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Synthesis of Cycloolefin−Maleic Anhydride Alternating Copolymers for 193 nm Imaging

F. M. Houlihan, T. I. Wallow,[†] O. Nalamasu, and E. Reichmanis*

Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

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ABSTRACT: A series of novel cycloolefin−maleic anhydride copolymers have been prepared and evaluated for 193 nm imaging applications. Free radical induced copolymerization of norbornene and maleic anhydride affords a hydrolytically robust alternating copolymer. Aqueous base solubility can be induced via incorporation of acrylic acid and/or acrylate esters that can be cleaved to afford the parent acid via acidolysis. The proportion of acrylate in the resulting terpolymers is a linear function of the starting monomer ratio. These terpolymers are thermally stable and hydrolytically robust. Due to their aqueous base solubility and UV transparency, they have potential in high resolution imaging applications. Sub-0.18 μm imaging has been demonstrated upon 193 nm pattern-wise exposure of selected materials.

I. Introduction

Photolithography using a 193 nm (Ar−F excimer laser) light source is a leading candidate for future microelectronics device fabrication using 0.18 and 0.13 μm design rules. The opacity of traditional UV and deep UV (248 nm) chemically amplified organic photoresists[1] at 193 nm precludes their use in single-layer schemes at this wavelength, and major research efforts to develop alternate materials are currently underway. To date, these efforts have focused on derivatized acrylate and methacrylate copolymers.[2] The fundamental design challenge that has emerged appears to be the necessary trade-off between plasma-etching resistance and requisite materials properties for lithographic performance. On the whole, high carbon content copolymers functionalized with pendant alicyclic moieties possess adequate etching resistance but tend to be brittle, display poor adhesion, and have suboptimal imaging characteristics due to poor aqueous base solubility. Decreased alicyclic carbon content results in improved lithographic performance at the cost of etching resistance. Recent approaches for addressing this fundamental design challenge include (i) careful tailoring of polymer properties to maximize lithographic performance with minimal sacrifice in etching performance[2a,b] and (ii) development of three-component systems in which high carbon content alicyclic additives not only serve as dissolution inhibitors but also enhance the resistance of the matrix as a whole to plasma environments.[2b]

While methacrylate-based resist platforms are attractive from an economic perspective, they suffer from the fundamental drawback of possessing a linear, oxygen-rich scaffold whose poor plasma-etching stability can be offset only partially by functionalization with more stable pendant groups. In a more ideal resist platform, greater intrinsic plasma-etching stability might be imparted through incorporation of alicyclic, plasma-etch-resistant moieties directly into the polymer backbone. In addition, minimizing oxygen content by designing oxygenated functionalities to play only necessary imaging, adhesion and solubilizing roles would be beneficial. Alternative routes to achieve the goal of an "all alicyclic backbone" are shown in Figure 1 for the alicyclic alkene, norbornene. These routes are the ring-opening metathesis polymerization[3,4] (ROMP), the metal-catalyzed vinyl polymerization,[5−7] and radical-promoted vinyl polymerization.[8] Because of the potential for metal ion contamination, neither ROMP nor metal-catalyzed vinyl polymerization were considered as routes for achieving an "all alicyclic backbone" polymer. Additionally, the ROMP polymers also contain olefinic units, and an additional reduction reaction prior to use may be required. Radical-induced homopolymerization of norbornene and derivatives with monoalkoxycarbonyl substitution such as *tert*-butyl bicyclo[2.2.1]hep-5-ene-2-carboxylate tends to give polymers with low molecular weights. A dialkoxycarbonyl substituted derivative, di-*tert*-butylbicyclo[2.2.1]hep-5-ene-2,3-dicarboxylate, has recently been reported[8] to give somewhat higher molecular weight, however, the starting material is not readily available.

In pursuing alternate 193 nm single-layer resist platforms, we have developed a new class of matrix resin that more closely approximates the structural ideal, yet relies on simple, metal-ion free, free radical polymerization methodologies.[9] Unlike the methacrylate systems, these materials, based on cycloolefin−maleic anhydride alternating copolymers, contain large quantities of alicyclic structures directly in the polymer backbone. While these copolymers retain some oxygenated functionalities in structural roles, oxygen content is decreased relative to methacrylate analogs. In addition to our own work related to cycloolefin−maleic anhydride alternating copolymers[9] and the use of poly(*tert*-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) as a dissolution inhibitor for poly(((*tert*-butoxycarbonyl)oxy)-α-methylstyrene) in an e-beam resist scheme,[8] reference to the potential application of substituted polynorbornenes obtained via addition polymerization for 193 nm lithography has appeared,[10a] which was followed recently by further work reported by these workers and others on this topic.[10b,c]

II. Results and Discussion

Alternating Copolymer Matrix Resins: Synthesis and Materials Properties. Alternating Copolymerizations. Cycloolefin−maleic anhydride alternating copolymers may provide an attractive alternative to methacrylate-based matrix resins. Compelling fea-

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[†] Current address: IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

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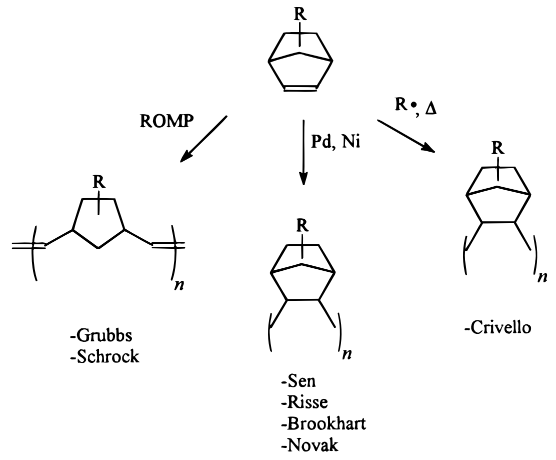


Figure 1. Norbornene polymerizations.

tures of these copolymers include (a) facile synthesis *via* standard radical polymerization, (b) a potentially large pool of cycloolefin feed stocks, and (c) a generic structural motif that incorporates alicyclic structures directly in the polymer backbone and provides a latent water-solubilizing group that may also be useful for further structural elaboration. A large number of cycloolefins are known to copolymerize with maleic anhydride.[11] As a rule, they yield high-T_g copolymers with a 1:1 alternating structure. Cyclic diolefins undergo transannular cyclopolymerizations that may be accompanied by substrate specific complications (*vide infra*). While we have screened a number of cycloolefins as substrates, our efforts to date have concentrated largely on norbornene, which copolymerizes cleanly and yields materials with promising properties.

