Photoresists with Reduced Environmental Impact: Water-Soluble Resists Based on Photo-Cross-Linking of a Sugar-Containing Polymethacrylate

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Received August 31, 1998; Revised Manuscript Received November 7, 1998

ABSTRACT: A family of water-soluble, negative-tone, high-resolution, chemically amplified photoresists based on partially or fully deprotected poly(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose) is described. Both the molecular weight of the parent ketal-protected polymer and the extent of its deprotection to a water-soluble polymer containing 3-*O*-methacryloyl-D-glucopyranose repeat units must be carefully controlled to provide good coating and imaging properties. The two ketal protecting groups of the poly(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) have different reactivity, and their complete removal requires long reaction times under hydrolytic conditions. The detailed deprotection chemistry of the polymer is readily understood through model studies with the fully and partially protected analogues of the polymer pendant groups: 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and 1,2-isopropylidene-α-D-glucopyranose. When combined with a water-soluble photochemical precursor of acid such as (4-methoxyphenyl)dimethylsulfonium trifluoromethanesulfonate, films of the deprotected or partially deprotected poly(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose) undergo acid-catalyzed cross-linking. The enhanced performance of the partially deprotected polymers over that of poly(3-*O*-methacryloyl-D-glucopyranose) suggests that the presence of remaining hydrophobic groups that afford water dispersibility rather than full solubility may be key to their performance. Imaged negative-tone features as small as 0.2 μm are obtained with these materials that have sensitivities of ca. 30 mJ/cm^2 with wholly aqueous casting and processing.

Introduction

Photopolymers, used in applications ranging from state-of-the-art semiconductor devices to lower resolution circuit boards, flat-panel displays, or antireflective coatings, have traditionally been cast from organic solvents and developed in solvents or aqueous solutions containing organic bases.[1] We have recently initiated a study of environmentally enhanced photopolymers that may be both cast and developed in pure water only.[2] With these novel designs, organic solvents are no longer necessary, and there is no need for aqueous base developers, an approach that could alleviate a number of concerns about the industrial use of organic solvents and strongly basic solutions within microelectronic facilities.

Chemically amplified[1,3,4] approaches to completely water-soluble resists[2,5] have been described in the literature. These materials incorporate water-soluble cationically active matrix resins with water-soluble or -dispersible[2,5,6] photoacid generators.[7] The matrix resin is cross-linked through processes catalyzed by the photochemically produced strong acid[7] during a subsequent thermal baking step. One system investigated in our laboratories was a family of negative-tone resists based on the acid-catalyzed cross-linking of poly(methyl methoxy[(1-oxo-2-propenyl)amino]acetate), also known as poly(methyl acrylamidoglycolate methyl ether) or poly(MAGME), with diols.[2a,b] Another interesting family of materials reported by Vekselman and Darling[5] incorporates polymers containing repeat units of maleic acid, where the initially water-soluble vicinal carboxylic acid group is converted under acidic catalysis to hydrophobic cyclic anhydride moieties. Both of these materials were cast from and developed in water alone to afford negative-tone images. However, resolutions below 1 μm are reportedly difficult to achieve.[2,5]

The resolution limits that frequently affect systems such as the poly(methyl methoxy[(1-oxo-2-propenyl)-amino]acetate) and other families of resists are usually attributable to the swelling of features during aqueous development. Any design functioning through cross-linking and utilizing the same solvent for both casting and developing is likely to encounter similar difficulties with swelling. The cross-linked regions typically retain a large degree of affinity for the developer, rapidly becoming swollen by immersion in the solvent.[3e] The material reported by Vekselman and Darling[5] should be able to resolve submicron features as it functions through a non-cross-linking change of polarity.[8]

Polymers containing sugar moieties attached to a suitable backbone[9−14] have been reported. These carbohydrate-containing polymers include poly(2-deoxy-2-methacrylamido-D-glucopyranose),[9,10] poly(2-acrylamido-2-deoxy-D-glucopyranose),[11] poly(1-acrylamido-1-deoxy-D-glucitol),[11] poly(1-deoxy-1-methacrylamido-D-glucitol),[11] poly(1-deoxy-1-methacrylamidomaltitol),[11] poly(sucrose-1′-methacrylate),[12] poly(1-*O*-methacryloyl-D-galactopy-

10.1021/ma981372j CCC: $18.00

ranose),[12] poly(6-*O*-acryloyl-D-galactopyranose),[13] poly(6-*O*-methacryloyl-D-galactopyranose),[10] poly(1-*O*-methacryloyl-D-glucopyranose),[10] poly(3-*O*-methacryloyl-D-glucopyranose),[14] and poly(6-*O*-methacryloyl-D-glucopyranose).[10] All of these materials are soluble or dispersible in pure water.

Sugars readily undergo a number of interesting acid-catalyzed reactions, some of which might be exploited for use in the design of water-soluble negative-tone resist materials. For example, acid-catalyzed dehydration occurs[15] with the loss of three molecules of water to afford furaldehydes. This chemistry was exploited by Lee and Fréchet[16] for use in a three-component chemically amplified resist incorporating D-xylose or α-D-glucose and triphenylsulfonium hexafluoroantimonate (a photoacid generator) in a poly(4-hydroxystyrene) matrix in 2-methoxyethanol. The photoliberated acid catalyzes the dehydration of the sugars to furaldehydes, which then cationically cross-link the poly(4-hydroxystyrene) matrix at low doses of deep-UV irradiation.[16]

Under acid catalysis, sugars can also form glycosidic linkages. This acetal linkage is readily formed by reaction of a sugar hemiacetal with a hydroxyl group from another sugar molecule. Wolfrom and co-workers[17] have investigated the condensation products formed from α-D-glucose under acidic conditions. In addition to furaldehydes and other products, 6-*O*-disaccharides joined by a glycosidic linkage at the primary C6 alcohol were isolated.[17]

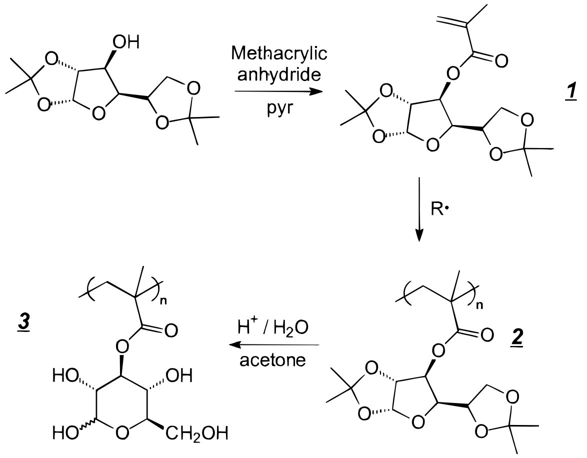
Polymers containing pendant sugar moieties should also be prone to these acid-catalyzed reactions, leading to cross-linked image formation. Of all of the polymers previously mentioned, only a few, such as poly(6-*O*-methacryloyl-D-glucofuranose), would be able to undergo dehydration to afford pendant furaldehydes. However, all of the listed sugar-containing polymers would be cross-linkable through glycoside formation. This chemistry, termed "acid-reversion", is briefly mentioned by Kimura and Hirai[14d] as a possible cause for the cross-linking reactions observed during the acid-catalyzed deprotection of poly(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose).

