. Yield: 80%. IR (KBr): 2910, 1860, 1780, 1730, 1460, 1370, 1250, 1150, 1050, 940 cm^{-1}. ^{1}H NMR (500 MHz): δ 2.08−2.21 (bm), 1.01−1.65

(bm). Anal. Calcd for $(C_{39}H_{52}O_9)_n$: C, 70.46; H, 7.88. Found: C, 70.35; H, 7.70.

Polymer ***36***. Reprecipitated into MeOH. Yield: 68%. IR (KBr): 2910, 1860, 1780, 1730, 1460, 1370, 1260, 1170, 1050, 970, 850 cm^{-1}. ^1H NMR (500 MHz): δ 2.13−2.21 (bm), 1.25−1.62 (bm). Anal. Calcd for $(C_{32}H_{44}O_9)_n$: C, 67.11; H, 7.74. Found: C, 66.96; H, 7.75.

Polymer ***37***. Reprecipitated into MeOH. Yield: 81%. IR (KBr): 2910, 1860, 1780, 1730, 1460, 1370, 1250, 1170, 1050, 940, 850 cm^{-1}. ^1H NMR (500 MHz): δ 2.13−2.21 (bm), 1.25−1.64 (bm). Anal. Calcd for $(C_{33}H_{46}O_9)_n$: C, 67.56; H, 7.90. Found: C, 67.72; H, 7.89.

Polymer ***38***. Reprecipitated into MeOH. Yield: 74%. IR (KBr): 2910, 1860, 1780, 1720, 1460, 1370, 1250, 1090 cm^{-1}. ^1H NMR (400 MHz): δ 2.0−2.5 (bm), 0.8−1.7 (bm). Anal. Calcd for $(C_{41}H_{56}O_9)_n$: C, 71.10; H, 8.09. Found: C, 71.29; H, 8.21.

Polymer ***39***. Reprecipitated into 2:1 MeOH:acetone. Yield: 66%. IR (KBr): 2910, 1860, 1780, 1720, 1460, 1380, 1250, 1090, 950, 890, 840 cm^{-1}. ^1H NMR (400 MHz): δ 0.80−2.60 (bm). Anal. Calcd for $(C_{48}H_{64}O_9)_n$: C, 73.44; H, 8.22. Found: C, 73.39; H, 8.09.

Polymer ***40***. Yield: 67%. IR (KBr): 2900, 1860, 1780, 1720, 1450, 1380, 1260, 1090, 950, 890, 840 cm^{-1}. ^1H NMR (400 MHz): δ 0.80−2.60 (bm). Anal. Calcd for $(C_{200}H_{264}O_{41})_n$: C, 72.26; H, 8.00. Found: C, 72.38; H, 8.00.

Polymer ***41***. Yield: 82%. IR (KBr): 3440, 2910, 1860, 1780, 1720, 1460, 1370, 1250, 1150, 1090, 930, 890, 840 cm^{-1}. ^1H NMR (400 MHz): δ 0.80−2.60 (bm). Anal. Calcd for $(C_{172}H_{232}O_{41})_n$: C, 68.89; H, 7.91. Found: C, 68.91; H, 7.78.

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