Norbornene−maleic anhydride copolymerizations were first described in a patent that provided two key insights:[12] (i) copolymerization provides a material with a 1:1 composition regardless of monomer feed ratio, and (ii) incorporation of small percentages (<10% is claimed) of other vinyl monomers without disruption of the essentially alternating nature is tolerated. Another early study constrained the generality of norbornene alternating copolymerizations in reporting that, of several functionalized norbornenes examined, only 5-norbornene-2-carbonitrile undergoes strictly alternating copolymerization with maleic anhydride.[13]

In practice, alternating copolymerization of norbornene and maleic anhydride occurs readily at 65 °C in a variety of solvents including THF, dioxane, acetone, and cyclohexanone using 2,2′-azobisisobutyronitrile (AIBN) as an initiator (Figure 2a). Poly(norbornene-*alt*-maleic anhydride) [P(NB/MA)] is a colorless powder with $T_g > 300$ °C and an onset of decomposition (under argon) of 370 °C. The polymer is soluble in ketones including cyclohexanone and methyl isobutyl ketone but is insoluble in esters including common spinning solvents such as ethyl-3-ethoxy propionate and propylene glycol methyl ether acetate. Experiments reveal that P(NB/MA) is hydrolytically robust: polymer prepared in cyclohexanone may be stored for at least a month without significant changes in overall characteristics. A less fortunate consequence of hydrolytic stability is that films spun from P(NB/MA) itself do not dissolve at useful rates in conventional aqueous base developer (0.262 N TMAH; OCG OPD-262) solution. Partial hydrolysis of P(NB/MA) yields more readily soluble materials, but this approach suffers from the drawbacks outlined below.

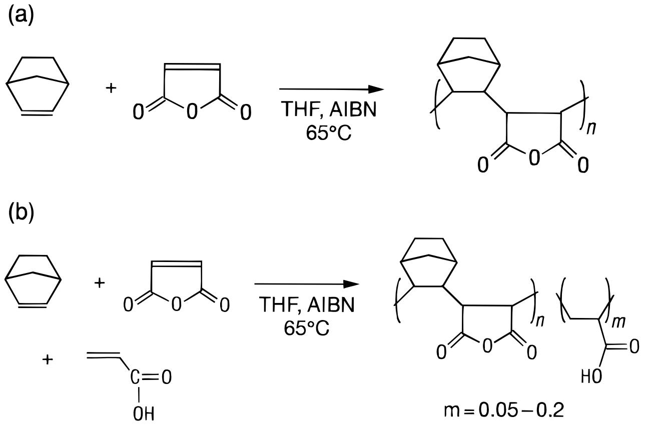


Figure 2. (a) P(NB/MA) synthesis. (b) P(NB/MA/AA) terpolymer synthesis.

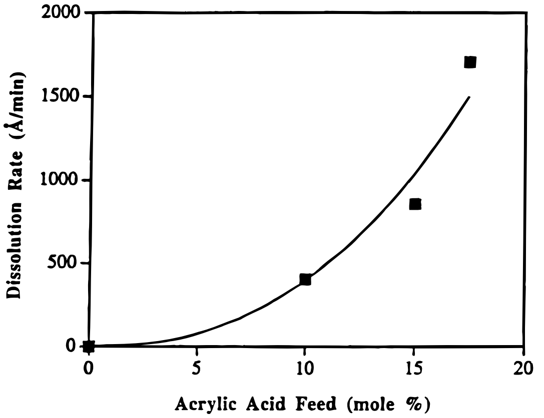


Figure 3. Dissolution rate of P(NB/MA/AA) resins in 0.131 N TMAH.

Terpolymerization with acrylic acid (Figure 2b) provides a controllable method of synthesizing aqueous base soluble resins: systematic variation of acrylic acid (AA) feed ratios from 5−20% yielded progressively more base-soluble yet hydrolytically robust formulations (Figure 3). No change in the dissolution rate in aqueous TMAH of films spun from a 14% wt poly(norbornene-*alt*-maleic anhydride-*co*-acrylic acid) [P(NB/MA/AA17.5)] (17.5 mol % AA) in cyclohexanone after a month of storage at ambient room temperature was observed. Compositions resulting from 15 and 17.5% acrylic acid feeds (P(NB/MA/AA15) and P(NB/MA/AA17.5) respectively) display the most useful development behavior and have been studied in some detail.[14] In addition to acrylic acid, the incorporation of *tert*-butyl acrylate (TBA) proceeds in a predictable manner. While the tertiary and quaternary polymers possess thermal and optical properties and organic solubilities indistinguishable from P(NB/MA), they exhibit much better adhesion to polar substrates such as silicon wafers. The radical polymerization reaction is well behaved for methacrylate-derived repeat unit loadings ranging from 0 to 0.3 mole fraction. Figure 4a shows that there is no significant deviation from a 1:1 ratio of the NB:MA repeat units as the relative amount of acrylate repeat unit is increased up to a mole fraction of 0.3. This is strong evidence that the alternating structure of the NB and MA repeat units is not disrupted by inclusion of large quantities of acrylate monomer. Additionally, Figure 4b shows that incorporation of TBA units into the polymer is a simple linear function of the mole fraction of TBA units in the feed. Gel permeation chromatographic analysis of these materials gives clean mono-

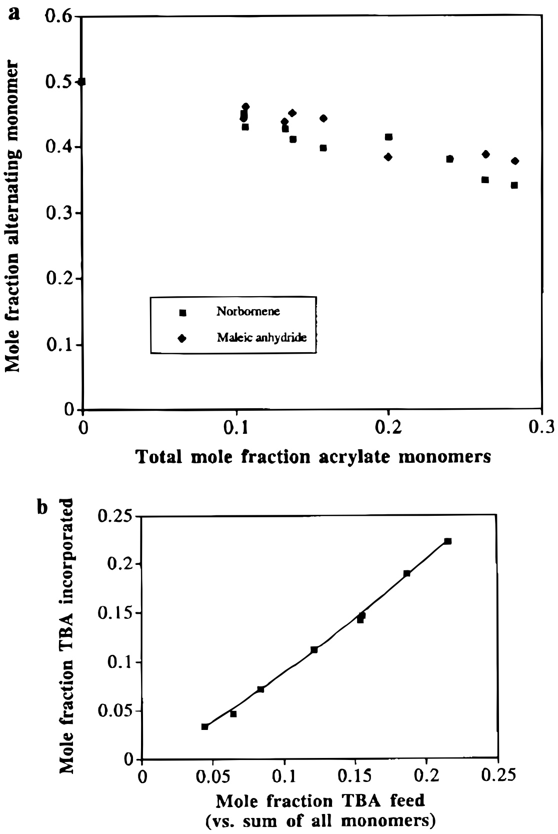
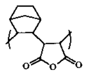
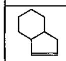
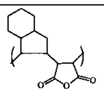
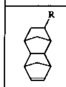
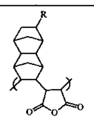
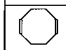
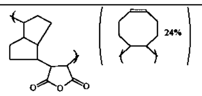
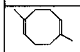
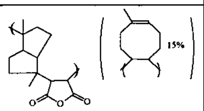
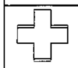
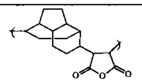
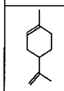
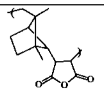


Figure 4. (a) "Doped" alternating copolymer compositions. (b) *tert*-Butyl acrylate incorporation into alternating copolymers.