We have now investigated water-soluble polymers containing pendant sugars as novel environmentally enhanced, chemically amplified, negative-tone resist materials, to be cast from and developed in water alone. Poly(3-*O*-methacryloyl-D-glucopyranose)[14a−c] (**3**), prepared through the deprotection of poly(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose)[14] (**2**) (Scheme 1), was selected for this study to be used in combination with a water-soluble onium salt as a negative-tone resist.

Experimental Section

Materials. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (diacetone-D-glucose), 1-dodecanethiol (DT), 1-methoxy-4-(methylthio)benzene, silver trifluoromethanesulfonate, and iodomethane (Aldrich) were used as received. Propanoyl chloride (Acros) was distilled prior to use. Pyridine (Fisher) was dried over KOH and distilled onto molecular sieves. Toluene (Fisher) was distilled over CaH_2. 2,2′-Azobisisobutyronitrile [AIBN] (Aldrich) was recrystallized from methanol before use. Triphenylsulfonium hexafluoroantimonate [TPSHFA] (IBM) was used without further purification. Weakly basic Amberlite IR-45 beads (Mallinckrodt) were washed with 0.5 M NaOH and rinsed until neutral with deionized water. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose (**1**) was prepared as previously described.[14a−c]

Scheme 1



Instruments and Equipment. 1D nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300 or a Bruker DRX500 spectrometer. 2D TOCSY spectra were acquired on a Bruker DRX500 spectrometer with 2048 × 128 complex points and 4500 Hz spectral width for two scans per t1 increment. 2D HMQC spectra were acquired on a Bruker DRX500 spectrometer with 2048 × 128 complex points and 4500 Hz (^1H) and 25 000 Hz (^{13}C) spectral widths for four scans per t1 increment. Shifts for NMR spectra are reported in ppm relative to TMS or to the chemical shift of the solvent. Infrared spectra were recorded on a Mattson Genesis II Fourier transform spectrometer using KBr powder, with a Pike diffuse reflectance accessory. A Hewlett-Packard 8452A diode array spectrophotometer was used to obtain UV spectra of dilute solutions and also films cast on quartz wafers. Differential scanning calorimetry (DSC) was performed on a Seiko Exstar6000 system at 10 °C/min. All reported glass transition temperatures were gathered on the second heating scan and are reported as the midpoint of the inflection tangent. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Melting points are uncorrected.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC). Water-soluble polymers were analyzed on a system consisting of a Waters M510 pump, a Rheodyne injector, and a M410 Waters refractive index detector. Three columns were connected in series: Suprema Guard (Polymer Standards Service (PSS), 20 μm), Suprema 30 (PSS, 10 μm), and Suprema 1000 (PSS, 10 μm). The mobile phase was a solution comprising 10 vol % acetonitrile in 90 vol % aqueous 10 mM ammonium chloride buffered to pH 9 with Borax, at a flow rate of 0.8 mL/min at 30 °C. The relative molecular weights were calculated using a calibration curve constructed from 15 narrow polydispersity PEG/PEO standards (PSS). Water-insoluble polymers were analyzed on a Waters 150-CV using the built-in refractive index detector. Four 5 μm PL gel columns (100 Å, 100 Å, 500 Å, and mixed bed C) were connected in series with THF as the mobile phase at a flow rate of 1 mL/min at 45 °C. Relative molecular weights were calculated using a calibration curve constructed from 16 narrow polydispersity polystyrene standards (Polymer Laboratories).

Coating was performed either on a Headway spinner or on an MTI Flexifab automated coating track. Film thickness measurements were performed using either a Tencor Alphastep 200 profilometer or a Prometrix SM300 film thickness mapper. Cauchy parameters for the Prometrix were determined using a Woollam variable angle scanning ellipsometer.

Initial imaging experiments were carried out using an Oriel 68811 power supply coupled to an Oriel deep-UV illumination system fitted with a 500 W HgXe lamp and an exposure timer. Photon flux was measured using an Oriel Merlin radiometer equipped with a silicon detector head. The output of the mercury lamp was filtered through a 254 nm narrow bandwidth filter from Oriel Corp. Final patterning experiments

Table 1. Effect of Chain Transfer Agents upon Polymers of 1

sample	AIBN (wt %)	CCl_4 (mol %)	DT (mol %)	M_n ($\times10^{-3}$)	M_w ($\times10^{-3}$)	M_w/M_n	T_g (°C)[a]	yield (%)[b]
2a	1.00			163	622	3.81	168	93
2b	1.00	1.87		123	356	2.79	167	83
2c	1.00	5.34		134	305	2.28	167	75
2d	1.00	8.54		92.4	225	2.44	167	70
2e	1.00		1.05	28.1	53.8	1.91	161	83
2f	1.00		2.72	14.2	20.2	1.42	157	40
2g	1.00		5.19	9.46	12.4	1.32	155	33
2h	2.00		2.70	7.07	15.4	2.18	147	87

[a] As determined by DSC. [b] All polymerizations were performed at 2.63 M concentration in dry toluene at 65 °C for 24 h.

Table 2. Poly(1,2:5,6-diisopropylidene-3-*O*-methacryloyl-α-D-glucofuranose) Deprotection[a]

sample	reflux time (h)[b]	deprotection (%)[c]	M_n ($\times10^{-3}$)	M_w ($\times10^{-3}$)
3a	25	~100	8.7	23.7
3b	15	~95	3.7	11.1
3c	2	~70	5.4	8.1

[a] Polymer **2h** used in all cases. [b] Time refluxed after attaining water solubility during deprotection reaction. [c] Determined from ^{1}H NMR.

