

Unique polymers *via* radical diene cyclization: polyspironorbornanes and their application to 193 nm microlithography

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The design of novel alkylated norcamphor derivatives that undergo cyclopolymerization is explored; the resulting polymers incorporate suitable functional groups for chemical amplification and show excellent imaging characteristics under lithographic exposure at 193 nm.

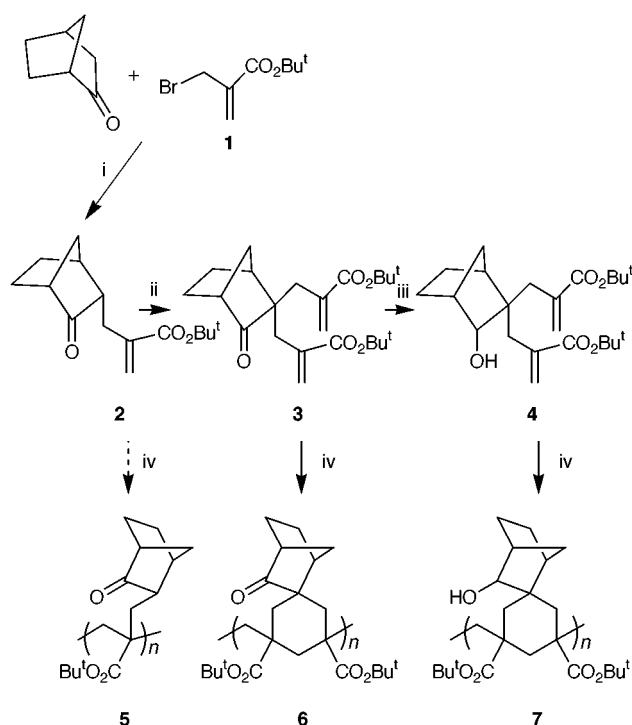
The rapid advance in the miniaturization of microelectronic devices requires the development of new imageable polymeric materials for 193 nm microlithography.¹ Highly sensitive, chemically amplified resists for 248 nm microlithography were described in the early 1980s,² and have been used commercially for more than a decade. They operate on the basis of acid-catalyzed deprotection of a polymer in a process that renders the final product soluble in aqueous base.³ The next generation of resists for 193 nm lithography requires much structural redesign to obtain optical transparency at 193 nm while preserving the etch resistance normally afforded by aromatic rings.

Acrylic and methacrylic acids⁴ have been suggested for this application due to their good transparency but their dry-etch resistance is limited. Since a high carbon to hydrogen (C/H) ratio is required to confer etch resistance⁵ to the polymeric structure, several carbon-rich, chemically amplified resist materials have recently been described.^{6,7} Here, we present a novel synthetic approach for the construction of carbon-rich polymers *via* the cyclopolymerization⁸ of suitably modified difunctional monomers.

In earlier work, Marvel *et al.*,⁹ and later Mathias *et al.*,¹⁰ have described the free radical polymerization of diacrylates to afford soluble cyclopolymer with virtually complete cyclization. We have now designed bifunctional acrylic-like monomers, incorporating both (i) *tert*-butyl esters as imageable functionalities for chemical amplification, and (ii) carbon-rich cage moieties for etch resistance. A suitable commercially available building block is racemic norcamphor. It can be alkylated *via* its enolate using *tert*-butyl 2-(bromomethyl)acrylate **1** to give the mono-substituted product **2** in good yield (Scheme 1).[†] This alkylation, as shown by 2D ¹H NMR spectroscopy, proceeds diastereoselectively, the *endo* face of the norbornene structure being less sterically hindered and more suitable for reaction with the bromide. The disubstituted monomer **3** could also be obtained under the same reaction conditions, although incomplete conversion of the starting monosubstituted camphor derivative **2** into **3** was observed, probably due to attack of the alkylating agent on the more sterically hindered *exo* face.

Isolation of pure monomer **3** required careful purification of the crude product by flash column chromatography. The structure of **3** was determined by standard spectrometric techniques and confirmed by X-ray crystallographic analysis. The ketone functionality of **3** could be selectively reduced with KBH₄ in MeOH to afford alcohol monomer **4** in good yields.