Table 1. Olefin−Maleic Anhydride Alternating Copolymers Screened as 193 nm Matrix Resins

Olefin		Copolymer Structure	Comments	MW M_n, M_w, M_z (polydispersity)
	NB		60-76% yields[b]	NB/MA/AA15 $1.6X10^3$, $3.7X10^3$, $6.0X10^4$(2.34) NB/MA/AA20 $1.1X10^3$, $2.5X10^3$, $4.0X10^3$(2.24) NB/MA/TBA20 $4.1X10^3$, $7.2X10^3$, $1.1X10^3$(1.76) NB/MA/TBA20/AA20 $2.1X10^3$, $5.1X10^3$, $8.0X10^3$(2.48)
	DDPD		17% yield	$1.2X10^3$, $1.5X10^3$, $1.9X10^4$ (1.24)
	R=-H, CH_3		no reaction	NA
	COD		45% yield[b]	$2.8X10^3$, $5.8X10^3$, $8.5X10^3$(2.06)
	DMCOD		21% yield[b]	$4.7X10^3$, $8.8X10^3$, $8.5X10^3$(1.88)
	CDDT		cross-linked	NA
	LMN		cross-linked	NA

[a] All copolymer structures are idealized: actual regio- and stereochemistry of cyclic systems is very heterogeneous. In the case of NB, molecular weight characteristics for selected acrylate ter- and quaternary polymers are given in the table. [b] See Experimental Section. [c] As deternined by ^{1}H NMR.

modal peaks with a polydispersity of <2.5 regardless of acrylate loading (Table 1). Finally, thin films cast on quartz display excellent transparency at 248 and 193 nm (e.g. absorbance per micrometer of P(NB/MA/AA15) with 20% (wt) *tert*-butyl lithocholate are 0.05 and 0.27 AU/μm respectively; while the same formulation with 1% (wt) triphenylsulfonium triflate gives 0.10 and 0.40 AU/μm respectively).

Alternative Monomers. In order to explore the general usefulness of cycloolefin−maleic anhydride copolymers for 193 nm imaging applications, several cycloolefins were screened (Table 1). 5,6-Dihydrodicyclopentadiene (DDPD) copolymerizes with maleic anhydride in low yield (17%) under conditions analogous to the norbornene copolymerization. Assuming further optimization is successful, this copolymer may be of interest as a higher-carbon content analog of P(NB/MA). Tetracyclododecene (TCCD) and methyltetracyclododecene (MTCCD) failed to copolymerize with maleic anhydride under all concentration and temperature regimes tested. 1,5-Cyclooctadiene (COD) and 1,5-dimethyl-1,5-cyclooctadiene (DMCOD) produced fully soluble copolymers; however, 1,2- copolymerization competed significantly with cyclopolymerization. Limonene (LMN) and 1,5,9-cyclododecatriene (CDDT) copolymerized to form cross-linked powders that could be swollen but not redissolved in cyclohexanone and other solvents. Dicyclopentadiene,[15] methylenenorbornene,[16] and vinylnorbornene[16] are known to undergo combinations of 1:1 and 1:2 copolymerizations with maleic anhydride and were not examined here. Table 1 summarizes the molecular weight characteristics of those materials that yielded soluble polymer. As for the NB/MA copolymers, these materials give polymers with polydispersities lower than 2.5.

P(NB/MA) Functional Group Transformations. Of the potentially useful post-polymerization functionalizations of P(NB/MA), hydrolysis, alcoholysis (to yield half-esters), imidization, amidization, and reduction were explored briefly.

P(NB/MA) proved to be surprisingly resistant to hydrolysis, both in solution and as a thin film. Prolonged heating (60 h at 60 °C) of an aqueous acetone solution did not result in extensive hydrolysis. Thin films cast on Si desorbed in 0.262 N TMAH long before dissolution occurred. The fully hydrolyzed diacid can be prepared by vigorous stirring of a P(NB/MA) slurry in 25% TMAH for *ca.* 16 h followed by acidification. The diacid is soluble in most alcohols but insoluble in acetone, methyl ethyl ketone (MEK), and cyclohexanone. Thin films dissolve instantaneously in 0.262 N TMAH. The diacid reverts to the anhydride on heating: TGA indicates an onset temperature of *ca.* 90 °C; a *ca.* 5% weight loss (58% reversion) occurs between 100−150 °C (heating rate = 10 °C/min). Alcoholysis requires unexpectedly forcing conditions: P(NB/MA) in a methanol/dimethylsulfoxide solution undergoes *ca.* 40% conversion to the corresponding half-ester in 64 h at 60 °C as determined by ^{1}H NMR; analogous conditions using 2-propanol resulted in less than 5% conversion. Similar to the diacid, the methyl half-ester reverts to the anhydride on heating.

Reactions with amines to yield poly(amic acids) and poly(imides) proceed much more readily; slow addition of amines at room temperature was sufficient to convert P(NB/MA) quantitatively. Model studies indicated that imides are strongly absorbing chromophores at 193 nm (succinimide exhibits $e = 1 \times 10^4$ L/mol·cm in water); poly(imides) are thus unsuitable for 193 nm applications. As amines are potent imidization catalysts for amic acids,[17] primary amines cannot be used for functionalizing P(NB/MA), since imidization competes with amidization. *N*-Methylcyclohexylamine, a secondary amine, yielded a stable poly(amic acid) with acceptable transparency (absorbance = *ca.* 0.5 m^{-1} at 193 nm) and aqueous base solubility.

Finally, P(NB/MA) can be reduced to a poly(norborne-*alt*-*cis*-4-hydroxy-2-butenoic acid) using $NaBH_4$ or, in an alternative metal-ion free procedure, Me_4NBH_4. Poly(norborne-*alt*-*cis*-4-hydroxy-2-butenoic acid) can be isolated without lactonization, is soluble in aqueous base, displays excellent film-forming properties, and is thermally stable to at least 150 °C in the absence of acid. Lactonization and insolubilization occur readily in films at 100−120 °C using triphenylsulfonium triflate as a photoacid generator.