Table 3. Resists Containing Polymers with Pendant Sugars

resist	polymer	casting solvent	PAG[a]	developer	sensitivity (mJ/cm^2)[b]	γ[c]
A	**2h**	PGMEA	TPSHFA	acetone	20	25
B	**3a**	water	**6**	water	110	6
C	**3b**	water	**6**	water	45	10
D	**3c**	water	**6**	water	30	9

[a] Photoacid generator. [b] All films were heated for 2 min at 110 °C after exposure to 254 nm. [c] Contrasts determined from the slope of the sensitivity curves.

were performed on an Integrated Solutions XLS 248 nm stepper with 0.53 lens numerical aperture. The illuminator type was conventional with 0.74 σ. All exposures were performed with a 4× binary mask.

Etch data on resist D were gathered on a Lam TCP 9400 prototype etcher with 300 W power and 150 sccm of HBr, 50 sccm of Cl_2 gas mix for 60 s and directly compared to films of commercially available resists APEX-E and SPR510L. Scanning electron microscopy (SEM) was performed with a Leo 1550 operating at 3 kV. Samples were coated with 15 Å of Au/Pd prior to examination on the SEM.

Resist Formulation and Processing. Resists were prepared either in deionized water or in 1-methoxy-2-propyl acetate, also known as propylene glycol methyl ether acetate or PGMEA, with ca. 20 wt % solids. Specific resist compositions are detailed in Table 3. Solution viscosities were varied through the addition of more solvent, as needed, to achieve 0.7 μm film thickness after casting onto silicon or quartz wafers at 3000 rpm and a hard contact postapply "bake" (PAB) or heating step of 3 min at 120 °C. Resist solutions were filtered through 0.45 μm Gelman GHP Acrodisc filters. Prior to coating, silicon wafers either were cleaned with a mixture of 70% concentrated H_2SO_4 and 30% H_2O_2 (30% in water) at 120 °C for 10 min followed by 5 min in boiling ultrapure water or were allowed to form thick oxide layers through thermal treatment. No priming treatment was used as this was found to have an adverse effect on adhesion. All formulations were found to give excellent films. A hard contact postexposure "bake" (PEB) or heating step of 2 min at 110 °C was used prior to development for 30 s in pure water or in acetone.

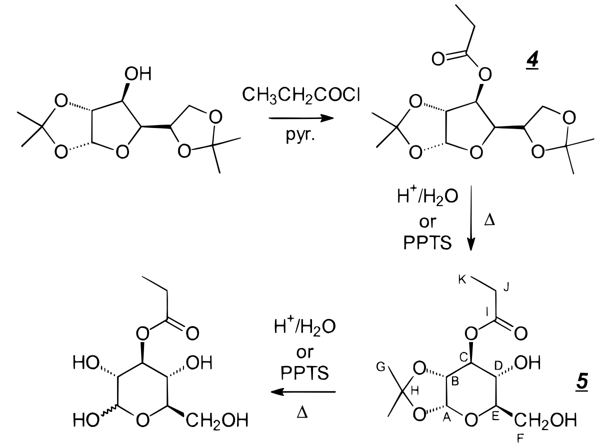
Preparation of Poly(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose)[14a−c] (2h). The monomer, **1**[14a−c] (17.20 g, 52.38 mmol), was dissolved in dry toluene (17.20 g) under nitrogen. AIBN (0.3440 g, 2.095 mmol) and DT (0.2880 g, 1.423 mmol) were added, and the reaction was heated to 65 °C for 20 h. The polymer solution was diluted with tetrahydrofuran (THF) and twice precipitated into methanol. After filtration and drying in vacuo, 14.87 g of a white powder was obtained (86%). GPC: $M_w = 15\,400$, $M_w/M_n = 2.18$. Tg (DSC): 147 °C. ^{1}H NMR ($CDCl_3$): δ 6.0−5.7 (br, 1H), 5.0−4.5 (br, 2H), 4.4−3.8 (br, 4H), and 2.0−0.8 (br, 17H) ppm. ^{13}C NMR ($CDCl_3$): δ 177, 114, 110, 105, 82, 80, 78, 72, 67, 46, 27, 26, 25, and 18 ppm. IR (KBr): 2292, 1738, 1384, 1374, 1258, 1219, 1165, 1076, 1024, 845, 639 cm^{-1}.

Preparation of Poly(3-*O*-methacryloyl-D-glucopyranose) (3a). Polymer **2h** (10.0 g) was dissolved in 750 mL of acetone. A 2 M solution of sulfuric acid (70 mL) was slowly added with rapid stirring, causing the solution to become opaque. The solution was heated to reflux until it became clear. Aliquots of water (30 mL) were added, each causing the solution to become cloudy. The solution was allowed to clarify between each addition. When the addition of further aliquots did not cause clouding, the acetone was removed under reduced pressure, and the solution was allowed to reflux for 25 h. After cooling and neutralization with Amberlite IR-45 basic beads, most of the water was removed under reduced pressure. The concentrated solution was precipitated into acetone. After filtration and drying in vacuo, 6.5 g of a white powder was obtained (86%). T_g (DSC): polymer decomposes before any transition is observed. GPC: $M_w = 23\,700$, $M_w/M_n = 2.73$. ^{1}H NMR (D_2O): δ 5.2 (br, 1H), 4.0−3.4 (br, 6H), 2.3−1.9 (br, 2H), and 1.5−1.0 ppm (br, 3H). ^{13}C NMR (D_2O + DMSO-d_6): δ 178, 94, 91, 76, 74, 71, 66, 59, 44, and 16 ppm. IR (KBr): 3400, 2947, 1718, 1650, 1457, 1260, 1176, 1086 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_7$ (based on repeat unit): C, 48.39; H, 6.50. Found: C, 48.57; H, 6.94.