Monomers **3** and **4** undergo smooth cyclopolymerization under free-radical conditions in deoxygenated solvents to give the cyclopolymerized products **6** and **7**, respectively (in up to 88% yield after precipitation from MeOH). The resulting polymers were soluble in a variety of organic solvents, and IR and NMR spectroscopic analyses revealed the absence of residual alkene groups in the two polymers, thus confirming that virtually complete cyclization had been achieved. Interestingly,



Scheme 1 Reagents and conditions: (i) NaOBu^t, THF, 0 °C, 70%; (ii) **1**, NaOBu^t, THF, 0 °C, 50%; (iii) KBH₄, MeOH, 0 °C, 50%; (iv) AIBN, solvent, 70 °C, 30 h.

the monosubstituted camphor derivative **2** did *not* polymerize under standard free radical conditions, probably as a result of the extreme steric hindrance that adjacent camphor derivatives would experience within the backbone of polymer **5**.

Differential scanning calorimetry analysis of polymers **6** and **7** showed no transitions below the decomposition temperature of the polymer, which occurs at *ca.* 240 °C and results from the thermolysis of the *tert*-butyl esters. Thermogravimetric analysis data for the polymers were in close agreement with the observed and calculated weight losses for the thermolysis of the *tert*-butyl ester functionalities. As can be seen in Table 1, variations in

Table 1 Cyclopolymerization of monomers **3** and **4** under free radical conditions

Monomer	Conc./mol		Additive/mol%		<i>M</i> _n ^a	<i>M</i> _w ^a	PDI ^b
	dm ⁻³	Solvent	AIBN	Thiol			
3	1.8	benzene	2	0	35 600	64 000	1.8
3	1.2	benzene	2	0	10 200	17 500	1.7
4	2	Bu ^t OH	2	0	34 200	57 700	1.7
4	1.2	Bu ^t OH	9	0	7 600	12 900	1.7
4	1.2	benzene	2	3	28 600	44 900	1.6
4	1.2	benzene	2	6	14 900	22 800	1.5

^a Molecular weights determined by size exclusion chromatography relative to polystyrene standards. ^b Polydispersity index.

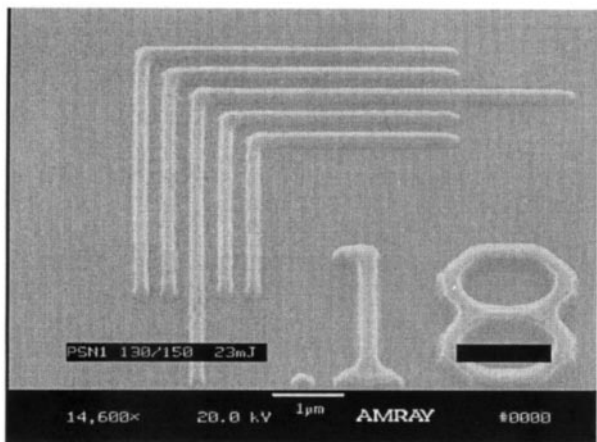


Fig. 1. Electron micrograph of 180 nm nested features obtained from films of polymer **6** and a photoacid generator after exposure to a 193 nm stepper.

monomer or initiator concentrations, solvent, or the use of dodecanethiol as a chain transfer agent,¹¹ brought about considerable variations in the molecular weight distribution. Control of molecular weight is useful for such polymers since low molecular weight polymers are often desirable for lithographic applications at 193 nm.

Camphor-derived polymers **6** and **7** produced high quality films on silicon wafers. Nevertheless, the absorbance of films of polymer **6** at 193 nm ($A = 0.66$ per μm of film thickness) was found to be relatively high. The corresponding polymer **7**, free of ketone or olefin moieties, showed a greatly reduced absorbance at 193 nm ($A = 0.23 \mu\text{m}^{-1}$). Films prepared from polymer **6** bearing ketone functionalities and 10 wt% of a photoacid generator¹² showed clearing doses in the order of 10 mJ cm^{-2} . Similar films prepared from polymer **7** and 5 wt% photoacid generator required doses of *ca.* 15 mJ cm^{-2} . This confirms that the removal of the somewhat basic ketone functionalities, in addition to lowering the absorbance of the films, contributes to enhance the photospeed of the corresponding resist formulations. Images with feature sizes of $0.18 \mu\text{m}$ (Fig. 1) and lower could be obtained. This study demonstrates the feasibility and flexibility of a cyclopolymerization protocol that allows the rapid adjustment of 'carbon density' within the polymeric structure for applications such as nanolithography. All of these bis-olefinic monomers cyclopolymerize readily and preliminary experiments suggest they can also be used in copolymerizations with a variety of co-monomers. We are currently pursuing further optimization of the fundamental design of these materials as well as of their imaging properties.