Dissolution Behavior. The latent water-solubilizing anhydride moieties in P(NB/MA) copolymers present both challenges and opportunities. As mentioned previously, they are remarkably hydrolytically stable and do not facilitate P(NB/MA) dissolution appreciably in aqueous TMAH. P(NB/MA/AA) dissolution in such media is similarly not dependent on anhydride hydrolysis; instead, it varies as a function of acrylic acid content. These findings suggest that the anhydrides remain predominantly latent (i.e., nonhydrolyzed) under the conditions employed (<120 s development time at room temperature in 0.262 N TMAH) or, conversely, that the developer, while basic enough to solubilize acidic functionalities as salts, lacks the reactivity to efficiently promote anhydride hydrolysis in the hydrophobic and sterically congested polymer. An alternative approach is to use modified developers containing nucleophilic additives capable of catalyzing anhydride hydrolysis. This latter approach presents several potential opportunities: (a) if successful, it may be applicable not only to 193 nm resins, but also to 248 nm resins containing similar latent functionalities such as acetoxystyrene residues; (b) it may present an alternative to the common, but environmentally unacceptable practice of using 2-propanol/water developer mixtures; and (c) it may influence development characteristics of resists in lithographically useful ways. Acylation catalysts, typically nucleophilic amines and imines that activate carboxylates by forming highly nucleophile-susceptible acyliminium intermediates, promote a wide variety of synthetically useful carboxylate transformations. Many are sufficiently water-soluble to evaluate as anhydride hydrolysis catalysts.

P(NB/MA/AA15), a terpolymer formulation whose dissolution rate is impracticably slow (780 Å/min at 20 °C) in 0.262 N TMAH, has proven useful in a preliminary evaluation of chemically active developers. Initial screening of imidazole, histidine, 1,2,4-triazole, 4-(dimethylamino)pyridine (DMAP), and guanidine demonstrated that imidazole and DMAP are potent dissolution-rate accelerants (Table 2). Dissolution rates were linear in all cases. Due to its combination of attractive properties (good rate acceleration, low cost, and low toxicity), imidazole was chosen for further study, even though DMAP appears to be a more potent accelerant. A concentration-dependence study reveals that P(NB/MA/AA15) dissolution rates are directly proportional to imidazole concentration and can be continuously varied by nearly an order of magnitude over a range of imidazole concentrations from 0 to 0.262 M (entries 7−9 in Table 2). The differing efficacies of imidazole and histidine may arise from neutralization of the TMAH developer: the imidazole substituent in histidine is unusually acidic (pK_a = 9.2 *vs.* imidazole pK_a = 14.5),[18a,b] apparently due to internal stabilization of the imidazolide anion by hydrogen bonding. Nevertheless, histidine-modified TMAH retains development activity slightly greater than that of TMAH itself. In contrast, 1,2,4-triazole (pK_a = 10.3)[18c] strongly attenuates dissolution, presumably by consuming TMAH to yield a catalytically inactive triazolide rather than an active histidine imidazolide. Guanidine appears to cross-link the matrix resin giving swelling instead of dissolution. Other comparison studies determined that surfactants play a small but significant role in accelerating dissolution. For instance, the dissolution rates of P(NB/MA/AA15) relative to that of this material in 0.262 N developer are as follows: 0.262 N (1.00), 0.131 N (0.54), and 0.131 N with 0.131 M imidazole (1.97). Addition of 200 ppm 3 M fluorochemical surfactant increases the relative dissolution rates of P(NB/MA/AA15) (0.262 N (1.19), 0.131 N (0.75), or 0.131 N with 0.131 M imidazole (1.97)).

Table 2. P(NB/MA/AA15) Dissolution Rates in the Presence of Potential Accelerants

entry	composition	relative rates[a]
1	0.131 N TMAH	1.0
2	0.131 N TMAH 0.131 N imidazole	3.76
3	0.131 N TMAH 0.131 N DMAP[b]	6.4
4	0.131 N TMAH 0.131 N 1,2,4-triazole	0
5	0.131M “buffered” guanidine[d]	*e*
6	0.262 N TMAH 0.131 N histidine[c]	1.32
7	0.262 N TMAH	1.85
8	0.262 N TMAH 0.131 N imidazole	7.46
9	0.262 N TMAH 0.262N imidazole	11.70

[a] Relative to absolute development rate for P(NB/MA/AA15) in 0.131 N TMAH. [b] 4-(Dimethylamino)pyridine. [c] One equivalent of TMAH required to neutralize histidine carboxylic acid. [d] A “buffered” 0.131 N guanidine solution prepared by mixing 100 mL 0.262 TMAH, 100 mL of water, and 2.360 g of guanidine carbonate. [e] Resins treated with this solution swelled instead of dissolving.

Another approach toward modifying the dissolution behavior of P(NB/MA/AA)-based resists is to use cholate-based dissolution inhibitors. Several simple monomeric cholate-based dissolution inhibitors have been examined such as *tert*-butyl deoxycholate (**1**), *tert*-butyl lithocholate (**2**) and *tert*-butyl 3-α-acetyllithocholate (**3**). Compound **2** is an effective dissolution inhibitor of P(NB/MA/AA) resins; a 25% (w/w) loading decreases dissolution rates by nearly an order of magnitude, independent of developer formulation (Table 3). Compound **3** behaves identically to **2** as a dissolution inhibitor; however, films containing **3** delaminate from Si much more readily, and these formulations were not examined in more detail. Lithocholic acid is a effective dissolution promoter: the P(NB/MA/AA15)/25% **2** three-component formulation has an ideal development selectivity of 42:1, assuming quantitative deprotection (entries 3 and 6, Table 3).

Lithographic Evaluation. Three strategies have been investigated to explore the utility of P(NB/MA) matrix resin chemistry for 193 nm lithographic applications. As shown in Figure 5, these are a two-component approach that utilizes a protected P(NB/MA/AA) polymer in conjunction with a photoacid generator (PAG), a three-component system using the parent acidic

Table 3. Dissolution Inhibition and Promotion by Cholate Derivatives

entry	composition of developer	additive[a]	relative rates[b]	relative rates[c]
1	0.131 N TMAH	**2** (12)	0.20	0.0533
2	0.131 N TMAH 0.131 N imidazole	**2** (12)	1.24	0.33
3	0.131 N TMAH	**2** (25)	0.13	0.346
4	0.131 N TMAH 0.131 N imidazole	**2** (25)	0.45	0.12[c]
5	0.131 N TMAH 0.131 N imidazole	**3** (25)	0.45	0.12[c]
6	0.131 N TMAH	LCA[d]	5.47	1.45

[a] Weight percent in parentheses. [b] Relative to absolute development rate for P(NB/MA/AA15) in 0.131 N TMAH. [c] Relative to absolute development rate for P(NB/MA/AA15) in 0.131 N TMAH/0.131 M imidazole. [d] Lithocholic acid; 21% (wt) corresponding to hypothetical complete acidolysis of **2** in a 25% (wt) formulation.