Preparation of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-propionyl-α-D-glucofuranose[18] (4). A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2.50 g, 9.60 mmol) and dry pyridine (1.00 mL, 12.4 mmol) in dry THF (5 mL) was cooled to 0 °C under nitrogen. Propanoyl chloride (1.00 mL, 11.5 mmol) was added dropwise. After the addition was completed, the reaction was allowed to warm to ambient temperature. After stirring for 4 h, water (25 mL) was added to quench the reaction. Following extraction of the aqueous phase with petroleum ether, the organic extracts were washed with 3% NaOH, 0.5 M HCl, water, and finally brine. The organic phase was dried over $MgSO_4$, and solvents were then removed under reduced pressure. The viscous yellow oil was filtered through a short plug of silica gel (eluent = 15% ethyl acetate in hexane) and then purified via distillation in vacuo to afford the pure product as a clear oil, which crystallized on standing to afford 2.19 g of colorless plates (72%). Mp = 49−50 °C (lit.[18b] 50 °C). ^{1}H NMR ($CDCl_3$): δ 5.85 (d, 1H, J = 3.7 Hz), 5.24 (d, 1H, J = 2.0 Hz), 4.46 (d, 1H, J = 3.7 Hz), 4.22 (m, 2H), 4.04 (m, 2H), 2.36 (q, 1H, J = 7.6 Hz), 2.35 (q, 1H, J = 7.5 Hz),1.52 (s, 3H), 1.41 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H), and 1.14 ppm (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 173.0, 112.2, 109.3, 105.0, 83.3, 79.8, 75.9, 72.4, 67.2, 27.5, 26.8, 26.7, 26.2, 25.2, and 9.0 ppm. IR (KBr): 2987, 1749, 1457, 1370, 1071, 1023, 843, 633, 513 cm^{-1}.

Model Deprotection Reaction of 4 under Acidic Conditions. A heterogeneous mixture of **4** (1.00 g, mmol) in 0.2 N sulfuric acid (10 mL) was stirred for 4 h at 55 °C. An aliquot of 0.1 mL was removed, cooled to ambient temperature, and neutralized with saturated $NaHCO_3$. Upon evaporation to dryness under reduced pressure, a white powder was obtained.

Scheme 2



The remaining solution was further heated to reflux for 20 h and worked up as described above. ^{1}H NMR analysis of the two crude powders in D_2O revealed a mixture of 1,2-*O*-isopropylidene-3-*O*-propionyl-α-D-glucopyranose (**5**) and 3-*O*-propionyl-D-glucopyranose in the sample withdrawn after 4 h, while the sample heated for a total of 24 h contained only 3-*O*-propionyl-D-glucopyranose. The ^{1}H NMR spectrum of the fully deprotected crude product correlated well with those of several other reported 3-*O*-acyl-D-glucopyranose derivatives.[19]

Preparation of 1,2-*O*-Isopropylidene-3-*O*-propionyl-α-D-glucopyranose (5). A solution of 1,2:5,6-di-*O*-isopropylidene-3-*O*-propionyl-α-D-glucofuranose (**4**) (1.00 g, 3.16 mmol) and pyridinium *p*-toluenesulfonate (PPTS, 0.80 g, 3.18 mmol) in methanol (10 mL) was heated at 65 °C for 2 h. The reaction mixture was cooled, methanol was removed under reduced pressure, and the crude oil was purified via silica gel flash chromatography (eluent = 50% ethyl acetate, 50% hexane), giving a white powder after drying in vacuo. This was recrystallized from toluene to afford 0.73 g of white needles (84%). Mp = 118−118.5 °C. ^{1}H NMR (D_2O) see Scheme 2: δ 6.04 (d, 1H, $J_{AB} = 3.8$ Hz, H_A), 5.28 (d, 1H, $J_{CD} = 2.9$ Hz, H_C), 4.75 (d, 1H, $J_{BA} = 3.8$ Hz, H_B), 4.27 (dd, 1H, $J_{DE} = 9.2$ Hz, $J_{DC} = 2.9$ Hz, H_D), 3.91 (m, 1H, H_E), 3.73 (q, 1H, $J_1 = 33.5$ Hz, $J_2 = 12.2$ Hz, H_F), 3.72 (q, 1H, $J_1 = 36.4$ Hz, $J_2 = 12.2$ Hz, $H_{F'}$), 2.43 (q, 1H, $J_{JK} = 7.6$ Hz, H_J), 2.42 (q, 1H, $J_{JK} = 7.5$ Hz, $H_{J'}$), 1.55 (s, 3H, H_G), 1.36 (s, 3H, $H_{G'}$), and 1.12 ppm (t, 3H, $J_{KJ = 7.6 Hz, HK}$). ^{13}C NMR (D_2O + DMSO-d_6): δ 174.7 (C_I), 112.3 (C_A), 104.8 (C_B), 83.0 (C_D), 79.4 (C_C), 76.5 (C_E), 68.1 (C_F), 27.4 (C_J), 26.6 (C_G), 26.1 ($C_{G'}$), and 9.0 ppm (C_K). IR (KBr): 3473, 3382, 1724, 1210, 1191, 1088, 1021, 924, 810, 632, 604, 542, 510 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 52.33; H, 7.40.

Preparation of (4-Methoxyphenyl)dimethylsulfonium Trifluoromethanesulfonate (6). 1-Methoxy-4-(methylthio)-benzene (1.00 g, 6.50 mmol) and silver trifluoromethanesulfonate (1.67 g, 6.50 mmol) were dissolved in dry THF (10 mL). The mixture was cooled with an ice bath, and iodomethane (0.937 g, 6.60 mmol) was added dropwise. After stirring for 30 min, the reaction mixture was filtered to remove the yellow AgI precipitate. The solvent was removed under reduced pressure, and 20 mL of diethyl ether was added to the flask. After stirring for 1 h, the product was filtered off as a white powder. This material was recrystallized from dichloromethane/diethyl ether to yield 1.24 g of colorless needles (65%). Mp = 83−84 °C. ^{1}H NMR (acetone-d_6): δ 8.05 (d, 2H), 7.22 (d, 2H), 3.91 (s, 3H), and 3.41 ppm (s, 6H). ^{13}C NMR ($CDCl_3$): 165, 132, 120 (q, CF_3), 117, 114, 56, and 30 ppm. IR (KBr): 3024, 1914, 1598, 1505, 1250, 1157, 1032, 837, 643, 573, 517 cm^{-1}. λ (H_2O): 244 nm. ϵ (244 nm, H_2O) = 15 200. Anal. Calcd for $C_{10}H_{13}F_3O_4S_2$: C, 37.73; H, 4.12; F, 17.90; S, 20.14. Found: C, 37.90; H, 4.24; F, 17.56; S, 19.86.

Results and Discussion

Molecular Weight Control of 2. The monomer, 1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose (**1**), was prepared as described in the literature.[14a−c] Initial attempts at the production of **2** via free-radical polymerization[14a−c] of **1** in toluene with 1 wt % AIBN gave very high molecular weight polymers, with M_n = 163 000 and M_w = 622 000. Acid-Catalyzed deprotection of these polymers to **3** yielded materials that had such high viscosities when dissolved in water (15 wt % solids) that filtration prior to spin-casting proved nearly impossible.