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Notes and references

† Selected data for **2**: $\delta_{\text{H}}(\text{CDCl}_3)$ 6.12 (s, 1H; C=CH), 5.46 (s, 1H; C=CH), 2.57 (m, 2H; norcamphor), 2.39 (br s, 1H; norcamphor), 2.16 (dd, 1H; norcamphor), 2.0–1.6 (m, 5H; norcamphor), 1.6–1.3 [m, 11H; norcamphor and $\text{C}(\text{CH}_3)_3$]; $\delta_{\text{C}}(\text{CDCl}_3)$ 218.7, 166.0, 140.1, 125.2, 80.8, 52.7, 49.6, 38.6, 34.6, 31.1, 28.0, 27.9, 23.9. For **3**: $\delta_{\text{H}}(\text{CDCl}_3)$ 6.13 (s, 2H; C=CH), 5.60 (s, 1H; C=CH), 5.49 (s, 1H; C=CH), 2.71 (dd, 2H; norcamphor), 2.6–2.1 (m, 5H; norcamphor), 1.9–1.3 [m, 23H; norcamphor and $\text{C}(\text{CH}_3)_3$]; $\delta_{\text{C}}(\text{CDCl}_3)$ 219.1, 167.1, 166.5, 139.4, 138.8, 127.1, 125.1, 80.8, 80.7, 54.4, 49.8, 44.2, 34.9, 34.1, 32.1, 28.0, 27.9, 24.9, 23.8. (calc. for $\text{C}_{23}\text{H}_{34}\text{O}_5$: C 70.7, H 8.7; found: C 70.7, H 8.8%). For **4**: $\delta_{\text{H}}(\text{CDCl}_3)$ 6.08 (s, 1H; C=CH), 6.05 (s, 1H; C=CH), 5.56 (s, 1H; C=CH), 5.51 (s, 1H; C=CH), 3.89 (br s, 1H; CHOH), 2.6–2.1 (m, 6H; norcamphor), 1.7–1.1 [m, 25H; norcamphor and $\text{C}(\text{CH}_3)_3$]; $\delta_{\text{C}}(\text{CDCl}_3)$ 167.9, 167.6, 140.4, 139.8, 126.1, 124.8, 80.5, 80.5, 77.6, 46.6, 44.6, 43.2, 38.4, 33.8, 30.2, 30.2, 27.9, 25.0, 18.8 (calc. for $\text{C}_{23}\text{H}_{36}\text{O}_5$: C 70.4, H 9.2; found: C 70.6, H 9.1%). For polymer **6**: TGDTA analysis: 235 °C; calc. loss 29%, found 31%; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2980, 1740, 1720, 1450, 1370, 1250, 1150, 850, 750; $\delta_{\text{H}}(\text{CDCl}_3)$ 3–1 (br s) (calc. for $(\text{C}_{23}\text{H}_{34}\text{O}_5)_n$: C 70.7, H 8.7; found: C 70.6, H 8.7%). For polymer **7**: TGDTA analysis: 238 °C; calc. loss 29%, found 29%; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3460, 2950, 1720, 1455, 1370, 1250, 1150, 850; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.5–3.5 (br s), 3–1 (br s).

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- Preliminary screening of photoacid generators showed triphenylsulfonium or diphenyliodonium nonafluorobutanesulfonate salts to give the best results in terms of resolution and sensitivity. The relative rate of etching of formulations containing polymer **6** in comparison to the commercial resist APEX was 1.25 (124 sccm HBr, 100 sccm Cl_2).

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