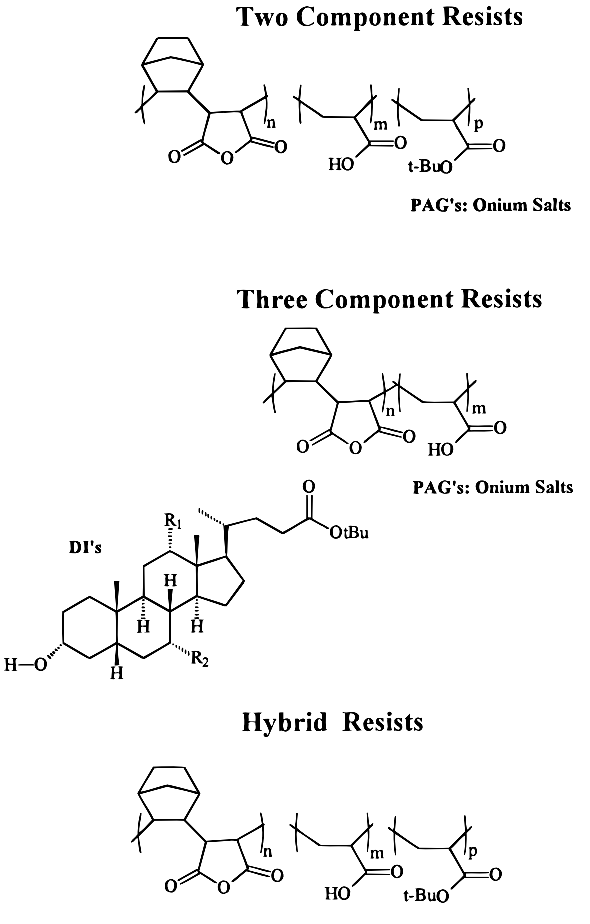


Figure 5. Resist systems evaluated based on P(NB/MA) polymer derivatives (R = H, OH) or in the case of oligomeric DI's an aliphatic diester moiety.[9b,c]

terpolymer, a dissolution inhibitor (DI), and a PAG, and a hybrid approach that uses both a DI and a partially protected matrix. Preliminary evaluations of these resists have been carried out at 248 nm using formulations that satisfy the transparency requirements for 193 nm. Of these, the discussion will be limited to the two-component system based on the P(NB/MA/AA15), and P(NB/MA/AA17.5) matrix resins (the former required imidazole-modified developers while the latter was compatible with standard aqueous base developer) and the three-component system based on poly(norbornene-*alt*-maleic anhydride-*co*-acrylic acid-*co*-*tert*-butyl acrylate) (both acrylate moieties at 20 mol % loading each) [P(NB/MA/AA20/TBA20)] matrix resins which are developable in standard aqueous base developer. The DIs were based on *tert*-butyl deoxycholate and *tert*-butyl lithocholate at loadings between 20 and 35% (w/w). Most experiments were carried out using triphenylsulfonium triflate (TPS-Tf) as PAG; triphenylsulfonium hexafluoroarsenate was used in some instances. Three-component resists were prepared in cyclohexanone while hybrid resists were prepared in propylene glycol methyl ether acetate (PGMEA).

Adhesion. P(NB/MA/AA17.5) formulations adhere to Si more strongly than those prepared from P(NB/MA/AA15). DIs have marked effects on adhesion as well: relatively hydrophilic **1** resulted in films which displayed good adhesion of high-resolution features; **2** exhibited some issues related to adhesion, especially at high loading (35% w/w).

Etching Studies. The relative reactive ion etching rates in a chlorine-based plasma (see experimental) compared to that of a conventional, novolac-based photoresist, Shipley 1811, were examined for a series of alternating alicyclic−maleic anhydride polymers [P(NB/MA), P(NB/MA/AA17.5), P(COD/MA), and P(DDPD/MA)}]; the relative rates established in this way were respectively 1.30, 1.37, 1.15, and 1.11 for the four materials examined. These results compare favorably with the needs of 193 nm lithographic patterning and show the general expected trend toward increased reactive ion etching resistance of materials with increased carbon/oxygen ratio and alicyclic content.[2]

Contrast. Both P(NB/MA/AA15) and P(NB/MA/AA17.5) display contrast factors (γ) ranging from 3 to 5.5 when formulated with DIs **1** or **2** (Table 4). Contrast factors do not appear to depend strongly on DI loading or on developer composition, although it appears that imidazole-modified developers provide higher contrast than aqueous TMAH.

Development Selectivity. Some dark development (development in the light unexposed region) occurs with these formulations regardless of DI. Increasing DI loading results in improved development selectivity; however, the development selectivities observed in exposed systems do not approach the ideal (42:1 at 25% loading) observed in model studies (entry 6, Table 3). Development selectivity is not discernibly correlated with DI composition or resist contrast.

PAG loading affects dose-response behavior as well. At high loadings (2.8% (w/w TBS−Tf), bimodal behavior is seen, with low doses producing the expected positive-tone behavior while high doses result in insoluble residues, apparently due to cross-linking of resist. As a result, only a narrow dose range exists for clearing the resist film (Figure 6). At lower PAG loadings (1.4%), this effect vanishes. This effect is probably caused by radical initiated cross-linking, stemming from radicals or radical cations generated by the onium salt. A similar onium salt loading related cross-linking effect[19] has been described for a resist formulated with poly(4-hydroxystyrene-*co*-styrene) and *tert*-butyl cholate.

Lithography. Scanning electron microscope (SEM) images of 0.35 μm line/space pattern (L/S) imaged with P(NB/MA/AA15)/20% **2**/TPS−AsF$_6$ films (entry 2, Table 4) show sloping sidewalls and line-thinning. In comparison increasing the loading of **2** (*tert*-butyl lithocholate) to 35% (entry 3, Table 4) results in much more vertical sidewalls. A similar loading effect is seen upon increasing the content of **1** (*tert*-butyl deoxycholate) from

Table 4. Lithographic Characteristics of Select P(NB/MA-acrylate)-Cholate Resists

entry	polymer	DI (wt % loading)[a]	PAG	clearing dose (mJ/cm^2)	contrast factor	development selectivity
1	P(NB/MA/AA15)[b]	**2** (20)	TPS−Tf	3.25	5.1	11
2	P(NB/MA/AA15)[b]	**2** (20)	TPS−AsF$_6$	3.5	3.8	
3	P(NB/MA/AA15)[b]	**2** (25)	TPS−AsF$_6$	3.0	5.5	28
4	P(NB/MA/AA17.5)[c]	**2** (25)	TPS−Tf	4.0	3.7	16−17
6	P(NB/MA/AA17.5)[c]	**1** (25)	TPS−Tf	5.0−6.0	4.1	14−18
8	P(NB/MA/AA20/TBA20)[d]	**2** (25)	DPI−Tf	28.5		46
9	P(NB/MA/AA20/TBA20)[d]	**1** (25)	DPI−Tf	17.5	2.7	22

[a] Solids basis. [b] Resist prepared in cyclohexanone and developed using 0.131 N TMAH/0.131 M imidazole. [c] Resist prepared in cyclohexanone and developed using ODP-262. [d] Resist prepared in PGMEA and developed using ODP-262.