A series of experiments were performed to control the molecular weight of the starting fully protected polymer, **2**, through the addition of CCl_4 or DT. The results of these experiments are summarized in Table 1. By using chain-transfer agents, it was possible to decrease the molecular weight of **2** to a useful range. Tetrachloromethane, even used in large amounts (>8 mol %), did not sufficiently lower the molecular weight of the final polymer. However, the incorporation of approximately 2.7 mol % DT with 1 wt % AIBN produced polymers within the molecular weight range useful for photoresist applications (<20 000) but afforded a lower yield of product (40%). Increasing the amount of AIBN to 2 wt % while keeping the amount of DT constant (2.7 mol %) succeeded in increasing the yield of product to 87%. The sample **2h** obtained under these conditions was used in all subsequent deprotections to **3**.

Deprotection of 2. Deprotection of **2** was performed in a refluxing mixture of acetone and water under acid catalysis. Dilute conditions (75 mL solvent per gram of polymer) were used to prevent cross-linking reactions during the reaction. It was necessary to maintain solubility of the polymer throughout the deprotection via the addition of small aliquots of water and/or the distillation of acetone. Any precipitated polymer was cross-linked, reducing the yield of useful product.

When addition of water no longer rendered the solution opaque, any remaining acetone was gradually distilled off to leave a dilute aqueous solution, which was further heated to reflux to ensure complete deprotection. Upon cooling, the acid catalyst was scavenged via the use of solid-supported weakly basic resin (Amberlite IR-45 beads). The deprotected polymer **3** was precipitated from the concentrated solution into acetone and dried in vacuo.

It was determined experimentally that the composition of the product varied with the duration of the final refluxing step. Refluxing for only a few hours after reaching complete aqueous solubility afforded partially deprotected polymers. Heating for longer periods of time removed more and more of these ketal groups, eventually giving a fully deprotected polymer. These results are summarized in Table 2. ^{1}H NMR spectral analysis of polymers **3a**−**c** was used to determine the extent of deprotection. For comparison, ^{1}H NMR spectra of polymers **2h**, **3a**, and **3c** are shown in Figure 1. Although it is difficult to determine the exact degree of deprotection due to the broad polymer NMR signals in D_2O, it appears that polymer **3a** was essentially fully deprotected while **3b** retained approximately 5% of its acetonide groups. Polymer **3c** still contained a significant number of acetonide groups (~30%) evidenced by chemical shifts at 1.4 (CH_3), 1.6 (CH_3), and 5.9 ppm (*H*-C1) (Figure 1).

The changes in molecular weight in samples **3a**, **3b**, and **3c** shown in Table 2 may, at first glance, appear surprising as these samples were all prepared from the same sample of polymer **2h**. However, it must be

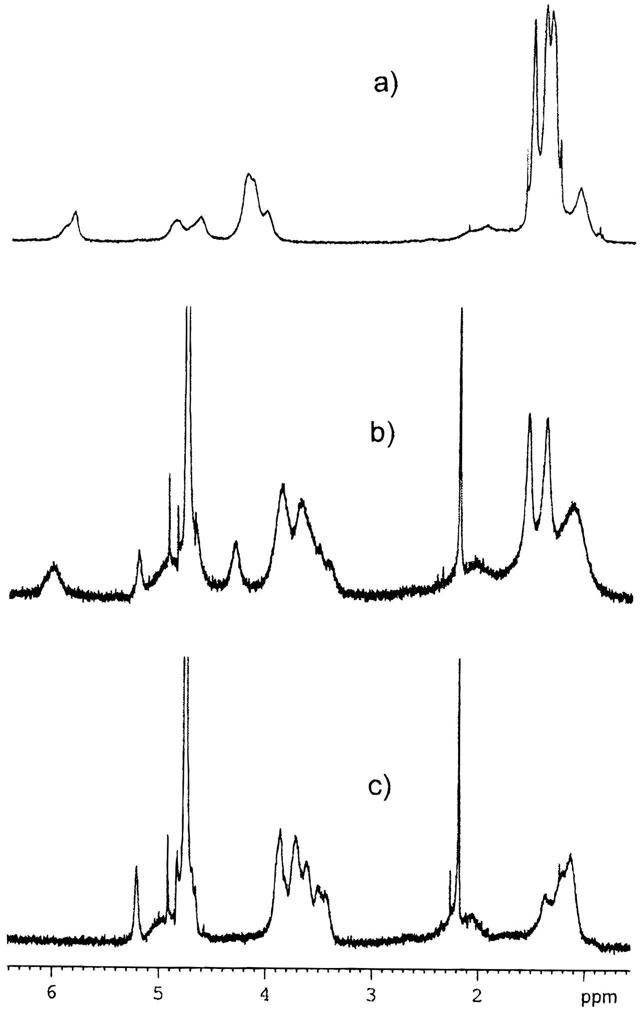


Figure 1. ^1H NMR spectra of (a) **2h** in $CDCl_3$, (b) **3c** in D_2O, and (c) **3a** in D_2O.

recalled that these are relative molecular weights calculated for polymers with varying contents of hydrophobic groups that may lead to differences in hydrodynamic volumes when dissolved in aqueous solution. In addition, the somewhat higher molecular weight measured for sample **3a** was obtained from a fully deprotected polymer. The harsh deprotection reaction conditions used may promote the occurrence of a small extent of unwanted coupling side reaction. Alternatively, aggregation of the hydrophilic polymer in aqueous solution may also be responsible for the higher molecular weight measured by GPC. However, these findings have no bearing on the usefulness of the polymer or its subsequent application as a water-soluble resist.

It was suspected that the two different isopropylidene protecting groups of the pendant sugar moiety were not removed with the same ease and that the signals at 4.3 and 5.9 ppm in the ^1H NMR spectrum of **3c** (Figure 1) were attributable to the cis-fused acetonide ring. Investigation of the literature shows that partially protected sugars can be obtained under controlled conditions since cis-fused acetonides are more difficult to hydrolyze than monocyclic isopropylidene ketals.[20]

A Model for the Polymer Deprotection Reaction. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-propionyl-α-D-glucofuranose (**4**) was prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (Scheme 2) as a model for polymer **2**. To model the polymer deprotection reaction, conditions similar to those used for the preparation of **3** were employed. A heterogeneous mixture of **4** in 0.2 N sulfuric acid was heated at 55 °C until homogeneity was reached after 4 h. A small sample was removed from the reaction medium, neutralized, and dried under reduced pressure. The remaining solution was further heated for a total of 24 h at 55 °C and then neutralized and dried as above. ^1H NMR analysis of samples of the two powders dissolved in D_2O revealed that the model compound was only partially deprotected after 4 h of reaction time. In contrast, the sample that had been treated for 24 h was completely deprotected as evidenced by the complete loss of the ketal methyl peaks in the NMR spectrum. The ^1H NMR spectrum of the partially deprotected sample displayed similarities to that of polymer **3c**, most noticeably the apparently selective loss of only one of the two acetonide protecting groups after shorter reaction times. These observations suggest that 1,2-*O*-isopropylidene-3-*O*-propionyl-α-D-glucopyranose (**5**) is formed quickly during the deprotection reaction, while removal of the second isopropylidene group to afford 3-*O*-propionyl-D-glucopyranose only occurs slowly, as shown in Scheme 2.

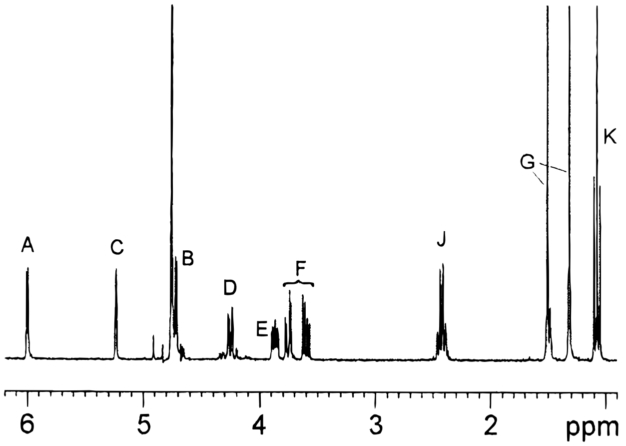


Figure 2. ^1H NMR spectrum of **5** in D_2O. See Scheme 2 for assignments.

To confirm this hypothesis, **5** was prepared from **4** using PPTS, a mild reagent reported as a selective reagent for the removal of acetonides.[21] Short reaction times (≤2 h) afforded the desired mono-ketal product, while an overnight run afforded only the product of complete deprotection (Scheme 2). Comparison of the ^{13}C NMR spectra of **4** and **5** confirms the loss of one isopropylidene ketal. An interesting study by Buchanan et al.[22] showed that ^{13}C NMR is a sensitive tool for the determination of isopropylidene rings. The chemical shifts of the quaternary ketal carbon in monocyclic rings are observed at 108.1−111.4 ppm, while those in acetonides cis-fused to furanoid rings are in the range 111.3−115.7 ppm.[22] Based on these assignments, comparison of the acetonide ketal ^{13}C chemical shifts shows that the monocyclic 5,6-*O*-acetonide is no longer present in **5**, confirming the selective deprotection reaction. Compound **4** has ketal ^{13}C signals with chemical shifts at 109.3 ppm (5,6-*O*-acetonide) and 112.2 ppm (1,2-*O*-acetonide) while compound **5** has only one signal at 112.3 ppm. In addition, two-dimensional NMR experiments (TOCSY ($^1H-^1H$ correlation) and HSQC ($^1H-^{13}C$ correlation)) were used to confirm the assignments shown in Scheme 2.

The ^1H NMR spectrum of **5** in D_2O is shown in Figure 2 for comparison with that of polymer **3c** (Figure 1). The

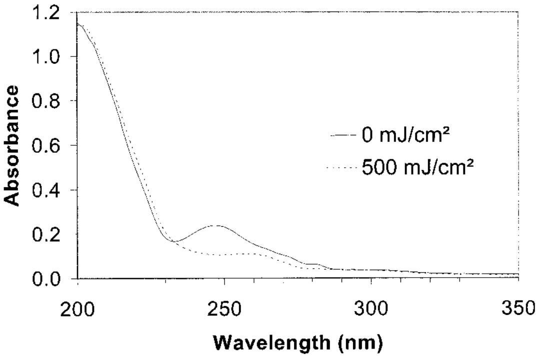
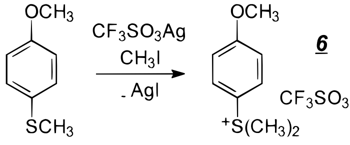


Figure 3. UV−vis spectra of a 7.72 × 10^{-5} M aqueous solution of **6**, before irradiation and after 500 mJ/cm^2 at 254 nm.

Scheme 3



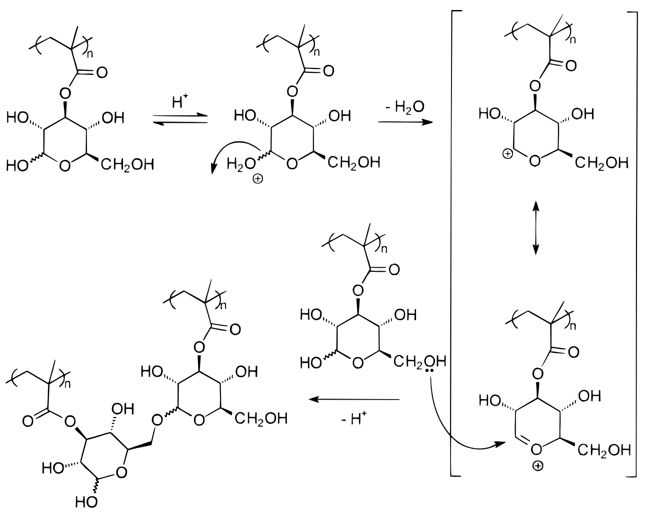
spectrum of **5**, labeled according to the assignments shown in Scheme 2, shows a large degree of similarity to that of polymer **3c**, indicating that polymer **3c** likely retains a large number of its cis-fused 1,2-*O*-isopropylidene groups, while the more accessible 5,6-*O*-isopropylidene protecting group is readily cleaved after only a few hours of acid-catalyzed deprotection.

Preparation of (4-Methoxyphenyl)dimethylsulfonium Trifluoromethanesulfonate (6). To test the performance of these sugar-containing polymers as chemically amplified water-processable photoresists, a water-soluble photoacid generator was required. (4-Methoxyphenyl)dimethylsulfonium trifluoromethanesulfonate (**6**) was prepared through a modification of a procedure by Sakamizu et al.,[6a] as outlined in Scheme 3. Absorbance spectra of dilute aqueous solutions (7.72 × 10^{-5} M) of compound **6** are shown in Figure 3, both before and after exposure to 500 mJ/cm^2 at 254 nm. The absorbance characteristics of this compound with an absorption maximum at 244 nm and an extinction coefficient (ϵ) of 15 200 at 244 nm in water are excellent for use in deep-UV chemically amplified resists. The solubility of this material in water and in many organic solvents is good.