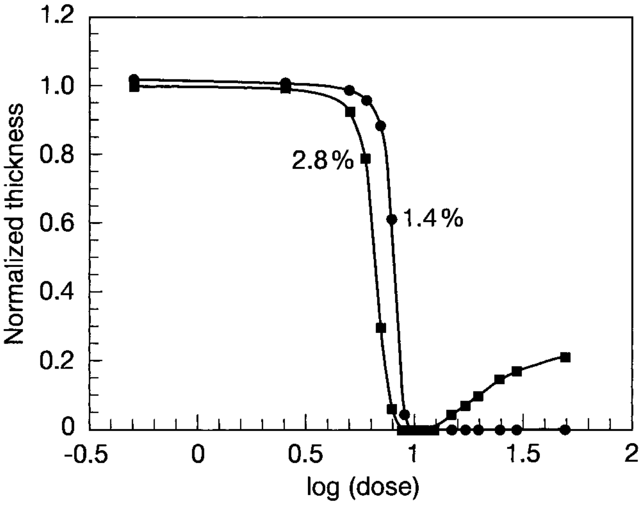


Figure 6. Development behavior of P(NB/MA/AA15)/20% **2** resist at high and low PAG loadings.

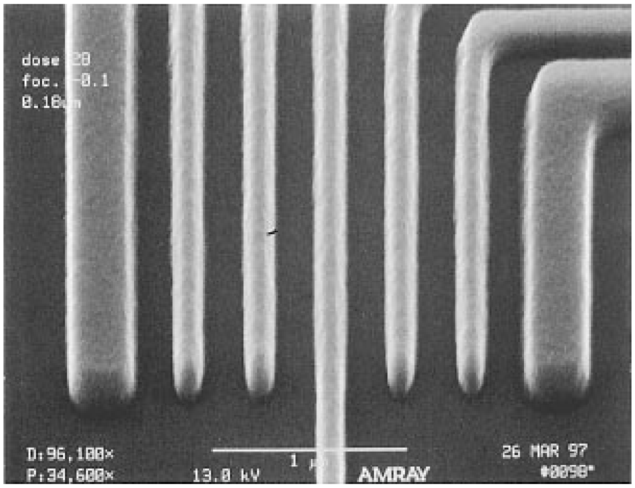


Figure 7. 0.18 μm L/S obtained using a hybrid resist formulation exposed at 193 nm with an ISI 193 nm stepper at a dose of 21 mJ/cm^2.

20 to 25 wt % in a P(NB/MA/AA17.5) resist matrix (entry 3, Table 4). However, line-thinning of L/S patterns appears to be more severe for formulations containing **2** rather than **1**.

Figure 7 shows an SEM image of 0.18 μm L/S obtained using a P(NB/MA/AA/TBA) formulation exposed at 193 nm. Note that use of this “hybrid” approach affords higher resolution patterns with a higher degree of precision and accuracy.

III. Conclusion

We have discovered a fundamentally new class of matrix resin applicable to imaging based on cycloolefin−maleic anhydride alternating copolymers. When formulated with cholate-based dissolution inhibitors and standard photoacid generators, these copolymers provide sensitive three-component resists that exhibit the potential for sub-0.25 μm imaging. The hydrolytic stability of the copolymers has provided an opportunity to explore new ideas for modifying aqueous developers with imidazole, an inexpensive, relatively nontoxic, and potent development accelerant.

This work demonstrates some of the challenges that recur frequently in designing 193 nm photoresists. As mentioned previously, the primary challenge in designing such materials involves balancing high alicyclic content for sufficient etching resistance with requisite materials properties, primarily adhesion and aqueous base solubility. Additional challenges arise from the general imperative that the resist display extremely reproducible high-resolution lithographic properties: specifically, this requires careful manipulation of a large number of physical properties that govern solubility, sensitivity, image fidelity, etc. Design principles governing different properties may not always work in concert; a functional resist design will, in the end, reflect multiple compromises and tradeoffs.

IV. Experimental Section

General Synthetic Procedures. Synthetic procedures were carried out using standard Schlenk-line techniques in oven-dried, Ar-purged glassware. Anhydrous solvents were purchased from standard sources and used as supplied. NMR analysis was performed using a Bruker AM-360 FT-spectrometer. Thermal analysis was carried out using a Perkin-Elmer DSC-7/TGA-7 thermal analysis system. UV−visible spectroscopy was conducted using a Hewlett-Packard Model 8452A UV−visible spectrophotometer whose dynamic range at 193 nm was monitored prior to resist absorbance measurements.

The repeating unit composition of the polymers was determined as follows. For polymers containing TBA, the first step is to determine the ratios of unreacted monomer in the solution after polymerization before workup. This is done by taking the ratio of the olefinic protons attributed to each type of unreacted monomer. Next, the TBA content of the recovered polymer is found by TGA. If the polymer yield is known, this allows the calculation of the total amount of reacted TBA. Subtraction from the starting amount of TBA gives the amount of TBA remaining after reaction. From this and the ratio of unreacted monomers, the amount of each monomer remaining can be found. Finally, if we know how much of each monomer was initially used, the amount incorporated into the polymer can be found. For poly(NB-*alt*-MA)-*co*-MA, which lacked TBA, the following was assumed. Since there is no discrimination between AA and TBA (Figure 4), it can be safely assumed that these two monomers have identical reactivity. Thus, a linear regression of the feed of TBA to its inclusion in the polymer was applied to incorporation of AA and used to estimate the composition of AA in the polymer. From this, the composition of the other monomers in the polymer was calculated in the manner described above.

Polymer Synthesis. P(NB/MA) Copolymer. (General example.) Norbornene (40.7 g; 432 mmol) was vacuum-transferred into a dry 500 mL Schlenk flask equipped with two PTFE-stoppered inlet valves and an efficient stir bar. Freshly sublimed maleic anhydride (42.4 g; 432 mmol), AIBN (0.706 g; 1.0 mol %), and THF (60 mL) were added under positive argon pressure. The mixture was degassed by three freeze−pump−thaw cycles, sealed, and immersed in an oil bath at 65 °C for 24 h. Upon cooling, the mixture was precipitated into five volumes of diethyl ether and filtered to collect the polymer. The solid was redissolved in 100 mL of acetone and precipitated into five volumes of diethyl ether. This process was repeated three times in total. The polymer was collected in the final filtration and dried at 50 °C *in vacuo* to yield 60.89 g (73%) of copolymer: ^{1}H NMR (DMSO-d_6) δ (ppm) (all very broad) 1.20, 1.35, 1.52, 2.25, 2.35, 3.15; ^{13}C NMR (DMSO-d_6) δ (ppm) (all very broad) 23.5, 28.1, 30.3, 34.0, 36.4, 39.7, 45.5, 47.0, 172.8.