Two-Component Resists with Sugar-Containing Polymers. Solutions (ca. 20 wt % solids) containing polymers **2h**, **3a**, **3b**, and **3c** and 5 wt % of a suitable photoacid generator (triphenylsulfonium hexafluoroantimonate or **6**) were prepared using either 1-methoxy-2-propyl acetate (PGMEA) or water as the solvent. (See Table 3 for specific resist solution compositions.) The viscosity of these resist solutions was varied through addition of more solvent as needed to achieve 0.7 μm film thickness upon casting at 3000 rpm. In all cases the films were heated (PAB) for 2 min at 110 °C. The absorbance of a 0.7 μm film of resist D was found to be 0.27 at 248 nm when cast on a quartz wafer. As the polymer itself is nearly transparent at this wavelength, the absorbance of these films can be tailored by varying the content of photoacid generator.

The sensitivity and contrast data for resists A through D are given in Table 3. The sensitivity of a resist is determined by plotting the film thickness remaining after development for a number of differing exposure doses (the contrast curve). If the resist is negative-tone, the sensitivity value is taken as the minimum dose needed to maintain full thickness. The value for full removal of the film is used for a positive-tone resist. The contrast (γ) is calculated from the slope of the contrast curve at its steepest point. The larger the value of γ, the better the contrast between exposed and unexposed regions, the better the features of the "printed" image.

Scheme 4



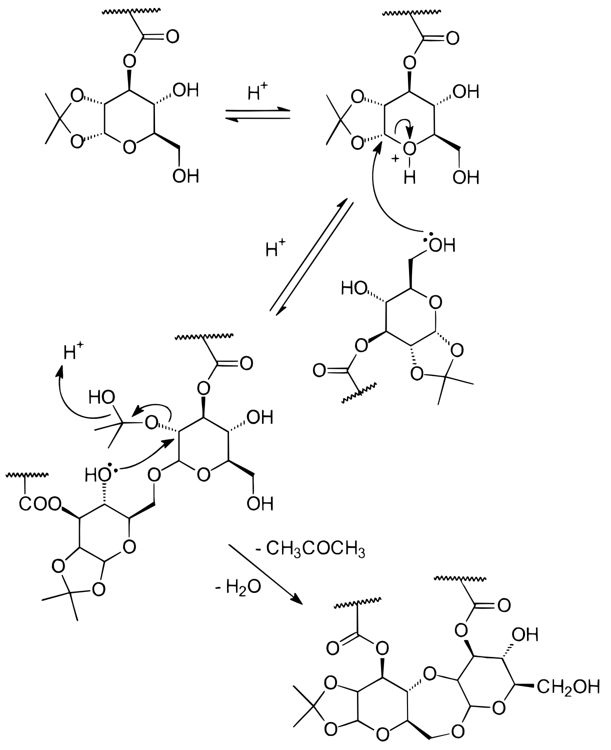
Resist A contains the fully protected polymer **2h** with 5 wt % of the photoacid generator (triphenylsulfonium hexafluoroantimonate) in 1-methoxy-2-propyl acetate (PGMEA); it displays the highest sensitivity and contrast after irradiation at 254 nm followed by heating (PEB) for 2 min at 110 °C and development in acetone. Although this material has the best performance, it clearly does not meet our criteria for a completely water-soluble resist material, being cast from and developed in organic solvents.

Resists B, C, and D, being cast from and developed in pure water with **6** incorporated as a chemical amplification catalyst, do meet our goal of environmental enhancement. After irradiation at 254 nm and heating (PEB) 2 min at 110 °C these resists can be developed in pure water to afford negative-tone images. All resists exhibit very good contrasts, ranging from a γ value of 6 for resist B to a high of $\gamma = 25$ for resist A. Resists C and D prepared from polymers **3b** and **3c** that still contain some isopropylidene groups were found to have improved sensitivities over resist B.

It appears that the presence of some remaining acetonide rings greatly improves the sensitivity and contrast of these water-soluble resist materials. Any deprotected polymer containing pendant sugars is able to cross-link through the formation of glycosidic linkages as shown in Scheme 4. However, our findings of enhanced performance with increased content of isopropylidene groups suggests that an additional cross-linking pathway may be available in materials containing ketal groups.

Chemically amplified resists based on acetal chemistries have been reported.[23−25] Some of these resists are based on acetal cleavage reactions affording either two alcoholic moieties and an aldehyde,[23] or an alcohol and a vinyl ether such as tetrahydropyran,[24] to give positive-tone images after development, while others rely on ring-opening cross-linking reactions of cyclic acetals with phenolic resins[25] to afford negative-tone images. Given the enhancement in sensitivity observed

Scheme 5



with increased content of acetonide groups, it is likely that the residual ketal groups present in our materials are also undergoing some type of cross-linking process, such as transacetalization.

A variety of different transacetalization reactions are possible with partially deprotected polymers such as **3c**. As illustrated in Scheme 5, a volatile byproduct, acetone, would be formed by some of these reactions, driving the equilibrium further toward the formation of a cross-linked product than possible in films relying solely on glycoside formation. The formation of glycosidic linkages produces only water as a byproduct. Since water is less volatile than acetone, its removal from the film requires harsher conditions to displace the equilibrium toward cross-linked product. It must be recalled that some water is already present in these hygroscopic resist films that are cast from aqueous solution; this makes water removal during the short postexposure heating step less efficient than would be observed for a less hydrophilic or drier resist film.

Molecular Weight Increase in Resist D. To confirm that the insolubilization of these materials indeed occurs via cross-linking of the matrix resin, the molecular weight of resist D was monitored as a function of increasing time of irradiation at 254 nm. The resist cast from water on silicon wafers was heated (PAB) to 120 °C for 3 min and then irradiated at 254 nm for varying amounts of time. After exposure, the wafers were heated (PEB) at 110 °C for 2 min, and the resist film was dissolved and subjected to GPC analysis. The results of this experiment are shown in Table 4. Samples exposed to more than 9 mJ/cm^2 became insoluble in the GPC mobile phase consisting of a solution of 10 vol % acetonitrile in 90 vol % of aqueous 10 mM ammonium chloride buffered to pH 9 with Borax. This series of experiments illustrates a rapid molecular weight increase with increased dosage, confirming that imaging of the sugar-containing resists occurs through a cross-linking mechanism of insolubilization.

Table 4. Effect of Deep-UV Irradiation on the Molecular Weight of Resist D[a]

dose (mJ/cm^2)	M_w ($\times 10^{-3}$)	M_z ($\times 10^{-3}$)	M_w/M_n
0	8.9	18.2	2.5
4.3	8.8	20.3	3.0
6.4	12.5	48.1	4.2
7.4	31.9	785	10.9
8.6	39.6	1700	34.8

[a] All films were heated for 2 min at 110 °C after irradiation at 254 nm.

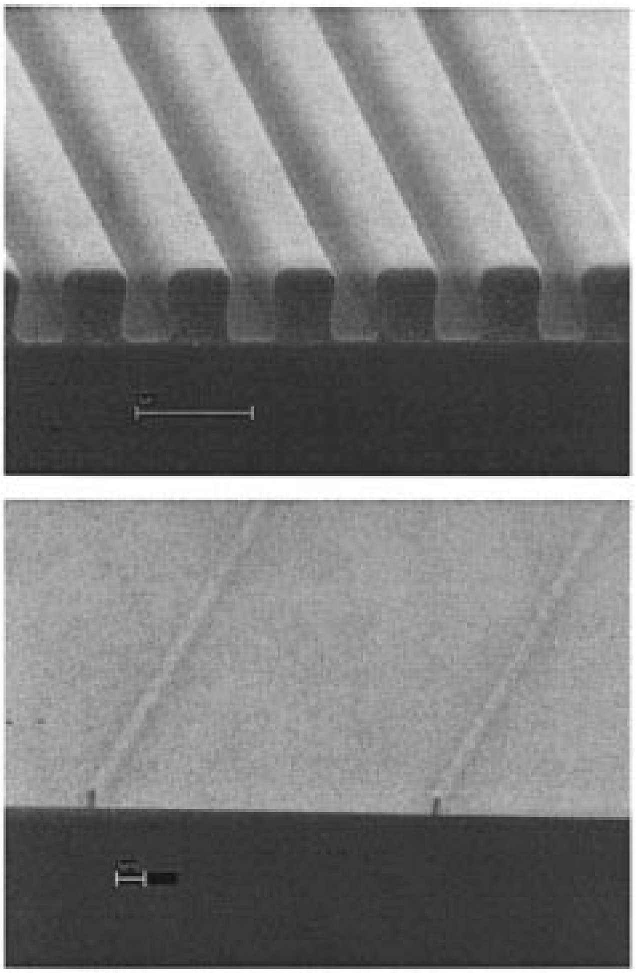


Figure 4. Features from patterning of resist D: (a) 0.45 μm line and space patterns with 73 mJ/cm^2 at 248 nm, 2 min at 110 °C, and development in water and (b) 0.225 μm and 0.200 μm isolated lines with 169 mJ/cm^2, 2 min at 110 °C, and development in water.

Imaging of Resist D. High-resolution imaging of resist D was carried out using an Integrated Solutions XLS 248 nm stepper. Figure 4 shows images of 0.225 μm isolated lines and 0.45 μm line and space patterns obtained from 0.7 μm films of resist D. This resist is able to resolve very small features, much smaller than any other water-soluble cross-linked systems that we have studied.[2] Swelling problems are still encountered, as illustrated by the 0.200 μm isolated line shown in Figure 4, but only at much higher resolutions (smaller features) than with previous water-soluble designs based on cross-linking.

It may be that these materials are not actually fully water-soluble, but rather are water-dispersible. The cross-linked areas of the film would thus not be as likely to take up water during development, resulting in

Table 5. Etching of Films of Resist D

starting thickness (Å)	final thickness (Å)	rate (Å/min)	rate vs SPR510L[a]	rate vs APEX-E[b]
8576	6058	2519	3.59	2.99

[a] SPR510L was etched at 702 Å/min. [b] APEX-E was etched at 842 Å/min.

improved features. Klein et al.[14c] discussed the aqueous solubility of **3** and found very small A_2 (second virial coefficient) values from viscosity and light scattering experiments, indicating that the hydrophobic part of the polymer assumes a large fraction of the polymer. They concluded that the sugar moieties were hydrophilic enough to bring the polymer into aqueous solution but not enough to fully solvate the entire chain in water.[14c]

Etch Testing. A film of resist D was tested for etch resistance. Exposure to 50 sccm of Cl_2 and 150 sccm of HBr in a Lam TCP 9100 prototype etcher for 60 s at 300 W gave the results shown in Table 5. Control experiments show that under these conditions commercially available resists SPR510L and APEX-E were etched at 702 and at 842 Å/min, respectively. The etching performance of this sugar-containing material is not unexpected, as it does not contain any of the structural units (aromatic or caged moieties) that are typically needed to withstand the very harsh conditions of reactive ion etching.[26]

Conclusions

We have successfully demonstrated the use of sugar-containing polymers as matrix resins for entirely water-soluble negative-tone resists. In preliminary experiments, these materials have displayed excellent imaging properties, almost rivaling those of the highest resolution materials cast from organic solvents. Because of the relatively poor etch performance, their use as high-performance photoresists in current processes is somewhat limited, although it should be possible to incorporate comonomers containing caged structures such as isobornyl methacrylate, an approach used by many researchers to boost the etch resistance of acrylate-based resists,[27] without compromising the water dispersibility of the matrix resin. With suitable modifications these sugar-containing polymers might be used as a basis for the design of antireflective coatings for which etch resistance is not an issue.

It is clear that there exists a relationship between the content of 1,2-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucopyranose moieties and the imaging properties of these materials. Future studies of these materials may include the preparation of 1,2-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucopyranose through the deprotection of the monomer **1** with PPTS as described for **5**. Polymerization and copolymerization of this interesting monomer may lead to resists with enhanced properties. In addition, water-soluble copolymers of 3-*O*-methacryloyl-D-glucopyranose (for water solubility) and 1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryloyl-α-D-glucofuranose (as the best cross-linker) might well provide improved sensitivities over the materials reported herein. Materials based either on 6-*O*-methacryloyl-D-glucose (possible cross-linking through furaldehyde formation) or on sugars other than α-D-glucose may also exhibit improved performances.

Acknowledgment. Financial support of this research by the Semiconductor Research Corporation, Sematech, and the Office of Naval Research is acknowledged with thanks. Thanks also to Rudi Nunlist and Corey Liu of the University of California at Berkeley for assistance with the 2D NMR experiments.

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MA981372J