P(DDPD/MA) Copolymer. 5,6-Dihydrodicyclopentadiene (10.0 g; 75 mmol) was vacuum-transferred into a dry 100 mL Schlenk flask equipped with two PTFE-stoppered inlet valves and an efficient stir bar. Freshly sublimed maleic anhydride (7.31 g; 75 mmol), AIBN (0.122 g; 1.0 mol %), and THF (17 mL) were added under positive argon pressure. The mixture was degassed by three freeze−pump−thaw cycles, sealed, and immersed in an oil bath at 65 °C for 24 h. Upon cooling, the mixture was added into five volumes of diethyl ether and filtered to collect the polymer. The solid was redissolved in 25 mL of methyl ethyl ketone and precipitated into five volumes of diethyl ether. This process was repeated three times in total. The polymer was collected in the final filtration and dried at 50 °C *in vacuo* to yield 2.92 g (17%) of copolymer: ^{1}H NMR (DMSO-d_6) δ (ppm) (all very broad) 1.28, 1.48, 1.84, 2.03, 2.26, 2.5−4.0 (multiple resonances), 3.32; ^{13}C NMR (DMSO-d_6) δ (ppm)(all very broad) 22.3, 25.4, 29−35 (multiple resonances), 38−50 (multiple resonances), 172.2.

P(COD/MA) Copolymer. 1,5-Cyclooctadiene (11.0 g; 102 mmol) was vacuum-transferred into a dry 100 mL Schlenk flask equipped with two PTFE-stoppered inlet valves and an efficient stir bar. Freshly sublimed maleic anhydride (10.0 g; 102 mmol), AIBN (0.164 g; 1.0 mol %), and dioxane (30 mL) were added under positive argon pressure. The mixture was degassed by three freeze−pump−thaw cycles, sealed, and immersed in an oil bath at 65 °C for 24 h. Upon cooling, dioxane was removed under vacuum, the polymer was redissolved in methyl ethyl ketone, and the mixture was precipitated into five volumes of diethyl ether and filtered to collect the polymer. The solid was redissolved in 25 mL of methyl ethyl ketone and precipitated into five volumes of diethyl ether. This process was repeated three times in total. The polymer was collected in the final filtration and dried at 50 °C *in vacuo* to yield 9.40 g (45%) of copolymer: ^{1}H NMR (DMSO-d_6) δ (ppm) (all very broad) 1.20, 1.43, 1.82, 1.89, 2.30, 2.8−4.0 (multiple resonances), 2.96, 3.02, 5.60; ^{13}C NMR (DMSO-d_6) δ (ppm) (all very broad) 21−31 (multiple resonances), 31.0, 32.7, 46.7, 48.3, 129.5, 173.0.

P(DMCOD/MA) Copolymer. 1,5-Dimethyl-1,5-cyclooctadiene (13.9 g; 102 mmol) was vacuum-transferred into a dry 100 mL Schlenk flask equipped with two PTFE-stoppered inlet valves and an efficient stir bar. Freshly sublimed maleic anhydride (10.0 g; 102 mmol), AIBN (0.164 g; 1.0 mol %), and dioxane (30 mL) were added under positive argon pressure. The mixture was degassed by three freeze−pump−thaw cycles, sealed, and immersed in an oil bath at 65 °C for 24 h. Upon cooling, the mixture was precipitated into five volumes of diethyl ether and filtered to collect the polymer. The solid was redissolved in 25 mL of methyl ethyl ketone and precipitated into five volumes of diethyl ether. This process was repeated three times in total. The polymer was collected in the final filtration and dried at 50 °C *in vacuo* to yield 5.03 g (21%) of copolymer: ^{1}H NMR (DMSO-d_6) δ (ppm) (all very broad) 0.88, 0.99, 1.47, 1.63, 1.8−2.5 (broad shoulder), 2.7−4.0 (multiple resonances), 2.98, 5.40; ^{13}C NMR (DMSO-d_6) δ (ppm) (all very broad) 17.2, 19.2, 23.5, 25.2, 27−40 (multiple resonances), 44.6, 48.7, 52.4, 55.0, 125.0, 134.0, 172.4.

P(NB/MA/AA15) Terpolymer (General Example of Terpolymer Synthesis). Norbornene (41.7 g; 443 mmol) was vacuum-transferred into a dry 500 mL Schlenk flask equipped with two PTFE-stoppered inlet valves and an efficient stir bar. Freshly sublimed maleic anhydride (36.90 g; 376 mmol), distilled acrylic acid (4.56 mL; 67 mmol), AIBN (0.722 g; 1.0 mol %), and THF (100 mL) were added under positive argon pressure. The mixture was degassed by three freeze−pump−thaw cycles, sealed, and immersed in an oil bath at 65 °C for 24 h. Upon cooling, the mixture was precipitated into five volumes of diethyl ether and filtered to collect the polymer. The solid was redissolved in 100 mL of acetone and precipitated into five volumes of diethyl ether. This process was repeated three times in total. The polymer was collected in the final filtration and dried at 50 °C *in vacuo* to yield 42.21 g of terpolymer: ^{1}H NMR (DMSO-d_6) δ (ppm) (all very broad) 1.20, 1.36, 1.52, 2.26, 2.36, 3.10, 3.31; ^{13}C NMR (DMSO-d_6) δ (ppm) (all very broad) 22.6, 28.1, 30.5, 36.1, 39.7, 45.5, 47.0, 173.0, 174.1.

P(NB/MA/TBA20/AA20) Polymer. This polymer was prepared in the same way as for the P(NB/MA/AA) resins using the following quantities: 16.41 g of NB (174 mmol), 17.09 g of MA (174 mmol), 2.39 mL of AA (2.59 g, 34.8 mmol), 5.10 mL of TBA (4.46 g, 34.8 mmol), 0.285 g of AIBN (1.74 mmol), and 40 mL of THF 18 h at 60 °C. In this manner, 15.97 g (39% yield) of polymer was recovered after precipitation into ether, filtration, and drying.

Dissolution Inhibitor Synthesis. *tert*-Butyl Lithocholate (2). A 500 mL flask equipped with a PTFE stopcock and PTFE-stoppered gas inlet valve was charged with 30.0 g (79.7 mmol) of lithocholic acid and a stir bar. The flask and contents were dried under vacuum at 50 °C overnight. Following an Ar purge, 200 mL of dry THF was added under an Ar backflow. The solution was chilled to 0 °C, and 28.3 mL (200 mmol) of trifluoroacetic anhydride was added dropwise. The mixture was allowed to warm to room temperature over the course of 90 min. The reaction was recooled to 0 °C, and 38.2 mL (400 mmol) of dry *tert*-butyl alcohol was added dropwise. The reaction was stirred at 0 °C under argon for 10 h. While the reaction mixture was maintained at 0 °C, 65 mL (0.6 mol) of concentrated aqueous NH_4OH was added to the mixture. Following addition, the mixture was maintained at 0 °C for 24 h. The flask contents were poured into a separatory funnel containing 300 mL each of ether and water; the ethereal layer was washed four times with 200 mL water, concentrated, and dried *in vacuo* to give a solid which was recrystallized from aqueous acetone to yield 32.8 g of **2** (75.8 mmol; 95% yield): ^{1}H NMR ($CDCl_3$) δ (ppm) 0.62 (s, 3 H), 0.88 (d, J not resolved, 3 H), 0.89 (s, 3 H), 0.94−1.86 (multiple resonances, 25 H), 1.42 (s, 9 H), 1.89 (m, 1 H), 2.11 (m, 1 H), 2.21 (m, 1 H), 3.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 12.0, 18.3, 20.8, 23.3, 24.2, 26.4, 27.2, 28.10, 28.15, 30.5, 31.0, 32.5, 34.6, 35.25, 35.35, 35.8, 36.4, 40.2, 40.4, 42.1, 42.7, 56.0, 56.5, 71.8, 79.8, 173.7.

***tert*-Butyl Deoxycholate (1).** A 500 mL flask equipped with a PTFE stopcock and PTFE-stoppered gas inlet valve was charged with 10.0 g (25.5 mmol) of deoxycholic acid and a stir bar. The flask and contents were dried under vacuum at 50 °C overnight. Following an Ar purge, 200 mL of dry THF was added under an Ar backflow. The solution was chilled to 0 °C, and 30 mL (212 mmol) of trifluoroacetic anhydride was added dropwise. The mixture was allowed to warm to room temperature over the course of 90 min. The reaction was recooled to 0 °C and 60 mL (630 mmol) dry *tert*-butyl alcohol was added dropwise. The reaction was stirred at 0 °C under argon for 10 h. While the reaction mixture was maintained at 0 °C, 42 mL (0.4 mol) of concentrated aqueous NH_4OH was added to the mixture. Following addition, the mixture was maintained at 0 °C for 24 h. The flask contents were poured into a separatory funnel containing 150 mL of ether and 400 mL of water; the ethereal layer was washed three times with 200 mL of water, concentrated, and dried *in vacuo* to give an oil: NMR analysis indicated an approximately 1:1 mixture of **1** and *tert*-butyl-12a-trifluoroacetyl deoxycholate. The mixture was redissolved in 100 mL of THF, cooled to 0 °C, treated with 10 mL of concentrated aqueous NH_4OH, allowed to warm to room temperature, and stirred for 6 h. NMR analysis indicated complete hydrolysis of the trifluoroacetate at this point, and the mixture was worked up as before to yield a colorless solid. Compound **1** does not appear to be crystalline and was prepared for further use by lyophilization from dioxane to give

7.80 g (17.4 mmol; 68%) of a powder which was pure by ^{1}H and ^{13}C NMR: ^{1}H NMR (CDCl$_3$) δ (ppm) 0.64 (s, 3 H), 0.88 (s, 3 H), 0.93 (d, J = 6.4 Hz, 3 H), 1.00−1.82 (multiple resonances, 24 H), 1.41 (s, 9 H), 2.12 (m, 1 H), 2.23 (m, 1 H), 3.58 (m, 1 H), 3.96 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ (ppm) 12.7, 17.3, 23.1, 23.6, 26.1, 27.1, 27.4, 28.1, 28.6, 30.4, 30.9, 32.6, 33.6, 34.1, 35.0, 35.2, 36.0, 36.4, 42.0, 46.5, 47.4, 48.2, 71.7, 73.1, 79.9, 173.7.

Development Studies. General Experimental Procedures. P(NB/MA), P(NB/MA/AA), and P(NB/MA/AA/TBA) films were spun on HMDS-primed Si wafers from 0.2- or 0.45-μm filtered cyclohexanone solutions. Concentrations in the range of 11−14% (w/w) yielded 0.7−1.0 *m*m films at 2000 rpm. Film thicknesses were determined using a Dektak^3 surface profilometer or a Nanometrics Nanospec/AFT film thickness gauge calibrated relative to Dektak measurements. Prior to development, films were baked at 120 °C for 120 s to ensure consistent solvent evaporation and film annealing. Following development, films were rinsed with copious amounts of water, then baked at 120 °C for 60 s to drive off adsorbed water. Modified developers were prepared from commercially available 0.262 N TMAH developer (OCG OPD-262) and used immediately. In most instances, time−course measurements were made; averaged development rates from these measurements are reported in the text and in Tables 2 and 3.

Lithographic Evaluation. Resist formulations were prepared in cyclohexanone and contained 11−14% w/w copolymer, depending on exact formulation (PGMEA for hybrid formulations). The resists were passed through 0.2 or 0.45 *m*m PTFE filter membranes prior to casting. The 0.7−0.9 μm films were cast on HMDS-primed Si wafers at 2000 rpm and annealed for 60 s at 120 °C prior to exposure. Following exposure, films were baked at 120 °C for 120 s. P(NB/MA/AA15) films were developed in 0.131 N TMAH/ 0.131 M imidazole for 120 s. P(NB/MA/AA17.5) films were developed in 0.262 N TMAH (OPD-262 or OPD-4262.) Development times ranged from 60 s (formulated with **1**) to 180 s (formulated with **3**). Contrast curves were plotted according to the conventions outlined in the literature[20] to obtain contrast (γ_p) which is defined as $[\log(D_p/D_p^o)]^{-1}$ where D_p and D_p^o are respectively the doses at which the irradiated resist area achieves full dissolution or first starts to undergo dissolution by action of developer.

The etching studies were done on a Lucas Labs 9410 Vortex Tool equipped with a Helicon source. The etching measurements were done with a Cl$_2$ pressure of 2.5 Torr at a flow of 80 cm^3/s with a chuck power of 50 W and an etch source power of 2500 W at a temperature of 23 °C for 60 s. Substrates for etching were spun onto 6" silicon wafers. Shipley HB1811—a commercial Novolak/Diazonapththoquinone resist (Shipley Co) commonly employed in lithographic manufacturing— was used as a reference. Hard baked films of HB1811 (2 min 250 °C) gave an etch rate of 25.2 A/s. All etching results reported are given relative to the etch rate of Shipley HB1811.

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